Synthesis and Surface Modification of CdSe and CdS Quantum Dots Exhibiting High Quantum Yield

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SYNTHESIS AND SURFACE MODIFICATION OF CDSE AND CDS QUANTUM DOTS EXHIBITING HIGH QUANTUM YIELD

by

Jeweliet A. Yost

(A Thesis)

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Figure B.9. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 1.04 mmol C$_3$H$_{10}$O$_2$.

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Figure C2. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C$_4$H$_{10}$O$_2$.

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Figure C7. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C₄H₁₀O₂.

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Figure C12. Photos of CdSe (OA & ODE) QDs dissolved in chloroform that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, 0.0.726 mmol C₄H₁₀O₂ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.

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Figure C16. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C₄H₁₀O₂.

Figure C17. Photos of CdSe (OA & ODE) QDs dissolved in toluene that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, 0.0726 mmol C₄H₁₀O₂ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.

Figure C18. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C₄H₁₀O₂.

Figure C19. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C₄H₁₀O₂.

Figure C20. Photos of CdSe (OA & ODE) QDs dissolved in chloroform that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, 0.0726 mmol C₄H₁₀O₂ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.

Figure C21. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C₄H₁₀O₂.

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Figure C23. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C₄H₁₀O₂.
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Figure C25. Absorbance spectra (a) and fluorescence spectra (b) of CdS (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C₄H₁₀O₂.

Figure C26. Absorbance spectra (a) and fluorescence spectra (b) of CdS (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C₄H₁₀O₂.

Figure C27. Absorbance spectra (a) and fluorescence spectra (b) of CdS (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C₄H₁₀O₂.

Figure C28. Photos of CdS (oleylamine) QDs dissolved in chloroform that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, and 0.0726 mmol C₄H₁₀O₂ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.

Figure C29. Absorbance spectra (a) and fluorescence spectra (b) of CdS (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C₄H₁₀O₂.

Figure C30. Absorbance spectra (a) and fluorescence spectra (b) of CdS (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C₄H₁₀O₂.

Figure C31. Absorbance spectra (a) and fluorescence spectra (b) of CdS (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C₄H₁₀O₂.

Figure C32. Photos of CdS (oleylamine) QDs dissolved in toluene that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, and 0.0726 mmol C₄H₁₀O₂ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.

Figure C33. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment...
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Figure C37. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C₄H₁₀O₂. ................................................................................................... C29

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Figure C40. Photos of CdS (OA & ODE) QDs dissolved in toluene that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, and 0.0726 mmol C₄H₁₀O₂ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment. ............................................................................................................ C32

Figure C41. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C₄H₁₀O₂. ................................................................................................... C32

Figure C42. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C₄H₁₀O₂. ................................................................................................... C33

Figure C43. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment
(yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C$_4$H$_{10}$O$_2$. .................................................................C34

Figure C44. Photos of CdS (OA & TOA) QDs dissolved in chloroform that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, and 0.0.726 mmol C$_4$H$_{10}$O$_2$ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment. .......................................................C34

Figure C45. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C$_4$H$_{10}$O$_2$. ............................................................................................................ C35

Figure C46. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C$_4$H$_{10}$O$_2$. ........................................................................................................... C36

Figure C47. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C$_4$H$_{10}$O$_2$. ........................................................................................................... C37

Figure C48. Photos of CdS (OA & TOA) QDs dissolved in toluene that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, and 0.0.726 mmol C$_4$H$_{10}$O$_2$ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment. ...................................................................................................................................C37

Figure D.1. TGA of CdSe (oleylamine) QDs heated from 30 °C to 600 °C at a constant rate of 10 °C/min under nitrogen. ...................................................... D1

Figure D.2. TGA of CdSe (OA & ODE) QDs heated from 30 °C to 600 °C at a constant rate of 10 °C/min under nitrogen. ...................................................... D1

Figure D.3. TGA of CdSe (OA & TOA) QDs heated from 30 °C to 600 °C at a constant rate of 10 °C/min under nitrogen. ...................................................... D2

Figure D.4. TGA of CdS (oleylamine) QDs heated from 30 °C to 600 °C at a constant rate of 10 °C/min under nitrogen. ...................................................... D2

Figure D.5. TGA of CdS (OA & ODE) QDs heated from 30 °C to 600 °C at a constant rate of 10 °C/min under nitrogen. ...................................................... D3

Figure D.6. TGA of CdS (OA & TOA) QDs heated from 30 °C to 600 °C at a constant rate of 10 °C/min under nitrogen. ...................................................... D3
List of Abbreviations

Atomic force microscopy (AFM)

Benzoyl peroxide ($C_{14}H_{10}O_4$)

Cadmium acetate ($Cd(Ac)_2$)

Cadmium carbonate ($CdCO_3A$)

Cadmium dimethyl ($CdMe_2$)

Cadmium oxide ($CdO$)

Cadmium selenide ($CdSe$)

Cadmium sulfide ($CdS$)

Cadmium telluride ($CdTe$)

Calcium hydride ($CaH_2$)

Dynamic light scattering (DLS)

Full-width half-maximum (FWHM)

Hydrazine ($N_2H_4$)

Hydrophilic-lipophilic balance (HLB)

Infrared (IR)

Light emitting diode (LED)

Octadecene (ODE)

Octadecylamine (ODA)

Oleic acid (OA)
Quantum dot (QD)
Quantum yield (QY)
Relative fluorescence units (RFU)
Rhodamine 6G (Rh6G)
Sodium borohydride (NaBH₄)
\textit{tert}-butylhydroperoxide (C₄H₁₀O₂)
Thermogravimetric analysis (TGA)
Total internal reflection fluorescence microscope (TIRFM)
Transmission electron microscopy (TEM)
Trioctylamine (TOA)
Trioctylphosphine oxide (TOPO)
Trioctylphosphine (TOP)
Trioctylphosphine selenium (TOPSe)
Ultra violet (UV)
Ultraviolet-visible spectroscopy (UV-VIS)
Abstract

The thesis investigates the effect of surface treatment with various reducing and oxidizing agents on the quantum yield (QY) of CdSe and CdS quantum dots (QDs). The QDs, as synthesized by the organometallic method, contained defect sites on their surface that trapped photons and prevented their radiative recombination, therefore resulting in a decreased QY. To passivate these defect sites and enhance the QY, the QDs were treated with various reducing and oxidizing agents, including: sodium borohydride (NaBH₄), calcium hydride (CaH₂), hydrazine (N₂H₄), benzoyl peroxide (C₁₄H₁₀O₄), and tert-butyl hydroperoxide (C₄H₁₀O₂). It was hypothesized that the reducing/oxidizing agents reduced the ligands on the QD surface, causing them to detach, thereby allowing oxygen from atmospheric air to bind to the exposed cadmium. This cadmium oxide (CdO) layer around the QD surface satisfied the defect sites and resulted in an increased QY. To correlate what effect the reducing and oxidizing agents were having on the optical properties of the QDs, we investigated these treatments on the following factors: chalcogenide (Se vs. S), ligand (oleylamine vs. OA), coordinating solvent (ODE vs. TOA), and dispersant solvent (chloroform vs. toluene) on the overall optical properties of the QDs. The QY of each sample was calculated before and after the various surface treatments from ultra-violet visible spectroscopy (UV-Vis) and fluorescence spectroscopy data to determine if the treatment was successful.

From our results, we found that sodium borohydride was the most effective surface treatment, with 10 of the 12 treatments resulting in an increased QY. Hydrazine, on the other hand, was the least effective treatments, as it quenched the QD fluorescence
in every case. From these observations, we hypothesize that the effectiveness of the QD surface treatments was dependent on reaction rate. More specifically, when the surface treatment reaction happened too quickly, we hypothesize that the QDs began to aggregate, resulting in a quenched fluorescence. Furthermore, we believe that the reaction rate is dependent on concentration of the reducing/oxidizing agents, solubility of the agents in each solvent, and reactivity of the agents with water. The quantum yield of the QDs can therefore be maximized by slowing the reaction rate of each surface treatment to a rate that allows for the proper passivation of defect sites.
Chapter 1. Introduction

Fluorescent quantum dots (QD) are semiconductor nanocrystals with dimensions on the order of a few nanometers. At the nano-scale, materials exhibit size-dependent absorbance and fluorescence emission properties that are not observed in macro-scale (bulk) semiconductors. The size, shape, and growth conditions of QDs can be tuned by varying reaction conditions, such as the reaction time, reaction temperature, and stabilizing ligands used. The ability to tune the size of QDs allows for their potential application in a number of photonic devices, including: emitters for color displays\(^1\), color modifiers for light emitting diodes (LEDs)\(^2\), optical fiber amplifiers\(^3,4\), low threshold lasers\(^5\), self-assembled photonic sphere arrays\(^6\), polymer-based photovoltaic cells\(^7\), optical temperature probes\(^8\), chemical sensors\(^7\), and high-speed signal-processing filters\(^9\).

Quantum dots, specifically CdSe QDs, are also becoming an important tool in medical imaging. Regardless of application, QDs with a high quantum yield (QY) are critical to development of many future technologies. This thesis focuses on developing and understanding the effect of surface treatments to produce cadmium selenide (CdSe) and cadmium sulfide (CdS) QDs with a high QY.

The preparation method for the synthesis of CdSe and CdS QDs utilized in this thesis involves the high temperature thermolysis of organometallic precursors via microwave heating. During this method, organic precursors are dissolved in a heated coordinating solvent and bound to unsaturated metal atoms on the QD surface to prevent the formation of bulk semiconductors.\(^{10}\) The nanoparticles are capped with a monolayer of organic ligands and are soluble only in non-polar hydrophobic solvents.\(^{10}\) Ligands play
at least four distinct roles in the overall electronic function of the QDs. First, they are present during the nucleation process and determine the reactivity and availability of the crystal precursors and ligands.\textsuperscript{11} Second, they control the rate of growth and final particle size distribution\textsuperscript{11} by keeping the particles isolated and facilitating homogenous growth during synthesis\textsuperscript{12}. Third, they provide colloidal stability, preventing aggregation and growth.\textsuperscript{11,13,14} Lastly, they interact electronically with surface sites and may passivate defects on the surface of QDs.\textsuperscript{12}

Quantum dots have a high surface area to volume ratio resulting in a large fraction of atoms on the surface of the nanocrystals. Incomplete surface coverage can lead to the formation of inhomogeneous defect sites on the QD surface. These defect sites are capable of trapping electrons or holes, which in turn prevents radiative recombination and ultimately degrades their QY. For this reason, proper passivation of the nanocrystal surface is necessary to achieve a high QY. The goal of this thesis is to develop methods to effectively passivate these surface defect points via treatment with various reducing and oxidizing agents. It is expected that treatment with reducing/oxidizing agents will lead to the formation of a cadmium oxide (CdO) layer around the QDs thereby passivating the defect sites and resulting in increased QY.\textsuperscript{16} The reducing agents that will be investigated include: sodium borohydride (NaBH\textsubscript{4}), calcium hydride (CaH\textsubscript{2}), and hydrazine (N\textsubscript{2}H\textsubscript{4}); while the oxidizing agents include: benzoil peroxide (C\textsubscript{14}H\textsubscript{10}O\textsubscript{4}) and \textit{tert}-butylhydroperoxide (C\textsubscript{4}H\textsubscript{10}O\textsubscript{2}).
To better understand the effect surface reactions of reducing and oxidizing agents have on the optical properties of the QDs, several variables were investigated more thoroughly. Specifically, the effect of cadmium precursor in the semiconductor (Se vs. S), stabilizing ligand (oleylamine vs. oleic acid (OA)), non-coordinating solvent (octadecene (ODE) vs. trioctylamine (TOA)), and dispersion solvent (chloroform vs. toluene) was studied. Untreated and treated QDs were subjected to ultra-violet visible (UV-Vis) spectroscopy, fluorescence spectroscopy, and thermogravimetric analysis (TGA) to provide information about the QD optical properties, size, and surface coverage of ligands. The QY of the QDs before and after treatment was used as a measure of success.

This thesis is organized into 8 chapters. Chapter 2 is a literature review section that provides an overview of the applications and synthesis methods of QDs and serves as motivation for the work completed in this thesis. Chapter 3 outlines the experimental methods used to synthesize and treat the QDs with various reducing/oxidizing agents. Chapters 4, 5, and 6 present and discuss the results obtained from carrying out these procedures, and Chapter 7 provides general conclusions from these results. Lastly, recommendations for future work are summarized in Chapter 8.
1.1 References


(4) Meissner, K. E.; Holton, C.; Spillman, W. B. *Physica E: Low-dimensional Systems and Nanostructures* 2005, 26, 377-381.


Chapter 2. Background

2.1 Quantum Dots versus Bulk Semiconductors

A bulk semiconductor is a material that has an electrical conductivity between a metal and an insulator. Quantum dots behave similarly to bulk semiconductors but differ in two distinct ways: (1) the bandgap of QDs can be tuned; and (2) the energy levels of QDs are considered to be discrete rather than continuous. Electrons in a bulk semiconductor exhibit different energies and are therefore in different energy levels. The energy levels are continuous because there is virtually no energy difference between the levels. Some of the energy levels are ‘unavailable’ to electrons and are referred to as the bandgap. Electrons occupying levels below the bandgap are in the valence band while those above the bandgap are in the conduction band (see Figure 2.1 below).

![Figure 2.1. Electron structure in a semiconductor material.](image)

In most bulk semiconductors, the valence band is occupied by electrons, while the conduction band is vacant. For electrons to move from the valence band to the
conduction band, they must acquire enough energy to cross the bandgap.\textsuperscript{1-3,5} To accomplish this, an external stimulus is required, such as heat, voltage, or photon flux.\textsuperscript{5} The electrons transferred from the valence band to the conduction band are called ‘free’ electrons because they have been ‘freed’ from the confines of the valence band.\textsuperscript{1} The minimum amount of energy a bulk semiconductor absorbs to raise an electron from the valence band to the conduction band corresponds to the energy of the bandgap ($E_g$).\textsuperscript{2,3} For bulk semiconductors, the bandgap energy is fixed and is dependent on the semiconductor material. The temporary valence location vacated when an electron moves to the conduction band is a positively charged ‘hole’.\textsuperscript{1,3-5} A material rich in holes (or lacking electrons) is a $p$-type material whereas an electron-rich material is $n$-type.\textsuperscript{1,2}

The promoted electrons in the conduction band remain there momentarily before returning to the valence band. As the electron returns to the valence band, it passes through the bandgap. Electromagnetic radiation with a wavelength corresponding to the energy it loses in the transition is emitted.\textsuperscript{2,3} Typically, electrons fall from the bottom of the conduction band to the top of the valence band. In other words, they travel from one edge of the bandgap to the other. Thus, because the bandgap is fixed in bulk semiconductors, this emission wavelength is also fixed. Often this emitted light is not in the visible spectrum; instead it is in the infrared (IR) or ultra violet (UV) region.\textsuperscript{2} The process of an electron returning to the valence band is known as radiative recombination.\textsuperscript{2,3}
Quantum dots are different from bulk semiconductors because their bandgap can be tuned to emit light at a particular wavelength. The size of the bandgap is dictated by the size of the particle. More specifically, the nanocrystal bandgap increases with decreasing size as $1/r^2$ (where $r$ refers to the QD radius). As a result, quantum dots of the same material can vary in color and optical properties depending on the QD size. The size may be precisely controlled by the reaction time, temperature, and choice of ligand used during their synthesis, which will be discussed in detail below. CdSe QDs, for instance, can be tuned to emit radiation across most of the visible and some of the IR spectrum (4500 to 6500 Å). Experimental observations of CdSe QDs have shown that as the average radius increases from 0.6 nm to 4.15 nm, the emitted color changes from blue (centered at 450 nm) to red (centered at 650 nm) (see Figure 2.2 below), and the photon energy of the first absorbance peak decreases from 3.02 eV to 1.88 eV and eventually approaches the bandgap energy of bulk CdSe ($E_g = 1.7$ eV). The electrons of QDs that are considered ‘blue shifted’ must travel a greater distance in terms of energy and therefore produce radiation at a shorter, ‘bluer’ wavelength. Because this thesis focuses on both CdSe and cadmium sulfide (CdS) QD cores, it is important to note that the bandgap of CdS is higher than that of CdSe ($E_g = 2.5$ eV).

![Figure 2.2. Schematic of QD particle size and color emitted.](image)
Another difference between QDs and bulk semiconductors is that the distance between the electron and ‘hole’ pair (called an exciton) in the bulk material is much smaller than the dimensions of the semiconductor crystal. With QDs, the exciton is about the same size as the dimensions of the particle and as a result, their energy levels are discrete rather than continuous. In this context, discrete refers to the finite separation between energy levels (also referred to as quantum confinement). The separation between energy levels increases as the particle size decreases. Quantum confinement occurs when the nanocrystal radius becomes comparable to the bulk exciton Bohr radius (~5 Å for CdSe). Under these conditions, the absorptive and emissive behavior of the semiconductor is changed because the addition or subtraction of just a few atoms can alter the boundaries of the bandgap.

2.2 Applications for Quantum Dots

The ability to tune the size of quantum dots allows for their potential application in a number of photonic devices, including: emitters for color displays, color modifiers for light emitting diodes (LEDs), optical fiber amplifiers, low threshold lasers, self-assembled photonic sphere arrays, polymer-based photovoltaic cells, optical temperature probes, chemical sensors, and high-speed signal-processing filters. Quantum dots, specifically CdSe, are also often applied to the medical field. Due to the known toxicity of Cd and Se to cells, however, in vitro biomedical applications of CdSe QDs are currently practiced, whereas in vivo applications are still in the research stage.
Examples of *in vitro* applications include: laboratory blood tests, urine analysis, tissue slide staining, and cell culture monitoring.\(^{19}\) Future work of this thesis focuses on the potential use of QDs in various *in vivo* applications which are described in detail below.

A primary application of QDs in the medical field involves bioconjugation, or the coupling of a QD to a small biomolecule, including oligonucleotides, peptides, proteins, and DNA. In fact, multiple biomolecules can be attached to the surface of a single QD due to the large surface area of the nanocrystals.\(^{20}\) It has been estimated that two to five protein molecules and 50 or more small molecules (such as oligonucleotides or peptides) can be conjugated to a single 4 nm QD.\(^{20}\) These bioconjugations are being used for the assembly of new materials, for developing homogeneous bioassays, and as multicolor fluorescent labels for detection and imaging.\(^{20}\) One specific example involves the attachment of antibodies that have the ability to bind many target proteins to QDs in order to form new luminescent tags which can help detect the presence of selected diseased tissues or illuminate the structure of diseased areas.\(^{20}\)

A further application of QDs is the multiplexed optical encoding and high-throughput analysis of genes and proteins. This involves embedding polystyrene beads with multicolor CdSe QDs at various color and intensity combinations.\(^{20}\) It is estimated that the use of six colors and 10 intensity levels can encode one million protein or nucleic acid sequences.\(^{20}\) Specific capturing molecules (such as peptides, proteins, and oligonucleotides) are then covalently linked to the beads and encoded by the bead’s spectroscopic signature.\(^{20}\) To read all of the QD-encoded beads, a single light source is all
that is required.\textsuperscript{20} To then determine whether an unknown analyte is captured or not, conventional assay methodologies are applied.\textsuperscript{20} This so-called ‘bar-coding’ technology can be used for gene profiling and high-throughput drug and disease screening. These ‘bar-coding’ technologies offer significant advantages over planar chip devices, including improved kinetic binding and dynamic range.\textsuperscript{20}

Quantum dots can also help read DNA sequences.\textsuperscript{20,21} Recent research has found that by attaching QDs and antibodies to polymer microspheres, the prevalence of targeted DNA sequences can be read by a standard flow cytometer.\textsuperscript{21} The surface of each microsphere could also be covered with specific antibodies that would bind to particular protein sequences.\textsuperscript{21} This method has significant potential as it is currently being compared to immuno-assay fluorescence arrays.\textsuperscript{21}

Quantum dots can further be used to accurately identify specific types of cancer. To diagnose a specific cancer type, slides are made from tumor tissue samples and selective chemical stains highlight one specific feature at a time, such as nuclei or aster cells.\textsuperscript{19} Quantum dots can allow for the simultaneous marking of numerous features with different colors, thus improving the amount and speed of information received by oncologists.\textsuperscript{19}

Oncologists are also exploring the use of quantum dots to guide cancer surgery. The intensity of scattered luminescence can guide a surgeon to selectively remove only tagged diseased tissue beyond the primary tumor.\textsuperscript{19,22} Traditionally, a radioactive blue dye is used to track the flow of cancer cells through the lymph system.\textsuperscript{23} However,
ionizing radiation is hazardous to both the patient and medical caregivers. As a potentially safer alternative, near-infrared (λ is approximately 850 nm) QDs are being explored to mark cancerous lymph nodes for surgical removal from mice and pigs.

2.3 Optical Properties

Despite the large number of potential QD applications in the medical field, the future work of this thesis focuses on the specific use of QDs in bio-imaging. Quantum dots are an emerging alternative to traditional organic dyes for solar cells and bio-imaging primarily because of their (1) small size, (2) ability to tailor the chemistry of the QD surface, (3) high quantum efficiency, (4) narrow spectral linewidth, (5) broad absorption tail, (6) stable emission, and (7) long fluorescence lifetime. The ability to tailor the QD chemistry is beneficial because varying the size, shape, and composition of QDs allows for the production of materials with specific emissive, absorptive, and light-scattering properties. This flexibility allows for the production of QDs whose emissive properties range across the entire visible spectrum from the same material.

The terms quantum yield, quantum efficiency, and photoluminescence are used interchangeably throughout this thesis to represent the brightness of the QDs. The quantum yield refers to the existence of nonradiative transition of electrons and holes between energy levels. In other words, it is the ratio of emitted photons to absorbed photons. The quantum yield of QDs is significantly higher than organic dyes causing them to be advantageous for bio-imaging applications. This is because the molar
extinction coefficients of QDs are about 10-50 times larger than those for organic dyes (5-10 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}).^{26} This causes the QD absorption rates to be 10-50 times faster at the same excitation photon flux than organic dyes.\textsuperscript{26} Due to this increased rate of light emission, individual QDs appear to be 10-20 times brighter than dyes.\textsuperscript{26}

One major disadvantage of organic dyes involves their broad, overlapping emission spectra that prevent their use in multicolor detection applications\textsuperscript{20,27} without the use of complex mathematical analysis of the data. Multicolor detection is used to track multiple molecular targets simultaneously using different colors and intensities, and is therefore a very important feature. For example, most complex human diseases such as cancer and atherosclerosis involve a large number of genes and proteins and would therefore require this type of detection.\textsuperscript{26} Quantum dots exhibit a narrow spectral linewidth\textsuperscript{6,28}, typically one third that of a conventional organic dye, therefore making them very attractive for these types of applications (see Figure 2.3).\textsuperscript{29} A narrow spectral linewidth means that the QDs can only be excited within a narrow window of wavelengths.\textsuperscript{30} Consequently, QDs of different sizes and colors can be excited by a single wavelength shorter than their emission wavelengths, with minimum signal overlap.
The fluorescence peak of traditional organic dyes is very close to their absorption peak.\textsuperscript{19} This causes each dye to require its own expensive, carefully-tuned, sharp-cutoff filter to block the excitation background from the imaging camera.\textsuperscript{19} In contrast, QDs have a broad absorption tail over wavelengths shorter than the peak emission wavelength.\textsuperscript{19} A single common long pass filter and a single excitation source are therefore all that is required for QDs that emit in several distinct wavelength ranges.\textsuperscript{31}

QDs offer another advantage over organic dyes because their emission wavelengths can be continuously tuned by varying the particle size and chemical
composition. Additionally, QDs are about 100 times more stable against photobleaching (also called fading) than organic dyes.\textsuperscript{28,30} Moreover, QDs show long-term stability against photochemical and current-induced degradation.\textsuperscript{6} This extreme stability reflects the strong chemical bonding found in QDs and makes them very attractive for the imaging of thick masses over long periods of time.\textsuperscript{30} It also allows for the acquisition of real-time\textsuperscript{20} images that are bright and well contrasted.\textsuperscript{32}

Another interesting characteristic of QDs is their long fluorescence lifetime on the order of several to tens of nanoseconds.\textsuperscript{29} This allows time-delayed fluorescence measurements, which can be used to suppress the autofluorescence of biological matrices.\textsuperscript{29} Additionally, the long fluorescence lifetime facilitates the use of time-gated detection to separate their signal from that of shorted lived species.\textsuperscript{32} More specifically, time-gated detection provides a technique to separate the QD fluorescence from background fluorescence.

### 2.4 Synthesis

#### 2.4.1 Synthetic Methods

Since QD emission is size dependent, the synthesis process must be carefully controlled to achieve the targeted radius with a narrow size distribution. There are two main approaches for the synthesis of QD cores depending on the nature of the solvent: (1) the wet chemistry method, and (2) high temperature thermolysis of organometallic precursors.\textsuperscript{6,19,20,33,34} The wet-chemistry method uses low-temperature polar solvents such
as water or methanol, whereas the organometallic synthesis method uses high
temperature, non-polar solvents such as trioctylphosphine oxide (TOPO). Typically, the
wet chemistry method produces lower quality QDs with smaller and wider emission
peaks as compared to those produced by the organometallic method.\textsuperscript{19,35} The QDs
produced in this thesis were synthesized via the latter method.

\textbf{2.4.1.1 Wet Chemistry Method}

The wet chemistry method involves the deposition of a precursor material with a
surfactant in a coordinating organic solvent.\textsuperscript{36} As the QDs grow, the organic solvent is
naturally coordinated to the surface of the QDs and acts as a dispersant.\textsuperscript{36} Accordingly,
the organic solvent allows the initial nucleus to grow to the level of nanometers.\textsuperscript{36} The
wet chemistry method allows for the control of QD core size by varying the organic
solvents used, reaction temperature, and reaction time.\textsuperscript{36,37}

The type of organic solvent used in the wet chemistry method is of the utmost
importance. The ideal solvent should: (1) have the ability to be coordinated to the surface
of the QD\textsuperscript{36}, (2) be sufficiently bulky to the extent that it can control the growth rate of
the cores\textsuperscript{36}, (3) be stable at the crystal growth temperature\textsuperscript{36}, and (4) be able to disperse
the QDs in a state where the solvent is coordinated to the surface of the core.\textsuperscript{36} For
example, in a study by Masala et al.\textsuperscript{35}, two different solvents were investigated:
ethylenediamine and pyridine. The QDs produced in the presence of ethylenediamine
were small and uniform (approximately 4 nm – 6 nm in diameter), whereas QDs with
poor crystallinity and low yield resulted in the presence of pyridine. From these results, ethylenediamine was recommended as the organic solvent of choice for this QD synthesis method.

Unfortunately, the synthesis temperature is limited by the boiling point of the organic solvent. When grown at a low temperature, QDs often have a poor degree of crystallinity as well as a high defect concentration leading to a low quantum efficiency. It is therefore necessary to choose a solvent with a higher boiling point to ensure that a high enough reaction temperature can be used to produce high quality QDs.

The particle size distribution of QDs synthesized from the wet chemistry method is usually so wide that size-selective precipitation is required to separate a distribution into sections with narrow emission peaks. Additionally, this method typically yields QDs with very poor crystallinity and low quantum yield. For these reasons, the wet chemistry method was not investigated in this thesis.

2.4.1.2 Thermolysis of Organometallic Precursors

The decomposition of molecular precursors at high temperatures in a coordinating solvent is one of the most successful and popular routes to prepare high-quality QDs. This approach was first developed in 1993 by Bawendi et al. who prepared CdE QDs (E = Se, S, and Te) through separate, rapid injections of a solution of cadmiumdimethyl (CdMe₂) in trioctylamine (TOA) and a solution of trioctylphosphine (TOP) and the corresponding chalcogenide (Se, S, or Te) into tri-octylphosphine oxide (TOPO) at
high temperatures (200 °C to 300 °C). The capping agent allowed particle stability in organic solvents, prevented particle aggregation, and electronically passivated the semiconductor surface.

This method, although successful at producing high-quality QDs, is hindered by the toxicity of the starting materials as well as the high temperature required by the reaction. In particular, the alkyl metal (CdMe₂) is pyrophoric, explosive at high temperatures, and emits highly toxic gases of metal oxide. It was later found that cadmium oxide (CdO) and cadmium salts with an anion of a weak acid, such as cadmium acetate (Cd(Ac)₂) and cadmium carbonate (CdCO₃A), proved to be adequate substitutes. Compared to the highly unstable CdMe₂, the cadmium salt substitutes offer several advantages, including: (1) the injection temperature can be much lower (220 °C to 300 °C), (2) both nucleation and growth are almost independent of injection therefore guaranteeing great reproducibility, and (3) the slow nucleation implies that the injection can be completed within a longer time, therefore allowing large amounts of stock solutions to be added to the reaction vessel, making the process more feasible for scale-up productions.

Today, a typical reaction involves the dissolution of the cadmium salt in a mixture of TOPO and another solvent (for example, amines such as n-dodecylamine, or fatty acids such as stearic acid) at 300 °C or below, followed by the addition of a solution of the chalcogenide (Se, S, or Te) in tri-n-octylphosphine (TOP). The chalcogenide and cadmium precursor combine to form stable nuclei that subsequently grow as the reaction
At the growth temperature, surfactant molecules adsorb and desorb rapidly from the QD surface, enabling the addition (as well as removal) of atoms from the nanocrystal, while aggregation is suppressed by the presence of one monolayer of surfactant at the nanocrystal surface. The QDs resulting from this method are typically monodisperse, with sizes ranging from 2 nm to 25 nm and quantum efficiencies of up to 85%.

Tri-n-octylphosphine is used as both a surfactant and selenium-delivery solvent when in the form of a trioctylphosphine selenium (TOPSe) solution during QD synthesis. During the synthesis process, TOP (a cationic precursor) coordinates to the chalcogenide (Se or S) ion. The phosphine then undergoes nucleophilic attack from either the carboxylic acid/phosphonic acid counter ion or excess TOP in solution, cleaving the P=Se bond. In this thesis, the cadmium precursor used was cadmium acetate (Cd(Ac)$_2$) therefore the carboxylic acid provided the counter ion. The presence of a ligand during synthesis (especially oleic acid (OA)) induces P=Se cleavage. The presence of TOP on selenium rich surfaces has also been shown to be the source of enhanced fluorescence.

The organometallic synthesis method was developed to produce superior crystallinity and higher quantum yield from higher temperature reactions, and to provide better size control and surface passivation than other synthesis methods. At these higher temperatures, there is more thermal energy to help each add-atom find more energetically favorable bonding positions in the crystal lattice, therefore reducing defects.
by annealing during growth, leading to increased overall quantum efficiency.19 Another advantage associated with the organometallic method is that a narrower size distribution of QDs may be achieved compared to other techniques because effective separation of the two synthesis stages (nucleation and growth) is achieved by the ‘hot injection technique’.34 The ‘hot injection technique’ involves the rapid injection of organometallic reagents into a hot coordinating solvent causing nucleation to immediately take place and continue until the temperature and ligand concentration drop below a critical threshold.8,46 The depletion of reagents through nucleation and the sudden temperature drop associated with the introduction of room temperature reagents prevents further nucleation8, thus yielding particles of one size.46 It is estimated that the diameter of CdSe QDs immediately after nucleation is about 1.75 nm and the fluorescence peak is around 500 nm.47 The subsequent growth of the QD, however, resulted in the red shift of the fluorescence peak to green, yellow, and red as the size of the QD continued to increase.47,38 The ‘hot injection technique’ was utilized in this thesis.

2.4.2 Impact of Reaction Parameters on the Synthesis of QDs

For any method, experimental conditions are of the utmost importance when trying to produce QDs with consistent shape, crystal structure, and size. Alisvisatos et al. explored the CdSe system extensively to demonstrate that parameters such as temperature, ligand concentration, and growth rate significantly influence QD size and morphology.35,41,46 The size of the QDs can easily be tuned by controlling the reaction
temperature, with larger particles forming at higher temperatures. Spherical QDs were found to form at high ligand concentrations and slow growth rates, whereas rod-, teardrop-, and tetrapod-like shaped QDs formed at lower ligand concentrations and increased growth rates. It is most desirable to produce spherical QDs because they can achieve the highest quantum efficiency (85% for CdSe QDs) as compared to significantly lower quantum efficiencies for the other morphologies (for example, rod-shaped CdSe QDs can achieve a quantum efficiency as low as 1%).

As mentioned above, the temperature necessary to maintain steady growth increases with increasing QD size. More specifically, as the size distribution narrows, the reaction temperature must be raised to maintain steady growth. At these higher temperatures, the CdSe cores begin to grow via Ostwald ripening, and their size distribution deteriorates, leading to broader spectral line widths. In Ostwald ripening, the higher surface free energy of small QDs makes them less stable to dissolution in a solvent than larger QDs. This difference in stability results in the sacrifice of small particles to larger particles. In other words, larger particles grow and smaller particles dissolve, thus widening particle size distributions. When the size distribution begins to broaden, the temperature necessary for slow, steady growth drops. These lower temperatures can lead to the incomplete decomposition of the precursors or to reduced crystallinity of the surface monolayer of ligands. It is therefore necessary to determine the ideal growth temperature individually for each CdSe core size to ensure that the size distribution of the cores remains constant and that surface ligand layers with a high degree of crystallinity are formed.
Ligand concentration also affects both the shape and size distribution of QDs. For diffusion-controlled growth, the distribution of incoming diffusion flux toward each nanocrystal depends strongly on the ligand concentration in the bulk solution. At high ligand concentrations, the chemical potential of the bulk solution is equally as high as the overall chemical potential of the entire crystal. In this type of environment, there is no net diffusion flux between the bulk solution and the diffusion sphere. To minimize the total surface energy of the nanocrystal, the ligands on each nanocrystal surface adjust their position which means a rod-shaped crystal will turn into a dot-shaped one. Ligand concentration also affects the size distribution of QDs. At higher ligand concentrations, the smaller particles grow faster than the larger ones, resulting in a nearly monodisperse size distribution. If the ligand concentration drops below a critical threshold, small QDs are depleted as larger ones grow and the distribution broadens similar to Ostwald ripening. Thus, the preparation of nearly monodisperse spherical QDs is best achieved at a high ligand concentration.

Manipulation of the growth kinetics can offer further control over the shape of QDs. This is possible because the growth of CdSe QDs is highly anisotropic when the system is kinetically over-driven by a high ligand concentration. In addition to being anisotropic, CdSe has a unique $c$-axis which leads to faster growth along this axis when the overall growth rate is fast. When the growth rate is slow, a nearly spherical shape that minimizes surface area is favored. A slow reaction rate is preferred because it forms the thermodynamically favored sphere rather than the kinetically favored rod.
In addition to the experimental conditions discussed above, the precursor ratio (amount of Cd compared to amount of Se) plays a significant role in determining the emission properties of the synthesized QDs. In a study by Qu and Peng, Cd:Se ratios were varied between 2:1 and 1:10 to determine effect of initial precursor concentrations. From their study it was concluded that the highest quantum yields resulted when there was an excess of one of the precursors. When either one of the precursors was initially in excess, the concentration of the reacting species in the solution was considered constant after the growth reaction proceeded for a short period of time. This provided a desirable condition for the construction of the most favorable surface structure/reconstruction for the QDs in solution. Thus, an excess of one of the precursors, either Cd or Se, is required to produce QDs with high quantum efficiency.

2.4.3 Effect of Ligands on the Synthesis of QDs

The quality of QD cores produced is also dependent on the molecule that binds to the central metal atom of the QD core by some attractive interaction, (chemisorption, electrostatic attraction, or hydrophobic interaction). This molecule is called a ligand. Typical CdSe QDs have a diameter between 2 nm to 5 nm, with approximately 100 to 1600 CdSe ion pairs, and approximately 40 to 250 capping ligands on the QDs surface. Ligands play at least four distinct roles in the overall electronic function of the QDs. First, they are present during the nucleation process and determine the reactivity and availability of the crystal precursors and ligands. Second, they control the rate of
growth and final particle size distribution\textsuperscript{50} by keeping the particles isolated and facilitating homogenous growth during synthesis.\textsuperscript{19} Third, they provide colloidal stability, preventing aggregation and growth.\textsuperscript{31,50,51} Lastly, they interact electronically with surface sites and may passivate defects on the surface of QDs.\textsuperscript{19}

Defects exist on the surface of QDs due to the large surface-to-volume ratio of QDs\textsuperscript{45,52,53} which causes the formation of dangling bonds from some of the surface atoms.\textsuperscript{7} Ligands serve to donate electrons to, or accept electrons from, these dangling bonds of incompletely coordinated metal ions (Cd\textsuperscript{2+} sites are electron acceptors, and Se\textsuperscript{2-} are electron donors) in order to preserve the core character of the QD.\textsuperscript{53,54} The surface defects often act as nonradiative recombination sites for electron-hole pairs produced by incident excitation light, thereby reducing the quantum efficiency of the QDs.\textsuperscript{7,55} In CdSe QDs, these nonradiative traps are positioned above the valence band.\textsuperscript{45} Ligands passivate varying amounts of these surface defects to influence the quantum efficiency of the QDs. If the surface ligand provides good passivation of surface defects, high quantum efficiency is expected.

The nature and density of the surface trapping sites depends strongly on the surface structure and shape of the QD, along with the nature of the defect sites on the QD surface.\textsuperscript{7,31} Furthermore, the atomic configuration of the QD surface significantly affects the degree of passivation provided by the ligands.\textsuperscript{7} This can be visualized by considering the steric effect of the surface configuration of the QDs on the packing of the surface ligands.\textsuperscript{7} Thus, the surface structure of QDs also plays a role in determining quantum
yield. The shape of the QD dictates the number of atoms on the QD surface and therefore the number of potential surface trapping sites. Figure 2.4 below illustrates the fraction of surface atoms on a CdSe QD for different shapes. Spherical QDs have the smallest number of total surface atoms and are thermodynamically the most stable\textsuperscript{56}. It is estimated that approximately 56\% of the atoms in a 3 nm spherical QD are at the surface.\textsuperscript{54} On the other hand, elongated structures, such as rods and wires, maintain a larger fraction of their constituent atoms on their surfaces. Thus, spherical particles have the least amount of potential defect sites on their surface causing them to have the highest quantum yield potential and therefore be the most desirable.

Figure 2.4. Fractions of atoms on the CdSe QD surface plotted against the total number of atoms. The wires (purple) are 1 \(\mu\)m in length, the disks (green) are 20 nm in length, and the spheres (blue) and rods (red) are 4 nm in diameter.\textsuperscript{56}

Because ligands play such a vital role on the overall quality of QDs, numerous efforts have been made to synthesize high quality spherical CdSe QDs using different capping ligands. Although there are several different types of ligands, this thesis
investigates the effect of two, oleic acid (OA) and oleylamine, which are discussed in further detail below.

2.4.3.1 Oleic Acid (OA)

As described above, a popular method of producing QD cores via the organometallic method involves the use of tri-n-octylphosphine oxide (TOPO) as the ligand of choice. Although nearly monodisperse QDs with high quantum yield were obtained with TOPO, it is expensive, hazardous, and toxic. Additionally, due to varying amounts of impurities in commercially obtained TOPO, it is difficult to consistently produce high-quality QDs using various TOPO batches. Oleic acid (OA) was chosen instead of TOPO as one of the ligands investigated in this thesis as it is an environmentally friendly, cheaper, and a safer capping ligand.

Research has shown that OA can yield much more stable QDs than other saturated fatty acids. This higher stability is attributed to the amorphous structure of the ligand layer which is less permeable to oxygen than a crystalline ligand layer. More specifically, crystalline packing of the hydrocarbon chains of the ligand creates gaps between each crystalline domain. These gaps act as the diffusion channels for oxygen molecules, consequently making the QDs less stable if they are coated with ligands with a saturated hydrocarbon chain. The stability of OA is also attributed to the double bond and associated ‘kink’ in its alkyl chain which serves to impart colloidal stability. Oleic acid further provides better protection against oxidation and emission loss than other
ligands with 18 carbons, including stearic acid and octadecylamine (ODA).\textsuperscript{19} This higher stability of QDs capped with OA was attributed to the amorphous structure of the OA ligand layer.\textsuperscript{19}

\textbf{2.4.3.2 Oleylamine}

In a study conducted by Talapin et al. it was found that smaller QDs with better size distributions were achieved when amines (such as oleylamine) were used as stabilizing and size-regulating ligands than the commonly used TOPO.\textsuperscript{45} Additionally, amines provided much better passivation of the defects on the surface of QDs leading to non-radiative recombination.\textsuperscript{45} Research has consistently shown that for both CdS and CdSe QDs, direct interaction between the QD surface and amine ligand effectively passivates the QD surface and blocks the trapping of electrons at the defect sites therefore leading to high quantum efficiency.\textsuperscript{60} The use of amines as capping ligands on CdSe QDs has also been shown to result in a surface reconstruction, specifically a lattice contraction during growth, which also may contribute to the elevated quantum efficiency.\textsuperscript{42}

The proper choice of amine is important in producing high quality QDs. In general, less sterically hindered amines create higher capping densities, which leads to improved surface capping and, hence, better passivation of traps.\textsuperscript{45} The boiling point of the chosen amine is also of importance as it can potentially limit its use. For example, the relatively low boiling point (~175 °C) of octylamine prevents its use in CdSe QD reactions, as they require a temperature of approximately 300 °C.\textsuperscript{45} Octylamine was
further ruled out as a capping ligand because QDs were found to have a tendency to partially precipitate from solution during heating.\textsuperscript{45} The use of secondary amines (including dioctylamine) was also found to be inadequate for QD synthesis because they resulted in a very weak stabilization and poorly controlled growth of the QDs.\textsuperscript{45} For this thesis, the amine ligand of choice was oleylamine because it has been shown to produce high quality QDs, is cost effective, and safe to handle.

During the synthesis of QDs, the trioctylphosphine (TOP) and chalcogenide (either Se or S) solution is rapidly injected into the ligand and cadmium precursor solution to begin the growth process of the QD core. After this injection, the solution color may change based on ligand stability. For example, the TOPSe/TOP S solution is very stable in oleylamine due to hydrogen bonding, therefore the color is not expected to change.\textsuperscript{61} Because oleylamine is a very stable ligand, the growth rate of the QDs is much slower, resulting in spherical nanoparticles with a uniform size distribution.\textsuperscript{61} FTIR spectra on oleylamine-capped CdSe QDs suggested that oleylamine binds through donation of the lone pair of electrons from the nitrogen atom to both cadmium and selenium surface sites.\textsuperscript{42} Amines are expected to bind to selenium sites preferentially over cadmium sites due to the higher binding energy for selenium terminated sites over cadmium terminated sites, 1.05 eV compared to 0.91 eV, respectively.\textsuperscript{42}
2.4.4 Effect of Solvent

2.4.4.1 Non-Coordinating Solvent

The non-coordinating solvent mixture strongly affects nucleation, which in turn affects QD growth. This thesis investigates the effect of the coordinating properties of two different solvents when coupled with oleic acid: non-coordinating octadecene (ODE), and weakly-coordinating trioctylamine (TOA).

Octadecene is a non-coordinating solvent that provides an environment for particle nucleation and growth.\textsuperscript{40,62} ODE has a relatively low melting point (below 20 °C), relatively high boiling point (about 320 °C), low cost, low toxicity, low reactivity to precursors, and excellent solvation power for many compounds at elevated temperatures.\textsuperscript{62,63} Each of these factors makes ODE an ideal solvent for the growth of high-quality QDs. Research has shown that nucleation of CdSe QDs from ODE is very fast and stops almost immediately after precursor injection.\textsuperscript{40,62} It is estimated that when ODE is used, nucleation and growth is completed within the first 100 s of the reaction.\textsuperscript{40} Because nucleation and growth happen so fast, QDs with a very narrow size distribution are formed in the presence of ODE. Additionally, it has been found that QDs prepared in ODE had a spherical shape.\textsuperscript{61}

In a study where CdS QDs were formed in the presence of OA coupled with ODE, the amount of nuclei formed during the reaction could be controlled.\textsuperscript{42} When too many nuclei were formed, the size distribution of QDs was defocused due to Ostwald ripening.\textsuperscript{42} Conversely, when there were too few nuclei, particle growth was too fast to
reach the required size distribution. The balance between these two extremes was able to be achieved by altering the concentration of the capping ligand (OA) and thus the amount of metal complex available for the reaction through control of the amount of ODE. Using ODE as a solvent also allows control over particle size, making it further advantageous.

Unlike ODE, TOA is a weakly-coordinating solvent, therefore it contains some coordinating groups. Similar to ODE, research has shown that in the presence of TOA, spherical QDs formed. Although little literature exists on TOA, this thesis sets out to compare the quantum yield of QDs prepared in the presence of TOA to those prepared in ODE.

2.4.4.2 Dispersion Solvent

Depending on the application, QDs may need to be suspended in a particular solvent. For example, biomedical applications typically require aqueous environments. Quantum dots synthesized from the wet chemistry method are soluble in water and other polar solvents. Those made from the organometallic synthesis, on the other hand, are soluble in a variety of volatile non-polar organic solvents because of the residual non-polar organic ligands bonded to the QD surface. The QDs studied in this thesis were synthesized via the organometallic method, therefore the focus of this section will be on non-polar solvents, specifically chloroform and toluene.
The dispersion solvent has an effect on the optical properties of the QDs. In a study conducted by Bullen et al., it was observed that chloroform yielded greater photoluminescence intensity than toluene. This difference in photoluminescence may be due to changes in the dissolved oxygen concentration in the different solvents. Oxygen is more soluble in chloroform than toluene. The concentration of oxygen at 20 °C is 8.63 mM in toluene and 11.6 mM in chloroform. This suggests that the primary effect of solvent changes is to alter the degree of adsorption of passivating ligands on the QD surfaces. When the solvent in which the QDs are dissolved is altered, the adsorption isotherm adjusts. If the ligand is more soluble in the new medium, desorption occurs. If the ligand is less soluble, it will tend to adsorb from solution and may enhance the luminescence even further. The as synthesized QDs with OA and oleylamine as the capping ligands are non-polar. Consequently, QDs are more soluble in nonpolar solvents such as toluene, hardly soluble in chloroform, and insoluble in n-butanol and water. In other words, because the QDs are less soluble in chloroform than toluene, it is expected that they will exhibit higher quantum efficiency when dissolved in chloroform.

Quantum dot concentration in a dispersion solvent affects quantum efficiency. In general, the more concentrated the QD concentration, the higher the quantum efficiency. This trend is explained by the effect of dilution on the surface chemistry of the QD. Assuming a simple reversible equilibrium exists between ligands adsorbed to the QD surface and free ligands in solution, a proposed reaction is:

\[
[Cd–L] \rightleftharpoons [Cd] + [L]
\] (1)
where \([\text{Cd–L}]\) is the concentration of Cd sites bound to ligand in solution, \([\text{Cd}]\) is the concentration of empty binding sites, and \([L]\) is the concentration of free ligand in solution.\(^{66}\) Because the proposed reaction is reversible, after dilution in a solvent the QDs and ligands should re-establish equilibrium and the fraction of bound surface sites should decrease.\(^{66}\) For this reason, decreased quantum efficiency is expected with decreasing QD concentration.\(^{66}\)

2.4.5 *Separation of Cores from Reaction Solution*

After synthesis, it is possible to precipitate QDs of a specific size from solution through the addition of methanol. The addition of methanol increases the average polarity of the solvent and reduces the energetic barrier to flocculation.\(^{8}\) Flocculation differs from precipitation because the colloids are suspended in a liquid prior to separation rather than actually dissolved in the solution. The largest particles in a dispersion experience the greatest attractive forces and therefore have a higher probability of overcoming the reduced barrier.\(^{8}\) For this reason, the large particles are enriched in the flocculate produced and it is possible to remove a specific subset of particles from the solution.\(^{8}\) In this thesis, methanol was used to precipitate cores of a specific size distribution.

2.5 *Surface Treatment*

As previously explained, the surface of QDs is coated with passivating ligands that stabilize the growing particle, sustain their dispersion in solution, and minimize the
number of surface atoms with reduced coordination number. Often, the surface coverage is incomplete and the unbound surface atoms constitute a distribution of localized sites that carry slight positive or negative charge. These sites act as inhomogeneous defects and are capable of trapping electrons or holes, preventing their radiative recombination and lowering the quantum efficiency. In addition to proper choice of ligand, these defect sites can be passivated through the addition of a reducing or oxidizing agent.

In a specific instance, Jang treated cadmium sulfide (CdS) QDs with sodium borohydride (NaBH₄). Sodium borohydride is a widely used reducing agent that is both inexpensive and safe with regards to storage and handling. The quantum efficiency of the CdS QDs increased from 1.4 % to 78 % after treatment, which is a 54 fold improvement. Additionally, they found that the shape and size of the QDs did not change after treatment, according to transmission electron microscopy (TEM) images. Figure 2.5 illustrates these findings. Jang and coworkers concluded that treatment of the QDs with NaBH₄ caused oxidation of the QD surfaces. The NaBH₄ reduced the oleic acid surfactants to the corresponding alcohols or sodium salts which caused the ligands to lose their coordinating properties and detach from the nanocrystal surface. Oxygen (from atmospheric air) then diffused to the exposed cadmium on the QD surface to form a cadmium oxide (CdO) layer around the CdS QD surface. This CdO layer effectively passivated the surface defects, resulting in a nanocrystal with an enhanced quantum yield. They further concluded that because the treatment was independent of reaction
conditions and reagents, it would have similar effects for other II-VI QDs (including CdSe).\textsuperscript{70}

Jang et al. expanded on their work to include cadmium telluride (CdTe) QDs produced via the wet-chemistry method. Ma et al. found that after NaBH\textsubscript{4} surface treatment, the photostability of the QDs as well as the quantum efficiency were improved.\textsuperscript{71} These results successfully demonstrated that the NaBH\textsubscript{4} treatment can be extended to water-soluble QDs because NaBH\textsubscript{4} is also water-soluble.\textsuperscript{71} With their data, they generated an XPS spectrum which confirmed that a CdO layer formed around the QD surface, as proposed by Jang.\textsuperscript{71} Due to the formation of this CdO layer, the surface defects were effectively passivated and the quantum efficiency of the treated cores was double that of the untreated cores.\textsuperscript{71} This increased quantum efficiency was justified due
to the fact that CdO has a valence binding energy of 5.4 eV, which is higher than the CdTe bandgap energy ($E_g = 1.44$ eV), therefore resulting in effective surface passivation.\textsuperscript{71} Surface treatment did not change the size of the QDs (and therefore color emitted), however, as confirmed by the consistency of the peak wavelength (585 nm) and bandwidth (40 nm) of the treated and untreated cores.\textsuperscript{71}

The CdO layer formed on the QD surface was also shown to shield the oxygen molecules from interacting with the QD core and preventing photo-oxidation.\textsuperscript{71} A total internal reflection fluorescence microscope (TIRFM) quantitatively illustrated that the original QDs were notably photobleached, while those treated with NaBH$_4$ were much more photostable.\textsuperscript{71} The decay times were estimated to be 5.4 s and 32.7 s, for untreated and treated QDs, respectively, providing further evidence of the photostability of QDs by surface treatment.\textsuperscript{71} Good photostability of QDs is required for their application as fluorescent probes to label targets in biological systems, specifically for experiments with long-term imaging.\textsuperscript{71}

In the surface treatment of QDs, the amount of NaBH$_4$ added as well as the reaction time is very important. An excess amount of NaBH$_4$ and/or prolonged reaction time can result in the detachment of ligands from the QD core, resulting in the aggregation and precipitation of QDs.\textsuperscript{71} Because of this strong dependence, these two reaction parameters will be explored in this thesis. Additionally, this thesis will evaluate the effect of other reducing agents (including calcium hydride (CaH$_2$) and hydrazine (N$_2$H$_4$)), as well as two oxidizing agents (including benzoyl peroxide (C$_{14}$H$_{10}$O$_4$) and tert-
butyl hydroperoxide (C$_4$H$_{10}$O$_2$) to develop more robust methods to alter the surface chemistry of CdSe and CdS QDs.
2.6 References


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Chapter 3. Materials and Methods

Chapter 3 will summarize the materials used and experimental methods practiced to complete the experimental work of this thesis. Specifically, this chapter is divided into several sections that will present the procedures used to synthesize CdSe and CdS QDs from two different ligands (oleylamine and oleic acid) as well as two non-coordinating solvents (octadecence (ODE) and trioctylamine (TOA)). Methods used to treat the surface of the as-synthesized QDs with various reducing/oxidizing agents will then be presented followed by the characterization techniques applied to evaluate the effect of each surface treatment. Lastly, the methods which quantum yield and bandgap energy ($E_g$) were calculated are presented.

3.1 Materials

3.1.1 Quantum Dot Core Synthesis with Oleylamine

The materials used to synthesize quantum dot cores include a glass vial (5 mL), plastic cap for the vial, a 50 mL round-bottom flask, a 50 mL centrifuge tube, 5 mL Norm-Ject® disposable syringes, syringe needles (21 G x 1½ in from Becton-Dickinson), stir bars, selenium (Acros Organics, 99.5+%), sulfur (E.M. Science), dihydrate cadmium acetate (Sigma-Aldrich, reagent grade, 98%), trioctylphosphine (TOP) (Sigma-Aldrich, 90%), oleylamine (Aldrich Chemical Company), and methanol (Aldrich Chemical Company, 99+%). A CEM microwave (Discover System Model, 908005) was used to heat the solution and facilitate the reaction. A Thermo Electron Corporation centrifuge
(Centra CL5R) and centrifuge tubes were used to separate the cores from solution, an Entela ultraviolet light (UVGL) was used to provide a long-wave (365 nm) ultraviolet light to test sample fluorescence, and a Shel Lab vacuum oven was used to dry the sample.

3.1.2 Quantum Dot Core Synthesis with Oleic Acid and ODE

The materials used to synthesize quantum dot cores include a glass vial (5 mL), plastic cap for the vial, a 50 mL round-bottom flask, a 50 mL centrifuge tube, 5 mL Norm-Ject® disposable syringes, syringe needles (21 G x 1½ in from Becton-Dickinson), stir bars, selenium (Acros Organics, 99.5+%), sulfur (E.M. Science), dihydrate cadmium acetate (Sigma-Aldrich, reagent grade, 98%), trioctylphosphine (TOP) (Sigma-Aldrich, 90%), oleic acid (Aldrich Chemical Company), octadecene (ODE) (Sigma-Aldrich, technical grade, 90%), and methanol (Aldrich Chemical Company, 99+%). A CEM microwave (Discover System Model, 908005) was used to heat the solution and facilitate the reaction. A Thermo Electron Corporation centrifuge (Centra CL5R) and centrifuge tubes were used to separate the cores from solution, an Entela ultraviolet light (UVGL) was used to provide a long-wave (365 nm) ultraviolet light to test sample fluorescence, and a Shel Lab vacuum oven was used to dry the sample.
3.1.3 Quantum Dot Core Synthesis with Oleic Acid and TOA

The materials used to synthesize quantum dot cores include a glass vial (5 mL), plastic cap for the vial, a 50 mL round-bottom flask, a 50 mL centrifuge tube, 5 mL Norm-Ject® disposable syringes, syringe needles (21 G x 1½ in from Becton-Dickinson), stir bars, selenium (Acros Organics, 99.5+%), sulfur (E.M. Science), dihydrate cadmium acetate (Sigma-Aldrich, reagent grade, 98%), trioctylphosphine (TOP) (Sigma-Aldrich, 90%), oleic acid (Aldrich Chemical Company), trioctylamine (TOA) (Aldrich, 98%), and methanol (Aldrich Chemical Company, 99+%). A CEM microwave (Discover System Model, 908005) was used to heat the solution and facilitate the reaction. A Thermo Electron Corporation centrifuge (Centra CL5R) and centrifuge tubes were used to separate the cores from solution, an Entela ultraviolet light (UVGL) was used to provide a long-wave (365 nm) ultraviolet light to test sample fluorescence, and a Shel Lab vacuum oven was used to dry the sample.

3.1.4 Surface Treatment with Reducing/Oxidizing Agents

The materials used to treat the QD cores with various reducing and oxidizing agents include 7 mL glass vials, a 1,000 µL Eppendorf pipette, pipette tips, spectroscopic grade toluene (J.T. Baker), and spectrophotometric grade chloroform (Sigma-Aldrich, 99.8%). The reducing agents used include sodium borohydride (NaBH₄) (Sigma-Aldrich, 98.5%), benzoyl peroxide (C₁₄H₁₀O₄) (Aldrich, 97%), calcium hydride (CaH₂) (Sigma-Aldrich, 90-95%), tert-butyl hydroperoxide (C₄H₁₀O₂) (Aldrich, 70 wt% in water), and
hydrazine (N₂H₄) (Sigma-Aldrich, 98%). Ultra-violet visible spectroscopy (UV-Vis) and fluorescence spectroscopy were performed using a Spectramax M5 Multi-Mode Microplate Reader (Molecular Devices) to measure sample absorbance and fluorescence, respectively. A Rotovapor R-210 (Buchi) was used to remove various solvents to isolate the cores. Lastly, a Entela ultraviolet light (UVGL) was used to provide a long-wave (365 nm) ultraviolet light to test sample fluorescence.

3.2 Methods

3.2.1 CdSe Quantum Dot Core Synthesis with Oleylamine

The first step in the synthesis of CdSe quantum dot cores with oleylamine involves carrying out two reactions in parallel. The first reaction is between selenium and trioctylphosphine (TOP); the second is cadmium acetate with oleylamine (Figure 3.1).

Figure 3.1. Synthetic scheme for the synthesis of CdSe quantum dot cores with oleylamine.
The Se/TOP reaction was carried out in a flame-dried 5 mL glass vial while the other reaction was carried out in a 50 mL round-bottom flask. Both reaction vessels were capped to ensure that the environment was rid of oxygen and water. The liquids were transferred from storage bottles to their respective glassware using 5 mL Norm-Ject® disposable syringes and syringe needles. The quantity of reactants used in the reactions was dependent on the batch size (see Table 3.1 below).

Table 3.1. Quantity of reactants required for various batch sizes.

<table>
<thead>
<tr>
<th>Batch Size</th>
<th>Selenium (g)</th>
<th>TOP (mol x 10^4 mL)</th>
<th>Cadmium Acetate (g)</th>
<th>Oleylamine (mol x 10^4 mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1X</td>
<td>0.008</td>
<td>1.06</td>
<td>0.04</td>
<td>0.94</td>
</tr>
<tr>
<td>2X</td>
<td>0.015</td>
<td>1.87</td>
<td>0.70</td>
<td>1.57</td>
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<tr>
<td>5X</td>
<td>0.039</td>
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<td>2.00</td>
<td>44.8</td>
</tr>
<tr>
<td>10X</td>
<td>0.077</td>
<td>9.75</td>
<td>4.00</td>
<td>89.7</td>
</tr>
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</table>

The solids in both solutions were dissolved by gently swirling with heating. It was important not to boil the solution during this step. Once the solids completely dissolved, a stir bar was added to the vial containing the Se/TOP mixture and placed in the CEM microwave at the settings summarized below. The settings of the CEM microwave were controlled by Synergy software.

a. Temperature: 120 °C  
b. Power: 300 Watts  
c. Ramp Time: 2 min  
d. Hold Time: 30 s  
e. Stirring: High
Once the reaction was complete, the vial was removed from the microwave. A stir bar was added to the round-bottom flask containing the oleylamine and cadmium acetate mixture and placed in the microwave. As with reactant quantities, the microwave settings were adjusted with batch size (see Table 3.2). During the reaction, the round-bottom flask was purged with dry nitrogen.

### Table 3.2. Microwave settings for various batch sizes.

<table>
<thead>
<tr>
<th>Batch Size</th>
<th>Step</th>
<th>Power (W)</th>
<th>Temperature (°C)</th>
<th>Ramp (min)</th>
<th>Hold (min)</th>
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<td>160</td>
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<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>150</td>
<td>2:00</td>
<td>1:30</td>
</tr>
</tbody>
</table>

When the temperature of the reaction reached 120 °C during the second heating step, the microwave was paused and the pre-heated Se/TOP mixture was injected into the round-bottom flask using a disposable syringe and needle. After the reaction was complete and the round-bottom flask cooled to room temperature, the solution was examined under the UV long-wave light to ensure that it fluoresced. Based on the settings specified in the above table, the cores will fluoresce a yellow or reddish color.

The excess oleylamine and unreacted cadmium precursor were separated from the QDs by extraction of the reaction solution with a volume of methanol equivalent to 4
times the reaction volume (reaction solution:methanol = 1:4) in a centrifuge tube. The centrifuge tube was gently shaken to start this precipitation before being placed in the Thermo Electron Corporation centrifuge. A centrifuge tube containing water of an equal volume was placed opposite the solution in the blue centrifuge tube holder. The centrifuge was run for 5 min at a 25 °C and a speed of 4500 relative centrifugal force (RCF). Once the separation was complete, the QD cores were visibly separated from the methanol. The methanol was then poured from the tube and disposed. Finally, the newly synthesized cadmium selenide cores were dried over night under vacuum (4000 Pa) at room temperature.

3.2.2 CdS Quantum Dot Core Synthesis with Oleylamine

The first step in the synthesis of CdS quantum dot cores with oleylamine involves carrying out two reactions in parallel. The first reaction is between sulfur and trioctylphosphine (TOP); the second is cadmium acetate with oleylamine (see Figure 3.2).

![Synthetic scheme for the synthesis of CdS quantum dot cores with oleylamine.](image)
The S/TOP reaction was carried out in a flame-dried 5 mL glass vial while the other reaction was carried out in a 50 mL round-bottom flask. Both reaction vessels were capped to ensure that the environment was rid of oxygen and water. The liquids were transferred from storage bottles to their respective glassware using 5 mL Norm-Ject® disposable syringes and syringe needles. The quantity of reactants used in the reactions was dependent on the batch size (see Table 3.3 below).

<table>
<thead>
<tr>
<th>Batch Size</th>
<th>Sulfur g</th>
<th>TOP ml</th>
<th>Cadmium Acetate g</th>
<th>Oleylamine mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1X</td>
<td>0.008</td>
<td>2.62</td>
<td>0.040</td>
<td>0.897</td>
</tr>
<tr>
<td>2X</td>
<td>0.015</td>
<td>4.61</td>
<td>0.700</td>
<td>15.7</td>
</tr>
<tr>
<td>5X</td>
<td>0.039</td>
<td>12.0</td>
<td>2.00</td>
<td>44.8</td>
</tr>
<tr>
<td>10X</td>
<td>0.077</td>
<td>24.0</td>
<td>4.00</td>
<td>89.7</td>
</tr>
</tbody>
</table>

The solids in both solutions were dissolved by gently swirling with heating. It was important not to boil the solution during this step. Once the solids completely dissolved, a stir bar was added to the vial containing the S/TOP mixture and placed in the CEM microwave at the settings summarized below. The settings of the CEM microwave were controlled by Synergy software.

a. Temperature: 120 °C
b. Power: 300 Watts
c. Ramp Time: 2 min
d. Hold Time: 30 s
e. Stirring: High
Once the reaction was complete, the vial was removed from the microwave. A stir bar was added to the round-bottom flask containing the oleylamine and cadmium acetate mixture and placed in the microwave. As with reactant quantities, the microwave settings were adjusted with batch size (see Table 3.4). During the reaction, the round-bottom flask was purged with dry nitrogen.

<table>
<thead>
<tr>
<th>Batch Size</th>
<th>Step</th>
<th>Power (W)</th>
<th>Temperature (°C)</th>
<th>Ramp (min)</th>
<th>Hold (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>2:00</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>160</td>
<td>1:30</td>
<td>0:30</td>
</tr>
<tr>
<td>2X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>2:00</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>160</td>
<td>1:30</td>
<td>0:30</td>
</tr>
<tr>
<td>5X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>3:00</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>175</td>
<td>2:00</td>
<td>1:30</td>
</tr>
<tr>
<td>10X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>3:00</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>200</td>
<td>2:00</td>
<td>1:30</td>
</tr>
</tbody>
</table>

When the temperature of the reaction reached 120 °C during the second heating step, the microwave was paused and the pre-heated S/TOP mixture was injected into the round-bottom flask using a disposable syringe and needle. After the reaction was complete and the round-bottom flask cooled to room temperature, the solution was examined under the UV long-wave light to ensure that it fluoresced. Based on the settings specified in the above table, the cores will fluoresce a yellow color.

The excess oleylamine and unreacted cadmium precursor were separated from the QDs by extraction of the reaction solution with a volume of methanol equivalent to 4
times the reaction volume (reaction solution:methanol = 1:4) in a centrifuge tube. The centrifuge tube was gently shaken to start this precipitation before being placed in the Thermo Electron Corporation centrifuge. A centrifuge tube containing water of an equal volume was next placed opposite the solution in the blue centrifuge tube holder. The centrifuge was run for 5 min at a 25 °C and a speed of 4500 relative centrifugal force (RCF). Once the separation was complete, the QD cores were visibly separated from the methanol. The methanol was then poured from the tube and disposed. Finally, the newly synthesized CdS cores were dried over night under vacuum (4000 Pa) at room temperature.

3.2.3 CdSe Quantum Dot Core Synthesis with Oleic Acid and Octadecene

The first step in the synthesis of CdSe quantum dot cores with oleic acid (OA) and octadecene (ODE) involves carrying out two reactions in parallel. The first reaction is between selenium and trioctylphosphine (TOP); the second is cadmium acetate, OA, and ODE (see Figure 3.3).

Figure 3.3. Synthetic scheme for the synthesis of CdSe quantum dot cores with OA and ODE.
The Se/TOP reaction was carried out in a flame-dried 5 mL glass vial while the other reaction was carried out in a 50 mL round-bottom flask. Both reaction vessels were capped to ensure that the environment was rid of oxygen and water. The liquids were transferred from storage bottles to their respective glassware using 5 mL Norm-Ject® disposable syringes and syringe needles. The quantity of reactants used in the reactions was dependent on the batch size (see Table 3.5 below).

Table 3.5. Quantity of reactants required for various batch sizes.

<table>
<thead>
<tr>
<th>Batch Size</th>
<th>Selenium</th>
<th>TOP</th>
<th>Cadmium Acetate</th>
<th>OA</th>
<th>ODE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g \times 10^4</td>
<td>mL</td>
<td>g \times 10^4</td>
<td>mL</td>
<td>g \times 10^2</td>
</tr>
<tr>
<td>1X</td>
<td>0.008</td>
<td>1.06</td>
<td>0.04</td>
<td>0.897</td>
<td>0.025</td>
</tr>
<tr>
<td>2X</td>
<td>0.015</td>
<td>1.87</td>
<td>0.70</td>
<td>15.7</td>
<td>0.050</td>
</tr>
<tr>
<td>5X</td>
<td>0.039</td>
<td>4.88</td>
<td>2.00</td>
<td>44.8</td>
<td>0.125</td>
</tr>
<tr>
<td>10X</td>
<td>0.077</td>
<td>9.75</td>
<td>4.00</td>
<td>89.7</td>
<td>0.250</td>
</tr>
</tbody>
</table>

The solids in both solutions were dissolved by gently heating. It was important not to boil the solution during this step. Once the solids completely dissolved, a stir bar was added to the vial containing the Se/TOP mixture and placed in the CEM microwave at the settings summarized below. The settings of the CEM microwave were controlled by Synergy software.

a. Temperature: 120 °C
b. Power: 300 Watts
c. Ramp Time: 2 min
d. Hold Time: 30 s
e. Stirring: High
Once the reaction was complete, the vial was removed from the microwave. A stir bar was added to the round-bottom flask containing the OA, ODE, and cadmium acetate mixture and placed in the microwave. As with reactant quantities, the microwave settings were adjusted with batch size (see Table 3.6). During the reaction, the round-bottom flask was purged with nitrogen.

<table>
<thead>
<tr>
<th>Batch Size</th>
<th>Step</th>
<th>Power (W)</th>
<th>Temperature (°C)</th>
<th>Ramp (min)</th>
<th>Hold (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>2:00</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>160</td>
<td>1:30</td>
<td>0:30</td>
</tr>
<tr>
<td>2X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>2:00</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>160</td>
<td>1:30</td>
<td>0:30</td>
</tr>
<tr>
<td>5X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>3:00</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>150</td>
<td>2:00</td>
<td>1:30</td>
</tr>
<tr>
<td>10X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>3:00</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>150</td>
<td>2:00</td>
<td>1:30</td>
</tr>
</tbody>
</table>

When the temperature of the reaction reached 120 °C, the microwave was paused and the pre-heated Se/TOP mixture was injected into the round-bottom flask using a disposable syringe and needle. After the reaction was complete and the round-bottom flask cooled to room temperature, the solution was examined under the UV long-wave light to ensure that it fluoresced. Based on the settings specified in the above table, the cores will fluoresce a yellowish color.

The excess OA and unreacted cadmium precursor were separated from the QDs by extraction of the reaction solution with a volume of methanol equivalent to 4 times the
reaction volume (reaction solution:methanol = 1:4) in a centrifuge tube. The centrifuge tube was gently shaken to start the precipitation, the cap was removed from the tube, and the solution was left until it separated into two distinct layers. The top layer composed of methanol and excess unreacted ligand was removed from the centrifuge tube and discarded using a pipette. Following the same procedure, the QD cores were washed a second time with methanol. Finally, the newly synthesized CdSe cores were dried overnight under vacuum (4000 Pa) at room temperature.

3.2.4 CdS Quantum Dot Core Synthesis with Oleic Acid and Octadecene

The first step in the synthesis of CdS quantum dot cores with oleic acid (OA) and octadecene (ODE) involves carrying out two reactions in parallel. The first reaction is between sulfur and trioctylphosphine (TOP); the second is cadmium acetate, OA, and ODE (see Figure 3.4).

![Figure 3.4. Synthetic scheme for the synthesis of CdS quantum dot cores with OA and ODE.](image-url)
The S/TOP reaction was carried out in a flame-dried 5 mL glass vial while the other reaction was carried out in a 50 mL round-bottom flask. Both reaction vessels were capped to ensure that the environment was rid of oxygen and water. The liquids were transferred from storage bottles to their respective glassware using 5 mL Norm-Ject® disposable syringes and syringe needles. The quantity of reactants used in the reactions was dependent on the batch size (see Table 3.7 below).

Table 3.7. Quantity of reactants required for various batch sizes.

<table>
<thead>
<tr>
<th>Batch Size</th>
<th>Sulfur g</th>
<th>Sulfur mol x 10^4</th>
<th>TOP mL</th>
<th>TOP mol x 10^4</th>
<th>Cadmium Acetate g</th>
<th>Cadmium Acetate mol x 10^4</th>
<th>OA mL</th>
<th>OA mol x 10^2</th>
<th>ODE mL</th>
<th>ODE mol x 10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1X</td>
<td>0.008</td>
<td>2.62</td>
<td>0.04</td>
<td>0.897</td>
<td>0.025</td>
<td>0.938</td>
<td>1.00</td>
<td>0.317</td>
<td>0.50</td>
<td>1.56</td>
</tr>
<tr>
<td>2X</td>
<td>0.015</td>
<td>4.61</td>
<td>0.70</td>
<td>15.7</td>
<td>0.050</td>
<td>1.88</td>
<td>2.00</td>
<td>0.634</td>
<td>1.00</td>
<td>3.13</td>
</tr>
<tr>
<td>5X</td>
<td>0.039</td>
<td>12.0</td>
<td>2.00</td>
<td>44.8</td>
<td>0.125</td>
<td>4.69</td>
<td>5.00</td>
<td>1.58</td>
<td>2.50</td>
<td>7.81</td>
</tr>
<tr>
<td>10X</td>
<td>0.077</td>
<td>24.0</td>
<td>4.00</td>
<td>89.7</td>
<td>0.250</td>
<td>9.38</td>
<td>10.0</td>
<td>3.15</td>
<td>5.00</td>
<td>15.6</td>
</tr>
</tbody>
</table>

The solids in both solutions were dissolved by gently swirling with heating. It was important not to boil the solution during this step. Once the solids completely dissolved, a stir bar was added to the vial containing the S/TOP mixture and placed in the CEM microwave at the settings summarized below. The settings of the CEM microwave were controlled by Synergy software.

a. Temperature: 120 °C
b. Power: 300 Watts
c. Ramp Time: 2 min
d. Hold Time: 30 s
e. Stirring: High
Once the reaction was complete, the vial was removed from the microwave. A stir bar was added to the round-bottom flask containing the OA, ODE, and cadmium acetate mixture and placed in the microwave. As with reactant quantities, the microwave settings were adjusted with batch size (see Table 3.8). During the reaction, the round-bottom flask was purged with nitrogen.

Table 3.8. Microwave settings for various batch sizes.

<table>
<thead>
<tr>
<th>Batch Size</th>
<th>Step</th>
<th>Power (W)</th>
<th>Temperature (°C)</th>
<th>Ramp (min)</th>
<th>Hold (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>2:00</td>
<td>0:10</td>
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<td></td>
<td>2</td>
<td>300</td>
<td>160</td>
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<td>0:30</td>
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<tr>
<td>2X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>2:00</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>160</td>
<td>1:30</td>
<td>0:30</td>
</tr>
<tr>
<td>5X</td>
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<td>300</td>
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<td>0:10</td>
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<td></td>
<td>2</td>
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<tr>
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<td>2</td>
<td>300</td>
<td>190</td>
<td>2:00</td>
<td>1:30</td>
</tr>
</tbody>
</table>

When the temperature of the reaction reached 120 °C during the second heating step, the microwave was paused and the pre-heated S/TOP mixture was injected into the round-bottom flask using a disposable syringe and needle. After the reaction was complete and the round-bottom flask cooled to room temperature, the solution was examined under the UV long-wave light to ensure that it fluoresced. Based on the settings specified in the above table, the cores will fluoresce a yellowish color.

The excess OA and unreacted cadmium precursor were separated from the QDs by extraction of the reaction solution with a volume of methanol equivalent to 4 times the
reaction volume (reaction solution:methanol = 1:4) in a centrifuge tube. The centrifuge tube was gently shaken to start the precipitation, the cap was removed from the tube, and the solution was left until it separated into two distinct layers. The top layer composed of methanol and excess unreacted ligand was removed from the centrifuge tube using a pipette and discarded. Following the same procedure, the QD cores were washed a second time with methanol. Finally, the newly synthesized cadmium sulfide cores were dried over night under vacuum (4000 Pa) at room temperature.

3.2.5 CdSe Quantum Dot Core Synthesis with Oleic Acid and Trioctylamine

The first step in the synthesis of CdSe QD cores with oleic acid (OA) and trioctylamine (TOA) involves carrying out two reactions in parallel. The first reaction is between selenium and trioctylphosphine (TOP); while the second is cadmium acetate, OA, and TOA (see Figure 3.5).

![Figure 3.5. Synthetic scheme for the synthesis of CdSe quantum dot cores with OA and TOA.](image)
The Se/TOP reaction was carried out in a flame-dried 5 mL glass vial while the other reaction was carried out in a 50 mL round-bottom flask. Both reaction vessels were capped to ensure that the environment was rid of oxygen and water. The liquids were transferred from storage bottles to their respective glassware using 5 mL Norm-Ject® disposable syringes and syringe needles. The quantity of reactants used in the reactions was dependent on the batch size (see Table 3.9 below).

<table>
<thead>
<tr>
<th>Batch Size</th>
<th>Selenium</th>
<th>TOP</th>
<th>Cadmium Acetate</th>
<th>OA</th>
<th>TOA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g</td>
<td>mL</td>
<td>g</td>
<td>mL</td>
<td>mol x 10⁴</td>
</tr>
<tr>
<td>1X</td>
<td>0.008</td>
<td>0.04</td>
<td>0.025</td>
<td>1.00</td>
<td>0.317</td>
</tr>
<tr>
<td>2X</td>
<td>0.015</td>
<td>0.70</td>
<td>0.050</td>
<td>2.00</td>
<td>0.634</td>
</tr>
<tr>
<td>5X</td>
<td>0.039</td>
<td>2.00</td>
<td>0.125</td>
<td>5.00</td>
<td>1.58</td>
</tr>
<tr>
<td>10X</td>
<td>0.077</td>
<td>4.00</td>
<td>0.250</td>
<td>10.0</td>
<td>3.15</td>
</tr>
</tbody>
</table>

The solids in both solutions were dissolved by gently swirling with heating. It was important not to boil the solution during this step. Once the solids completely dissolved, a stir bar was added to the vial containing the Se/TOP mixture and placed in the CEM microwave at the settings summarized below. The settings of the CEM microwave were controlled by Synergy software.

- f. Temperature: 120 °C
- g. Power: 300 Watts
- h. Ramp Time: 2 min
- i. Hold Time: 30 s
- j. Stirring: High
Once the reaction was complete, the vial was removed from the microwave. A stir bar was added to the round-bottom flask containing the OA, TOA, and cadmium acetate mixture and placed in the microwave. As with reactant quantities, the microwave settings were adjusted with batch size (see Table 3.10). During the reaction, the round-bottom flask was purged with nitrogen.

<table>
<thead>
<tr>
<th>Batch Size</th>
<th>Step</th>
<th>Power (W)</th>
<th>Temperature (°C)</th>
<th>Ramp (min)</th>
<th>Hold (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>2:00</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>160</td>
<td>1:30</td>
<td>0:30</td>
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<tr>
<td>2X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>2:00</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>160</td>
<td>1:30</td>
<td>0:30</td>
</tr>
<tr>
<td>5X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>3:00</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>150</td>
<td>2:00</td>
<td>1:30</td>
</tr>
<tr>
<td>10X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>3:00</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>150</td>
<td>2:00</td>
<td>1:30</td>
</tr>
</tbody>
</table>

When the temperature of the reaction reached 120 °C during the second heating step, the microwave was paused and the pre-heated Se/TOP mixture was injected into the round-bottom flask using a disposable syringe and needle. After the reaction was complete and the round-bottom flask cooled to room temperature, the solution was examined under the UV long-wave light to ensure that it fluoresced. Based on the settings specified in the above table, the cores will fluoresce a reddish color.

The excess OA and unreacted cadmium precursor were separated from the QDs by extraction of the reaction solution with a volume of methanol equivalent to 4 times the
reaction volume (reaction solution:methanol = 1:4) in a centrifuge tube. The centrifuge tube was gently shaken to start the precipitation, the cap was removed from the tube, and the solution was left until it separated into two distinct layers. The top layer composed of methanol was then removed from the centrifuge tube and discarded using a pipette. Following the same procedure, the QD cores were washed a second time with methanol. To separate the washed QD cores from methanol, the Thermo Electron Corporation centrifuge was used. A centrifuge tube containing water of an equal volume was placed opposite the solution in the blue centrifuge tube holder. The centrifuge was run for 5 min at a 25 °C and a speed of 4500 relative centrifugal force (RCF). Once the separation was complete, the QD cores were visibly separated from the methanol. The methanol was then poured from the tube and disposed. Finally, the newly synthesized CdSe cores were dried over night under vacuum (4000 Pa) at room temperature.

3.2.6 CdS Quantum Dot Core Synthesis with Oleic Acid and Trioctylamine

The first step in the synthesis of CdS quantum dot cores with OA and trioctylamine (TOA) involves carrying out two reactions in parallel. The first reaction is between sulfur and trioctylphosphine (TOP); while the second is cadmium acetate, OA, and TOA (see Figure 3.6).
The S/TOP reaction was carried out in a flame-dried 5 mL glass vial while the other reaction was carried out in a 50 mL round-bottom flask. Both reaction vessels were capped to ensure that the environment was rid of oxygen and water. The liquids were transferred from storage bottles to their respective glassware using 5 mL Norm-Ject® disposable syringes and syringe needles. The quantity of reactants used in the reactions was dependent on the batch size (see Table 3.11 below).

Table 3.11. Quantity of reactants required for various batch sizes.

<table>
<thead>
<tr>
<th>Batch Size</th>
<th>Sulfur</th>
<th>TOP</th>
<th>Cadmium Acetate</th>
<th>Oleic Acid</th>
<th>TOA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g</td>
<td>mol x 10^4</td>
<td>mL</td>
<td>mol x 10^4</td>
<td>g</td>
</tr>
<tr>
<td>1X</td>
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<td>0.04</td>
<td>0.897</td>
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<tr>
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<td>0.70</td>
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</tr>
<tr>
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<td>12.0</td>
<td>2.00</td>
<td>44.8</td>
<td>0.125</td>
</tr>
<tr>
<td>10X</td>
<td>0.077</td>
<td>24.0</td>
<td>4.00</td>
<td>89.7</td>
<td>0.250</td>
</tr>
</tbody>
</table>

The solids in both solutions were dissolved by gently swirling with heating. It was important not to boil the solution during this step. Once the solids completely dissolved, a
stir bar was added to the vial containing the S/TOP mixture and placed in the CEM microwave at the settings summarized below. The settings of the CEM microwave were controlled by Synergy software.

  f. Temperature: 120 °C
  g. Power: 300 Watts
  h. Ramp Time: 2 min
  i. Hold Time: 30 s
  j. Stirring: High

Once the reaction was complete, the vial was removed from the microwave. A stir bar was added to the round-bottom flask containing the oleic acid, TOA, and cadmium acetate mixture and placed in the microwave. As with reactant quantities, the microwave settings were adjusted with batch size (see Table 3.12). During the reaction, the round-bottom flask was purged with nitrogen.
Table 3.12. Microwave settings for various batch sizes.

<table>
<thead>
<tr>
<th>Batch Size</th>
<th>Step</th>
<th>Power (W)</th>
<th>Temperature (°C)</th>
<th>Ramp (min)</th>
<th>Hold (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>2:00</td>
<td>0:10</td>
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<td>2</td>
<td>300</td>
<td>160</td>
<td>1:30</td>
<td>0:30</td>
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<tr>
<td>2X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>2:00</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>160</td>
<td>1:30</td>
<td>0:30</td>
</tr>
<tr>
<td>5X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>3:00</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>175</td>
<td>2:00</td>
<td>1:30</td>
</tr>
<tr>
<td>10X</td>
<td>1</td>
<td>300</td>
<td>100</td>
<td>3:00</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>300</td>
<td>175</td>
<td>2:00</td>
<td>1:30</td>
</tr>
</tbody>
</table>

When the temperature of the reaction reached 120 °C during the second heating step, the microwave was paused and the pre-heated S/TOP mixture was injected into the round-bottom flask using a disposable syringe and needle. After the reaction was complete and the round-bottom flask cooled to room temperature, the solution was examined under the UV long-wave light to ensure that it fluoresced. Based on the settings specified in the above table, the cores will fluoresce a yellowish color.

The excess OA and unreacted cadmium precursor were separated from the QDs by extraction of the reaction solution with a volume of methanol equivalent to 4 times the reaction volume (reaction solution:methanol = 1:4) in a centrifuge tube. The centrifuge tube was gently shaken to start the precipitation, the cap was removed from the tube, and the solution was left until it separated into two distinct layers. The top layer composed of methanol and unreacted ligand was then removed from the centrifuge tube using a pipette and discarded. Following the same procedure, the QD cores were washed a second time with methanol. To separate the washed QD cores from methanol, the Thermo Electron
Corporation centrifuge was used. A centrifuge tube containing water of an equal volume was placed opposite the solution in the blue centrifuge tube holder. The centrifuge was run for 5 min at a 25 °C and a speed of 4500 relative centrifugal force (RCF). Once the separation was complete, the QD cores were visibly separated from the methanol. The methanol was then poured from the tube and disposed. Finally, the newly synthesized CdS QDs were dried over night under vacuum (4000 Pa) at room temperature.

3.2.7 *Treatment with a Reducing/Oxidizing Agent*

The CdSe and CdS cores were treated with various reducing/oxidizing agents to increase their quantum efficiency. This step was completed by dissolving the dried cores in spectrophotometric grade chloroform. It is important to note that regular grade chloroform resulted in negative fluorescence peaks, therefore spectrophotometric grade was required. The absorbance of the QD solution was measured via ultra-violet visible spectroscopy (UV-Vis) using a Spectramax M5 Multi-Mode Microplate Reader. For dilute solutions, the solution absorbance is linearly proportional to QD concentration. The lower the arbitrary units (a.u.), the more dilute the solution. A solution absorbance between 0.08 and 0.10 a.u. was desirable for this investigation, therefore the volume of chloroform added to each batch of QD cores was varied to adjust the absorbance to this range.

Once absorbance of the QD solution was between 0.08 and 0.10 a.u., the master batch was divided into 16 different sub-batches in 7 mL glass sample vials. The volume
of each sample was approximately 5 mL. This thesis investigates the effect of 5 different reducing/oxidizing agents: (1) sodium borohydride (NaBH₄), (2) calcium hydride (CaH₂), (3) hydrazine (N₂H₄), (4) benzoyl peroxide (C₁₄H₁₀O₄), and (5) tert-butyl hydroperoxide (C₄H₁₀O₂). To determine the optimal quantity of agent to be used for each batch, these 16 prepared samples were used to test 3 different concentrations of each of the 5 agents. One additional sample was left untreated and used as a reference throughout the treatment process. For solid agents, the masses investigated were: 0.001 g, 0.003 g, and 0.006 g. For liquid agents, the volumes investigated were: 0.05 mL, 0.10 mL, and 0.15 mL. Preliminary results showed that QDs fluoresced brighter in chloroform than toluene, therefore, chloroform was used as the solvent when determining concentration. The optimum quantity of reducing/oxidizing agents for each of the batch types was defined as the quantity at which the highest quantum yield was achieved. These quantities are summarized in Table 3.13 below, while the plots and pictures supporting the chosen quantities can be found in Appendix A.

<table>
<thead>
<tr>
<th></th>
<th>CdSe</th>
<th>CdS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oleylamine</td>
<td>OA/ODE</td>
</tr>
<tr>
<td>NaBH₄</td>
<td>0.006 g</td>
<td>0.006 g</td>
</tr>
<tr>
<td></td>
<td>0.159 mmol</td>
<td>0.159 mmol</td>
</tr>
<tr>
<td>CaH₂</td>
<td>0.001 g</td>
<td>0.001 g</td>
</tr>
<tr>
<td></td>
<td>0.024 mmol</td>
<td>0.024 mmol</td>
</tr>
<tr>
<td>N₂H₄</td>
<td>0.150 mL</td>
<td>0.050 mL</td>
</tr>
<tr>
<td></td>
<td>4.74 mmol</td>
<td>1.58 mmol</td>
</tr>
<tr>
<td>C₁₄H₁₀O₄</td>
<td>0.001 g</td>
<td>0.006 g</td>
</tr>
<tr>
<td></td>
<td>0.004 mmol</td>
<td>0.025 mmol</td>
</tr>
<tr>
<td>C₄H₁₀O₂</td>
<td>0.050 mL</td>
<td>0.150 mL</td>
</tr>
<tr>
<td></td>
<td>0.519 mmol</td>
<td>1.56 mmol</td>
</tr>
</tbody>
</table>
After the concentration for each of the reducing/oxidizing agents was determined, 6 additional 7 mL glass vials were filled with 5 mL aliquots of the QD solution. To 5 of these samples, the optimum amount of reducing/oxidizing agents as summarized in Table 3.13 was added. The additional sample was left untreated and used as a reference throughout the treatment process. An absorbance and fluorescence spectrum of each of the 5 treated samples was measured 1 min, 1 d, 5 d, and 10 d after treatment. These spectra were compared to those of the untreated sample and used to evaluate the effect each reducing/oxidizing agent had on the quantum yield of the various QD batches.

The rotary evaporator was then used to evaporate the remaining chloroform from the QD solution. The isolated solid QD cores were then resuspended in photrex grade toluene. The volume of toluene added was varied until a solution absorbance between 0.08 a.u. and 0.10 a.u. was achieved as measured by the SpectraMax M5. Similar to chloroform, photrex grade toluene was required to eliminate negative fluorescence peaks that appeared in fluorescence spectra of QDs dissolved in regular grade toluene. The QD and toluene solution was divided into 6, 5 mL samples. Following the same procedure as described above, these toluene samples were treated with each of the 5 reducing/oxidizing agents and the absorbance and fluorescence of these samples was measured at the specified time intervals. Preliminary results showed that QDs fluoresced brighter in chloroform than toluene, therefore chloroform was used as the solvent when determining the optimum amount of reducing/oxidizing agents to be used. It was assumed that the optimum amount of agents was not dependent on solvent, therefore, Table 3.13 was applied to the toluene samples as well.
3.3 Characterization Techniques

Following synthesis and treatment, QD samples were analyzed for absorbance, fluorescence, and ligand surface coverage using the techniques described in detail below.

3.3.1 Ultra-Violet Visible (UV-Vis) Spectroscopy

Ultra-violet visible (UV-Vis) spectroscopy is a technique used to analyze compounds in the ultraviolet (UV) and visible (Vis) regions. UV-Vis measures electronic transitions and can be used to determine the wavelength and maximum absorbance of compounds. Spectra are produced when electrons in atoms or molecules move from one energy level to another higher energy level. In doing so, they absorb energy equal to the gap between the two energy levels. Compounds that absorb light in the visible region have color (such as QDs), while those that absorb only in the UV region are colorless.

Inside a UV-Vis spectrophotometer, there are two light sources: one giving off UV light and one giving off visible light. Typically, a tungsten light bulb is used as the visible light source while a deuterium light is used for UV light. The light sources produce white light that includes energies of all wavelengths (or colors) of light. A mirror directs this light into the diffraction grating which splits the colors into their constituent wavelengths. The instrument scans through the spectrum, sending different wavelengths of light through the sample in sequence. The single beam of light passing through the sample is then directed to a detector by mirrors. This detector compares the sample’s intensity to the reference intensity and sends a signal proportional to their ratio to the
computer that controls the instrument. The logarithm of this ratio gives the absorbance of the sample. Absorbance is a measure of how much light is being absorbed by the sample at a particular wavelength.

In this thesis, UV-Vis was used to measure the absorbance of the QD solution samples using a Spectramax M5 Multi-Mode Microplate Reader (Molecular Devices). SoftMax Pro software was used to collect the absorbance data from 350 nm to 750 nm and generate plots of absorbance units (a.u.) versus wavelength (nm). As previously mentioned, sample absorbance is proportional to the QD concentration. The lower the a.u., the more dilute the sample. Absorbance data was therefore used as a measure of sample concentration. Additionally, the intensity of the absorbance peak at 365 nm was used in calculating the quantum yield of each sample as described in detail in the following section. Lastly, the absorbance value corresponding to 365 nm was used to normalize the fluorescence data, as described in detail below.

3.3.2 Fluorescence Spectroscopy

Fluorescence spectroscopy is a type of electromagnetic spectroscopy used to analyze the fluorescence from a sample. This technique involves using a beam of ultraviolet light to excite the electrons in molecules of certain compounds and causes them to emit light of a lower energy. In this thesis, fluorescence spectroscopy was used to measure the fluorescence of the QD samples using a Spectramax M5 Multi-Mode Microplate Reader (Molecular Devices). The optimum excitation wavelength is defined
as the excitation wavelength that yields an emission wavelength that is separated from the
excitation peak wavelength by more than 80 nm.\textsuperscript{1} As seen in Figure 3.7 below, an
excitation wavelength of 365 nm resulted in an approximate 200 nm separation between
the emission wavelength (560 nm) and the excitation peak wavelength (365 nm). The
optimum excitation wavelength was therefore found to be 365 nm for all samples in this
thesis.

Figure 3.7. Sample fluorescence spectrum with excitation wavelength of 365 nm and no cutoff.

As seen in Figure 3.7 above, the intensity of the excitation light peak (at 365 nm)
is significantly greater than that of the emitted light peak (at 560 nm). This difference in
intensity is caused by interference due to scattered or stray light and background
interference.\textsuperscript{1,2} Sources of background include stray excitation light, sample constituents,
and solvents.\textsuperscript{1} To restrict these interferences, a long-pass emission cutoff filter is
necessary.\textsuperscript{1} The optimum emission cutoff filter should block as much of the residual
excitation light as possible without reducing the fluorescence signal.\textsuperscript{1} The cutoff
wavelength value should be between the excitation wavelength and the maximum emission wavelength. For this thesis, the cutoff wavelength was chosen to be 420 nm. Figure 3.8 below illustrates the effect of using an emission cutoff filter. This figure includes a fluorescence spectrum of the same sample as shown in Figure 3.7 excited at 365 nm with a cutoff filter at 420 nm.

Solutions of QDs were loaded into quartz cuvettes for fluorescence measurements. The cuvettes were made of quartz to allow passage of the UV excitation radiation, and were transparent on all four sides. It was necessary that the sides be transparent, since the fluorescence emission is detected in a direction perpendicular to the direction of the incident excitation radiation. SoftMax Pro software was used to collect the fluorescence data of the reference solution (which in this case was the blank solvent) as well the fluorescence of the QD solutions from 350 nm to 750 nm and generate plots of relative fluorescence units (RFU) versus wavelength (nm). The reference fluorescence
data was subtracted from the QD fluorescence data to correct for the solvent effect. To normalize this fluorescence data to absorbance data, the fluorescence values corresponding to a specific sample were divided by the absorbance of the same sample at the excitation wavelength of 365 nm. The area of the normalized fluorescence peak was used in calculating the quantum yield of each sample as described in detail in the following section.

3.3.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) measures the weight change of a sample as it is heated to the temperature at which it degrades. A thermal degradation profile of a sample can be determined by plotting the residual mass versus temperature. In this thesis, TGA was utilized to measure the ligand surface coverage of the QDs. TGA was performed using a TA Instruments SDT-Q600, which employs two cantilever balances in a furnace purged with nitrogen. An aliquot of a QD sample solution was placed in an alumina ceramic pan and placed in an oven at a temperature of 70 °C until the solvent evaporated. This step was repeated until the bottom of the ceramic pan was covered with a layer of the QD powder. The alumina ceramic pan filled with this QD powder was placed on one cantilever. A second, empty ceramic pan was placed on the other cantilever as a reference. The sample was then heated from 30 °C to 600 °C at a constant rate of 10 °C/min. The mass remaining after heating to the set temperature was believed to be that of the metal core without organic ligands. The mass lost due to heating was therefore
assumed to be that of the ligands, thereby allowing for the estimation of ligand surface coverage.

3.4 Calculating Quantum Yield

The quantum yield (QY) of a compound is defined as the fraction of molecules that emit a photon after direct excitation by the source. This value is of importance as it is a measure of the extent of interferences and therefore is a quantitative measure of a compound’s brightness. The QY of untreated QD cores and those treated with a reducing/oxidizing agent was calculated by comparison with a known reference. In this thesis, Rhodamine 6G (Rh6G) was chosen as the reference because its QY is known (0.95), and it emits a photon at a similar wavelength as the QDs synthesized in this thesis (~ 530 nm) when excited at 365 nm. Reference solutions were made by dissolving Rh6G in water until the absorbance of each solution was between 0.08 a.u. and 0.10 a.u., as measured using the SpectraMax M5. A solution absorbance within this range was desired so that the concentration of the reference solution was comparable to the concentration of the QD sample solutions. The fluorescence of the reference solutions was also measured using the SpectraMax and peaks were generated. A custom MATLAB script was developed to calculate the area under each measured fluorescence peak. The QY of each QD sample was calculated using the following relation:

\[
QY_{\text{QD}} = QY_{\text{Rh6G}} \left( \frac{FL_{\text{QD}}}{AB_{\text{QD}}} \right) \left( \frac{AB_{\text{Rh6G}}}{FL_{\text{Rh6G}}} \right) \left( \frac{\eta_{\text{nd}}^2}{\eta_{\text{H}_2O}^2} \right) \tag{1}
\]
Where $QY_{Rh6G}$ is the quantum yield of the reference solution, Rh6G (0.95); $FL_{QDs}$ and $FL_{Rh6G}$ are the areas under the fluorescence peaks of the quantum dot and reference (Rh6G) solutions, respectively; $AB_{QDs}$ and $AB_{Rh6G}$ are the intensities of the absorbance peaks of the quantum dot and reference (Rh6G) solutions at 365 nm, respectively; $\eta_{sol}$ is the refractive index of the solvent ($\eta_{toluene} = 1.497$ and $\eta_{chloroform} = 1.446$); and $\eta_{H2O}$ is the refractive index of water ($\eta_{H2O} = 1.333$).

3.5 Calculating Band Gap Energy ($E_g$)

The bandgap energy ($E_g$) is the energy between the valence and conduction band in a semiconductor. As described in the background section, the $E_g$ is the minimum amount of energy required to promote an electron from the valence band to the conduction band. When the electron returns to the valence band, energy corresponding to the energy of the bandgap is emitted. This value is of importance when referring to QDs because, unlike in bulk semiconductors, the $E_g$ can be tuned to emit light of a particular wavelength. In other words, QDs of the same material can emit light at an array of wavelengths. The size of the bandgap is dictated by the size of the particle. For this reason, the $E_g$ will be used throughout this thesis to quantitatively account for changes in QD size after surface treatment with various reducing and oxidizing agents.

To calculate $E_g$, the absorbance data for each sample was plotted versus energy. The bandgap energy was defined as the minimum energy required for radiative
recombination from the valence band to the conduction band and was simply read off each graph (see Figure 3.9).\textsuperscript{4} To convert wavelength to energy, the following relation was used:

\[
E = \frac{hc}{\lambda}
\]  

(2)

Where \(E\) is energy in eV (1 eV = 1.602 x 10\textsuperscript{-19} J); \(h\) is Planck’s constant (6.63 x 10\textsuperscript{-34} J\textsuperscript{s}); \(c\) is the speed of light (3.00 x 10\textsuperscript{8} m/s); and \(\lambda\) is wavelength in m.

Figure 3.9. Typical absorbance spectra used to estimate the bandgap energy (\(E_g\)).\textsuperscript{4}
3.6 References


(4) Choi, K. *Purdue University*; West Lafayette, IN, 2007.
Chapter 4. Results and Discussion: CdSe

Chapter 4 will present and discuss the results of the experimental work performed on CdSe QDs. This chapter will be divided into three sections: (1) CdSe QDs synthesized with oleylamine, (2) CdSe QDs synthesized with oleic acid (OA) and octadecene (ODE), and (3) CdSe QDs synthesized with OA and trioctylamine (TOA). Each section will summarize the effect of treating the surface of the various QD batches with three reducing and two oxidizing agents. More specifically, the effect of each treatment on the quantum yield (QY) of the QDs will be investigated. The QY refers to the nonradiative transition of electrons and holes between energy levels, and is therefore a measure of brightness. The QY reported for each treatment was calculated following the procedures presented in Chapter 3 of this thesis. Rhodamine 6G (Rh6G) was chosen as the reference in the QY calculation because its QY is known (0.95), and it emits a photon at a similar wavelength as the QDs synthesized in this thesis (~ 530 nm) when excited at 365 nm.

It is important to note that the calculated QY is representative of the entire QD mixture, not just the QDs because the QD solution was not purified after treatment. For this reason, a major limitation of this study is that the measured absorbance and fluorescence spectra of each sample were of the mixture, not the pure components. For example, the absorbance of the mixture ($A_{mixture}$) can be represented by the following equation:

$$A_{mixture} = A_{QDs} + A_{ligand} + A_{treatment} + A_{solvent}$$ (3)
Where $A_{\text{mixture}}$ is the intensity of the absorbance peak of the QD mixture at 365 nm; $A_{\text{QDs}}$ is of the QDs; $A_{\text{ligand}}$ is of the ligand; $A_{\text{treatment}}$ is of the reducing/oxidizing agents; and $A_{\text{solvent}}$ is of the solvent.

When performing UV-Vis on the reaction mixture, the blank solvent was used as the reference and subtracted from the total absorbance, therefore the absorbance of the solvent can be neglected in the equation 3 ($A_{\text{solvent}} = 0$). Furthermore, UV-Vis was performed on a mixture containing each ligand and solvent combination. Again, the blank solvent was used as the reference, therefore the measured absorbance was representative of only the ligand. Figure 4.1 below contains the absorbance spectra of a sample QD mixture (CdSe QDs capped with oleylamine in chloroform) represented by the solid line and a solution of ligand (oleylamine) and chloroform represented by the dashed line.

![Absorption spectra](image)

**Figure 4.1.** Absorbance spectra of a CdSe (oleylamine) QDs dissolved in chloroform (solid) and a solution of oleylamine and chloroform (dashed).

Absorbance is directly related to concentration via Beer’s Law:
Where \( A \) is the intensity of the absorbance peak; \( \varepsilon \) is the molar absorptivity (L/mol·cm) \( C \) is the molar concentration (mol/L) of the component in solution; and \( L \) is the path length (cm) of the radiation beam used for measuring the absorbance spectrum. As seen in equation 3, the absorbance of the QD mixture \( (A_{\text{mixture}}) \) is the sum of the intensities of the absorbance peaks at 365 nm of each component. The absorbance of the ligand is significantly less than that of the QD mixture at 365 nm (see Figure 4.1), therefore we can conclude that there is a small concentration of ligand in the QD mixture. Furthermore, even though the intensity of the absorbance peaks in Figure 4.1 were both approximately 0.06, indicating that the concentration of the components in the solutions were approximately the same, there were more components in the QD mixture solution than the solution comprised of only ligand and solvent. For this reason, we can conclude that the concentration of ligand in the QD mixture was orders of magnitude less than that in the solution only composed of ligand and solvent. The absorbance of the ligand \( (A_{\text{ligand}}) \) in equation 3 can therefore be assumed to be negligible \( (A_{\text{ligand}} = 0) \). The absorbance measured for each QD mixture as summarized in the following sections is therefore representative of the mixture of the absorbance of the QDs and that of the treatment, or:

\[
A_{\text{mixture}} = A_{\text{QDs}} + A_{\text{treatment}}
\]  

The measured fluorescence spectra included in this study are also representative of the QD mixture rather than just the QDs. For this reason, when the fluorescence of the
QDs was quenched, we were unable to conclude what caused this quenching. For example, if the quenching was caused by excess free ligand in the QD solution, it may be possible to restore the fluorescence by purifying the QDs after treatment and removing this residual ligand. In a study by Tansakul et al. it was found that the quenched QD fluorescence could be restored, therefore proving that quenching may be reversible.\textsuperscript{24} It is recommended that future work performed on this study explore whether the quenching is reversible by purifying the QDs after treatment.

In addition to comparing the QY of the QDs before and after surface treatment, a change in QD size distribution was also investigated. In a study by Zezza et al., it was concluded that the sharpness of the absorbance peak is indicative of the particle size distribution.\textsuperscript{1} Specifically, the sharper the absorbance peak, the narrower the size distribution.\textsuperscript{1} Furthermore, Bullen et al. found that a high full-width half-maximum (FWHM) value indicates the onset of Ostwald ripening which causes a slow “defocusing” of the size distribution.\textsuperscript{2} It can therefore be concluded that a sharp absorbance peak and low FWHM value is indicative of a narrow size distribution.

Lastly, the bandgap energy ($E_g$) was calculated before and after each surface treatment following the procedure provided in Chapter 3. The bandgap energy is the minimum amount of energy a QD absorbs to raise an electron from the valence band to the conduction band. The electron remains in the conduction band momentarily before returning through the bandgap to the valence band at which time it emits electromagnetic radiation with a wavelength corresponding to the bandgap.\textsuperscript{3,4} The size of the bandgap is
therefore dictated by the size of the QD. Specifically, $E_g$ increases with decreasing particle size.\textsuperscript{5} Furthermore, QD size is representative of the color emitted, with smaller QDs emitting blue and large QDs emitting red.

The reducing agents to be investigated include: sodium borohydride (NaBH$_4$), calcium hydride (CaH$_2$), and hydrazine (N$_2$H$_4$), while the oxidizing agents include: benzoyl peroxide (C$_{14}$H$_{10}$O$_4$) and \textit{tert}-butyl hydroperoxide (C$_4$H$_{10}$O$_2$). Three different concentrations of each reducing/oxidizing agent were investigated prior to experimentation to determine which concentration yielded the highest calculated QY for each batch of QDs (see Appendix A). This concentration was defined as the optimum concentration and was used to treat each batch of QDs, as described in the following sections.

4.1 CdSe (Oleylamine) Quantum Dot Cores

4.1.1 Treatment with Sodium Borohydride (NaBH$_4$) in Chloroform

Figure 4.2 displays the absorbance and fluorescence spectra of a CdSe (oleylamine) QD and sodium borohydride (NaBH$_4$) solution dissolved in chloroform at a 1.99 x $10^{-5}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Figure 4.2 below. From these values, it can be seen that the QY of the QDs increased slightly after treatment with NaBH$_4$ and reached a maximum 1 d after treatment before
decreasing to below that of the untreated QY 10 d later. Figure 4.2e confirms this decrease in QY 10 d after treatment as the treated QDs (right) are less bright than the untreated QDs (left). Additionally, no notable change in the sharpness of the absorbance peak or FWHM value was observed therefore ruling out a significant broadening of the QD size distribution after treatment. Lastly, the $E_g$ did not change after treatment indicating that there was no change in the size of the QDs. In conclusion, treatment of CdSe (oleylamine) QDs dissolved in chloroform with NaBH$_4$ resulted in a 66.7 % increase in the QY of the QDs 1 d after treatment.

Figure 4.2. Absorbance spectra (a) and fluorescence spectra (b) of a 6.39 x 10$^{-7}$ M solution of CdSe (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with NaBH$_4$ (1.99 x 10$^{-5}$ molar ratio of QDs to NaBH$_4$). Photos of untreated QDs (left) and QDs treated with NaBH$_4$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 4.1. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E\textsubscript{g}) of a CdSe (oleylamine) QD and NaBH\textsubscript{4} solution dissolved in chloroform at a 1.99 \times 10^{-5} molar ratio.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>E\textsubscript{g} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.003</td>
<td>38.7</td>
<td>2.19</td>
</tr>
<tr>
<td>Initial</td>
<td>0.003</td>
<td>40.3</td>
<td>2.19</td>
</tr>
<tr>
<td>1 d</td>
<td>0.005</td>
<td>42.5</td>
<td>2.19</td>
</tr>
<tr>
<td>5 d</td>
<td>0.004</td>
<td>45.7</td>
<td>2.19</td>
</tr>
<tr>
<td>10 d</td>
<td>0.002</td>
<td>49.4</td>
<td>2.20</td>
</tr>
</tbody>
</table>

4.1.2 Treatment with Sodium Borohydride (NaBH\textsubscript{4}) in Toluene

Figure 4.3 displays the absorbance and fluorescence spectra of a CdSe (oleylamine) QD and sodium borohydride (NaBH\textsubscript{4}) solution dissolved in toluene at a 3.27 \times 10^{-5} molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E\textsubscript{g}) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 4.2 below. From these values, it can be seen that the QY of the QDs increased immediately after treatment with NaBH\textsubscript{4} before decreasing to below that of the untreated QY 10 d later. The pictures in Figure 4.3 confirm these results as the treated sample (right) is brighter than the untreated sample (left) 1 d after treatment (c) and less bright 10 d after treatment (e). Additionally, the absorption edge continued to become less sharp and the FWHM continued to increase with time, indicating a broadening of the QD size distribution after treatment. Lastly, the E\textsubscript{g} did not change after treatment indicating that there was no change in the size of the QDs. In conclusion, treatment of CdSe
(oleylamine) QDs dissolved in toluene with NaBH₄ resulted in a 64.0 % increase in the QY of the QDs immediately after treatment.

Figure 4.3. Absorbance spectra (a) and fluorescence spectra (b) of a 1.04 x 10⁻⁶ M solution of CdSe (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with NaBH₄ (3.27 x 10⁻⁵ molar ratio of QDs to NaBH₄). Photos of untreated QDs (left) and QDs treated with NaBH₄ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.2. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E₉) of a CdSe (oleylamine) QD and NaBH₄ solution dissolved in toluene at a 3.27 x 10⁻⁵ molar ratio.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>E₉ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.050</td>
<td>39.3</td>
<td>2.15</td>
</tr>
<tr>
<td>Initial</td>
<td>0.082</td>
<td>39.7</td>
<td>2.16</td>
</tr>
<tr>
<td>1 d</td>
<td>0.025</td>
<td>39.3</td>
<td>2.15</td>
</tr>
<tr>
<td>5 d</td>
<td>0.046</td>
<td>46.2</td>
<td>2.17</td>
</tr>
<tr>
<td>10 d</td>
<td>0.029</td>
<td>47.5</td>
<td>2.18</td>
</tr>
</tbody>
</table>
4.1.3 Treatment with Calcium Hydride (CaH₂) in Chloroform

Figure 4.4 displays the absorbance and fluorescence spectra of a CdSe (oleylamine) QD and calcium hydride (CaH₂) solution dissolved in chloroform at a 1.33 x 10⁻⁴ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 4.3 below. From these values, it can be seen that the QY of the QDs decreased after treatment with CaH₂. Additionally, the spectra in Figure 4.4 illustrate that the fluorescence peak flattened and the absorbance increased after treatment. In a study by Mandal et al., an increase in absorbance was found to be indicative of aggregation because absorbance measurements are sensitive to scattering from colloidal suspensions that form as QD aggregates grow in size. Furthermore, they found that a significant decrease in QD fluorescence also resulted from aggregation. It can therefore be concluded that the flattening of the fluorescence peak coupled with the significant increase in absorbance observed 10 d after treatment with CaH₂, indicates that the QDs began to aggregate at this time. Furthermore, because the QDs were no longer fluorescent 10 d after treatment (see Figure 4.4e), it can be concluded that the QDs precipitated out of solution. Lastly, the E_g did not change after treatment indicating that there was no change in the size of the QDs. In conclusion, treatment of CdSe (oleylamine) QDs dissolved in chloroform with CaH₂ caused the QDs to stop fluorescing 10 d after treatment.
Figure 4.4. Absorbance spectra (a) and fluorescence spectra (b) of a $6.39 \times 10^{-7}$ M solution of CdSe (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with CaH$_2$ ($1.33 \times 10^{-4}$ molar ratio of QDs to CaH$_2$). Photos of untreated QDs (left) and QDs treated with CaH$_2$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.3. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdSe (oleylamine) QD and CaH$_2$ solution dissolved in chloroform at a $1.33 \times 10^{-4}$ molar ratio.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.003</td>
<td>40.0</td>
<td>2.19</td>
</tr>
<tr>
<td>Initial</td>
<td>0.003</td>
<td>43.7</td>
<td>2.19</td>
</tr>
<tr>
<td>1 d</td>
<td>0.003</td>
<td>40.6</td>
<td>2.19</td>
</tr>
<tr>
<td>5 d</td>
<td>0.002</td>
<td>43.3</td>
<td>2.20</td>
</tr>
<tr>
<td>10 d</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>
4.1.4 Treatment with Calcium Hydride (CaH₂) in Toluene

Figure 4.5 displays the absorbance and fluorescence spectra of a CdSe (oleylamine) QD and calcium hydride (CaH₂) solution dissolved in toluene at a 2.17 x 10⁻⁴ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 4.4 below. From these values, it can be seen that the QY of the QDs steadily decreased with time after treatment with CaH₂. The pictures included in Figure 4.5 confirm this expected decrease in QY, as the treated sample (right) is less fluorescent than the untreated sample (left). Additionally, the absorption edge continued to become less sharp and the FWHM increased with time, indicating a broadening of the QD size distribution after treatment. Lastly, the E_g increased slightly after treatment indicating that there was a slight decrease in the size of the QDs. In conclusion, treatment of CdSe (oleylamine) QDs dissolved in toluene with CaH₂ resulted in a quenching of the QDs fluorescence.
Figure 4.5. Absorbance spectra (a) and fluorescence spectra (b) of a $1.04 \times 10^{-6}$ M solution of CdSe (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with CaH$_2$ ($2.17 \times 10^{-4}$ molar ratio of QDs to CaH$_2$). Photos of untreated QDs (left) and QDs treated with CaH$_2$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.4. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdSe (oleylamine) QD and CaH$_2$ solution dissolved in toluene at a $2.17 \times 10^{-4}$ molar ratio.

<table>
<thead>
<tr>
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<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.057</td>
<td>39.1</td>
<td>2.15</td>
</tr>
<tr>
<td>Initial</td>
<td>0.042</td>
<td>40.3</td>
<td>2.15</td>
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<tr>
<td>1 d</td>
<td>0.026</td>
<td>39.9</td>
<td>2.15</td>
</tr>
<tr>
<td>5 d</td>
<td>0.020</td>
<td>46.6</td>
<td>2.19</td>
</tr>
<tr>
<td>10 d</td>
<td>0.023</td>
<td>53.6</td>
<td>2.23</td>
</tr>
</tbody>
</table>
4.1.5 Treatment with Hydrazine (N$_2$H$_4$) in Chloroform

Figure 4.6 displays the absorbance and fluorescence spectra of a CdSe (oleylamine) QD and hydrazine (N$_2$H$_4$) solution dissolved in chloroform at a 6.74 x 10$^{-7}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 4.5 below. From these values, it can be seen that the QY of the QDs decreased after treatment with N$_2$H$_4$. A possible explanation for the observed decrease in QY involves the solubility of N$_2$H$_4$ in chloroform. Specifically, N$_2$H$_4$ is nearly insoluble in chloroform$^8$ and is a liquid at room temperature. Therefore, an emulsion formed immediately after the addition of N$_2$H$_4$ to the untreated QD solution, as seen in Figure 4.6c where N$_2$H$_4$ formed large droplets that were poorly dispersed in the continuous chloroform phase. We hypothesize that oleylamine was able to act as a surfactant and stabilize the hydrazine droplets, as its surface tension (31.4 mN/m$^9$) is in between that of N$_2$H$_4$ (66.39 mN/m$^9$) and chloroform (27.5 mN/m$^9$). As mentioned above, N$_2$H$_4$ formed large, unevenly dispersed droplets in the chloroform which led to the assumption that oleylamine was a poor surfactant. This assumption was confirmed as the hydrophilic-lipophilic balance (HLB) of oleylamine was found to be approximately 10$^{10}$, indicating that it is a hydrophilic surfactant.$^{11}$ Chloroform is a hydrophobic solvent, therefore a hydrophobic surfactant with a low HLB value is required to yield a stable emulsion with small, evenly dispersed droplets of N$_2$H$_4$. 
When the reducing/oxidizing agents were soluble in a given solvent, it was assumed that the reduction/oxidation of the QDs happened immediately. Because N$_2$H$_4$ is nearly insoluble in chloroform, an emulsion formed immediately after treatment. Immediately after addition, a small amount of soluble N$_2$H$_4$ reacted with the QDs and reduced their surface to etch and destroy the QDs thereby quenching the QD fluorescence. The remainder of the N$_2$H$_4$ formed large, unevenly dispersed N$_2$H$_4$ droplets stabilized by the residual oleylamine. The solution appeared blue-green when excited by a 365 nm UV lamp because the oleylamine emits light at 450 nm upon excitation (see Figure 4.7). After 10 d a visible layer forms at the top of the chloroform solution, presumably due to instability of the emulsion (see Figure 4.6e). In conclusion, CdSe (oleylamine) QDs dissolved in chloroform died immediately after the addition of N$_2$H$_4$. 
Figure 4.6. Absorbance spectra (a) and fluorescence spectra (b) of a 6.39 \times 10^{-7} \text{ M} solution of CdSe (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with N_2H_4 (6.74 \times 10^{-7} \text{ molar ratio of QDs to N}_2\text{H}_4). Photos of untreated QDs (left) and QDs treated with N_2H_4 (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.5. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdSe (oleylamine) QD and N_2H_4 solution dissolved in chloroform at a 6.74 \times 10^{-7} \text{ molar ratio.}

<table>
<thead>
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<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>E_g (eV)</th>
</tr>
</thead>
<tbody>
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<td>Untreated</td>
<td>0.006</td>
<td>39.5</td>
<td>2.19</td>
</tr>
<tr>
<td>Initial</td>
<td>0.001</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1 d</td>
<td>0.003</td>
<td>107</td>
<td>2.37</td>
</tr>
<tr>
<td>5 d</td>
<td>0.004</td>
<td>107</td>
<td>2.40</td>
</tr>
<tr>
<td>10 d</td>
<td>0.004</td>
<td>106</td>
<td>2.40</td>
</tr>
</tbody>
</table>
Figure 4.7. Normalized fluorescence spectrum of a solution composed of chloroform, oleylamine, and \( \text{N}_2\text{H}_4 \).

4.1.6 Treatment with Hydrazine (\( \text{N}_2\text{H}_4 \)) in Toluene

Figure 4.8 displays the absorbance and fluorescence spectra of a CdSe (oleylamine) QD and hydrazine (\( \text{N}_2\text{H}_4 \)) solution dissolved in toluene at a 1.10 x 10\(^{-6} \) molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (\( E_g \)) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 4.6 below. From these values, it can be seen that the QY of the QDs was quenched immediately after treatment with \( \text{N}_2\text{H}_4 \). This quenching of the fluorescence was confirmed by the flattening of the fluorescence spectrum and the pictures in Figure 4.8 where the treated samples (right) no longer fluoresce. Hydrazine is soluble in toluene, therefore it was assumed that the reducing agent reacted with the QDs immediately after treatment and the concerns discussed in section 4.1.5 above were not applicable. In conclusion, treatment of CdSe (oleylamine) QDs dissolved in toluene with \( \text{N}_2\text{H}_4 \) caused the QDs to stop fluorescing immediately after treatment.
Figure 4.8. Absorbance spectra (a) and fluorescence spectra (b) of a $1.04 \times 10^{-6}$ M solution of CdSe (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with N$_2$H$_4$ ($1.10 \times 10^{-6}$ molar ratio of QDs to N$_2$H$_4$). Photos of untreated QDs (left) and QDs treated with N$_2$H$_4$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.6. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdSe (oleylamine) QD and N$_2$H$_4$ solution dissolved in toluene at a $1.04 \times 10^{-6}$ molar ratio.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.041</td>
<td>39.6</td>
<td>2.15</td>
</tr>
<tr>
<td>Initial</td>
<td>0.003</td>
<td>42.3</td>
<td>2.05</td>
</tr>
<tr>
<td>1 d</td>
<td>0.001</td>
<td>70.9</td>
<td>---</td>
</tr>
<tr>
<td>5 d</td>
<td>0.001</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>10 d</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>
4.1.7 Treatment with Benzoyl Peroxide (C\textsubscript{14}H\textsubscript{10}O\textsubscript{4}) in Chloroform

Figure 4.9 displays the absorbance and fluorescence spectra of a CdSe (oleylamine) QD and benzoyl peroxide (C\textsubscript{14}H\textsubscript{10}O\textsubscript{4}) solution dissolved in chloroform at a 7.99 x 10\textsuperscript{-4} molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E\textsubscript{g}) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 4.7 below. From these values, it can be seen that the QY of the QDs decreased after treatment with C\textsubscript{14}H\textsubscript{10}O\textsubscript{4}. Although the QY was calculated to be at a maximum 10 d after treatment, a decrease in fluorescence was actually observed (see Figure 4.9e).

Similar to treatment with N\textsubscript{2}H\textsubscript{4} (as described in section 4.1.5 above), the fluorescence peak centered at 560 nm in Figure 4.10 represents the true emission of the QDs. The peaks centered at 450 nm, on the other hand, are representative of the mixture of chloroform, oleylamine, and C\textsubscript{14}H\textsubscript{10}O\textsubscript{4}, not the QDs. Focusing on the peak representing the QDs, it can therefore be seen that the fluorescence of the QDs decreased immediately after treatment, decreased further and experienced a blue-shift 5 d after treatment, and was completely quenched 10 d after treatment. Figure 4.9e illustrates this quenching of the QD fluorescence 10 d after treatment, as the treated sample (right) is not fluorescent. Additionally, the absorption edge continued to become less sharp with time and the FWHM increased, indicating a broadening of the QD size distribution after treatment. Lastly, the E\textsubscript{g} increased 5 d after treatment indicating that there was a slight decrease in the size of the QDs at this time. In conclusion, treatment of CdSe
(oleylamine) QDs dissolved in chloroform with C<sub>14</sub>H<sub>10</sub>O<sub>4</sub> caused the QDs to stop fluorescing 10 d after treatment.

Figure 4.9. Absorbance spectra (a) and fluorescence spectra (b) of a 6.39 x 10<sup>-7</sup> M solution of CdSe (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with C<sub>14</sub>H<sub>10</sub>O<sub>4</sub> (7.99 x 10<sup>-4</sup> molar ratio of QDs to C<sub>14</sub>H<sub>10</sub>O<sub>4</sub>). Photos of untreated QDs (left) and QDs treated with C<sub>14</sub>H<sub>10</sub>O<sub>4</sub> (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.7. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E<sub>g</sub>) of a CdSe (oleylamine) QD and C<sub>14</sub>H<sub>10</sub>O<sub>4</sub> solution dissolved in chloroform at a 6.39 x 10<sup>-7</sup> molar ratio.

<table>
<thead>
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<th>QY</th>
<th>FWHM (nm)</th>
<th>E&lt;sub&gt;g&lt;/sub&gt; (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.005</td>
<td>39.3</td>
<td>2.19</td>
</tr>
<tr>
<td>Initial</td>
<td>0.003</td>
<td>39.7</td>
<td>2.19</td>
</tr>
<tr>
<td>1 d</td>
<td>0.002</td>
<td>39.3</td>
<td>2.19</td>
</tr>
<tr>
<td>5 d</td>
<td>0.003</td>
<td>53.3</td>
<td>2.23</td>
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<tr>
<td>10 d</td>
<td>0.007</td>
<td>102</td>
<td>2.40</td>
</tr>
</tbody>
</table>
4.1.8 Treatment with Benzoyl Peroxide (C_{14}H_{10}O_{4}) in Toluene

Figure 4.11 displays the absorbance and fluorescence spectra of a CdSe (oleylamine) QD and benzoyl peroxide (C_{14}H_{10}O_{4}) solution dissolved in toluene at a 1.30 x 10^{-3} molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 4.8 below. From these values, it can be seen that the QY of the QDs increased 1 d after treatment with C_{14}H_{10}O_{4} before decreasing to below that of the untreated QY 5 d later. This increase in QY 1 d after treatment is illustrated in Figure 4.11c as the treated sample (right) is brighter than the untreated sample (left).

Similar to treatment with C_{14}H_{10}O_{4} in chloroform (as described in section 4.1.7 above), the fluorescence peak centered at 550 nm in Figure 4.11 represents the emission of the QDs. The peaks measured 5 d (green) and 10 d (purple) after treatment, on the other hand, are centered at 450 nm and are therefore representative of the mixture of
toluene, oleylamine, and \( \text{C}_{14}\text{H}_{10}\text{O}_4 \), not the QDs (see Figure 4.12 below). Focusing on the peak representing the QDs, it can therefore be seen that the fluorescence of the QDs increased 1 d after treatment and was completely quenched 5 d after treatment. Figure 4.11d and e confirm these observations as the treated sample (right) is not fluorescent 5 d and 10 d after treatment, respectively. Additionally, the absorption edge continued to become less sharp with time and the FWHM increased, indicating a broadening of the QD size distribution after treatment. In conclusion, treatment of CdSe (oleylamine) QDs dissolved in toluene with \( \text{C}_{14}\text{H}_{10}\text{O}_4 \) resulted in a 22.9 % increase in the QY of the QDs 1 d after treatment, however, the fluorescence of the QDs was quenched 5 d after treatment.
Figure 4.11. Absorbance spectra (a) and fluorescence spectra (b) of a $1.04 \times 10^{-6}$ M solution of CdSe (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with $\text{C}_{14}\text{H}_{10}\text{O}_{4}$ (1.30 x $10^{-3}$ molar ratio of QDs to $\text{C}_{14}\text{H}_{10}\text{O}_{4}$). Photos of untreated QDs (left) and QDs treated with $\text{C}_{14}\text{H}_{10}\text{O}_{4}$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.8. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdSe (oleylamine) QD and $\text{C}_{14}\text{H}_{10}\text{O}_{4}$ solution dissolved in toluene at a $1.30 \times 10^{-3}$ molar ratio.

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<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
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<td>Untreated</td>
<td>0.035</td>
<td>40.4</td>
<td>2.15</td>
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<tr>
<td>Initial</td>
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<td>39.5</td>
<td>2.15</td>
</tr>
<tr>
<td>1 d</td>
<td>0.043</td>
<td>41.0</td>
<td>2.19</td>
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<tr>
<td>5 d</td>
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<td>84.5</td>
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<tr>
<td>10 d</td>
<td>0.007</td>
<td>71.6</td>
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4.1.9 Treatment with tert-Butyl Hydroperoxide (C₄H₁₀O₂) in Chloroform

Figure 4.13 displays the absorbance and fluorescence spectra of a CdSe (oleylamine) QD and tert-Butyl Hydroperoxide (C₄H₁₀O₂) solution dissolved in chloroform at a 6.14 x 10⁻⁶ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 4.9 below. From these values, it can be seen that the QY of the QDs decreased immediately after treatment with C₄H₁₀O₂ before ceasing to fluoresce 1 d later. Figure 4.13c illustrates this quenching of the QD fluorescence 1 d after treatment, as the treated sample (right) is not fluorescent.

Similar to treatment with C₁₄H₁₀O₄ (as described in sections 4.1.7 and 4.1.8 above), the fluorescence peak centered at 550 nm in Figure 4.10 represents the true emission of the QDs. The peaks measured after treatment, on the other hand, are centered at 450 nm and are therefore representative of the mixture of chloroform, oleylamine, and
C_{4}H_{10}O_{2}, not the QDs. For this reason, the quenching of the fluorescence of the QDs 1 d after treatment was confirmed. In conclusion, treatment of CdSe (oleylamine) QDs dissolved in chloroform with C_{4}H_{10}O_{2} resulted in a quenching of the QD fluorescence 1 d after treatment.

Figure 4.13. Absorbance spectra (a) and fluorescence spectra (b) of a 6.39 x 10^{-7} M solution of CdSe (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with C_{4}H_{10}O_{2} (6.14 x 10^{-6} molar ratio of QDs to C_{4}H_{10}O_{2}). Photos of untreated QDs (left) and QDs treated with C_{4}H_{10}O_{2} (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 4.9. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdSe (oleylamine) QD and C$_4$H$_{10}$O$_2$ solution dissolved in chloroform at a 6.14 x 10$^{-6}$ molar ratio.

<table>
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<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
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</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.002</td>
<td>44.0</td>
<td>2.19</td>
</tr>
<tr>
<td>Initial</td>
<td>0.001</td>
<td>48.0</td>
<td>2.19</td>
</tr>
<tr>
<td>1 d</td>
<td>0.001</td>
<td>32.8</td>
<td>2.40</td>
</tr>
<tr>
<td>5 d</td>
<td>0.003</td>
<td>43.5</td>
<td>2.38</td>
</tr>
<tr>
<td>10 d</td>
<td>---</td>
<td>---</td>
<td>2.35</td>
</tr>
</tbody>
</table>

Figure 4.14. Normalized fluorescence spectrum of a solution composed of chloroform, oleylamine, and tert-butyl hydroperoxide (C$_4$H$_{10}$O$_2$).

4.1.10 Treatment with tert-Butyl Hydroperoxide (C$_4$H$_{10}$O$_2$) in Toluene

Figure 4.15 displays the absorbance and fluorescence spectra of a CdSe (oleylamine) QD and tert-butyl hydroperoxide (C$_4$H$_{10}$O$_2$) solution dissolved in toluene at a 1.00 x 10$^{-5}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These values, as summarized in Table 4.10, show that the QY of the QDs decreased immediately after treatment with C$_4$H$_{10}$O$_2$. 
This decrease in QY is illustrated in Figure 4.15c where the treated QDs (right) are less bright than the untreated QDs (left).

Similar to treatment with C₄H₁₀O₂ in chloroform (as described in section 4.1.9 above), the fluorescence peak centered at 550 nm in Figure 4.15 represents the true emission of the QDs. The peak measured 5 d (green) and 10 d (purple) after treatment, on the other hand, is centered at 450 nm and is therefore representative of the mixture of toluene, oleylamine, and C₄H₁₀O₂, not the QDs (see Figure 4.16 below). Focusing on the fluorescence peak representing the QDs, it can therefore be seen that the fluorescence was quenched 5 d after treatment. Figure 4.15d and e confirm this quenching of the QD fluorescence as the treated sample (right) is not fluorescent 5 d and 10 d after treatment, respectively. Additionally, the absorption edge continued to become less sharp with time and the FWHM increased, indicating a broadening of the QD size distribution after treatment.¹,¹² In conclusion, treatment of CdSe (oleylamine) QDs dissolved in toluene with C₄H₁₀O₂ resulted in a quenching of the QD fluorescence 5 d after treatment.
Figure 4.15. Absorbance spectra (a) and fluorescence spectra (b) of a 1.04 x 10^{-6} M solution of CdSe (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with C_4H_{10}O_2 (1.00 x 10^{-5} molar ratio of QDs to C_4H_{10}O_2). Photos of untreated QDs (left) and QDs treated with C_4H_{10}O_2 (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.10. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdSe (oleylamine) QD and C_4H_{10}O_2 solution dissolved in toluene at a 1.00 x 10^{-5} molar ratio.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>46.6</td>
<td>2.15</td>
</tr>
<tr>
<td>Initial</td>
<td>0.002</td>
<td>---</td>
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</tr>
<tr>
<td>1 d</td>
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<td>52.4</td>
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<tr>
<td>5 d</td>
<td>0.062</td>
<td>75.6</td>
<td>2.35</td>
</tr>
<tr>
<td>10 d</td>
<td>0.097</td>
<td>76.9</td>
<td>2.39</td>
</tr>
</tbody>
</table>
4.1.11 Summary of CdSe/Oleylamine Treatments

Figure 4.17 compares the effect of treating CdSe (oleylamine) QDs with various reducing and oxidizing agents in chloroform versus toluene. From these photographs, it can be seen that the QDs dissolved in toluene were visibly brighter than those in chloroform. This observation was confirmed as the QY of the QDs before treatment in chloroform was approximately 0.004 while the QY in toluene was approximately 0.050. Because both sets of QDs came from the same master batch of cores, this difference in QY may be due to the solubility of the oleylamine in the various solvents. Thuy et al. have shown that the QY is higher when the capping ligand is less soluble in a given solvent.\textsuperscript{13} Because the QY was higher in toluene than chloroform, we therefore hypothesize that oleylamine is less soluble in toluene than chloroform. The $E_g$ of the untreated QDs in chloroform and toluene were 2.19 eV and 2.15 eV, respectively, which suggests that the QD size and therefore color emitted is independent of solvent.
The effect of reducing and oxidizing agents on the QY of CdSe (oleylamine) QDs was found to be independent of solvent for 4 of the 5 treatments. More specifically, it was found that the QY of the QDs declined after treatment with CaH$_2$, N$_2$H$_4$, and C$_4$H$_{10}$O$_2$ and improved after treatment with NaBH$_4$ in both chloroform and toluene. Treatment with C$_{14}$H$_{10}$O$_4$, on the other hand, increased the QY of the QDs when dissolved in toluene, but not in chloroform. The reason for this dependence on solvent is not known, however, a possible explanation focuses on the solubility of the oxidizing agent in the dispersion solvent, as explained in detail below.
Treatment of QDs with a reducing/oxidizing agent is expected to reduce the surface ligands thereby causing them to lose their coordinating properties and detach from the QD surface. Oxygen from atmospheric air is then able to diffuse to the exposed cadmium on the QD surface to form a cadmium oxide (CdO) layer around the QDs. This CdO layer serves to passivate defects on the QD surface, thereby enhancing the QY of the QDs. A possible explanation for the observed decrease of the QY after treatment with C_{14}H_{10}O_{4} in chloroform is that the oxidizing agent reacted with the QDs at a rate so fast that oxygen was not able to diffuse to the QD surface and form a CdO layer. Instead, C_{14}H_{10}O_{4} caused the oleylamine ligands to quickly detach from the QD surface and therefore caused aggregation in chloroform (as measured by the increase in absorbance), and resulted in a quenched QY. In toluene, however, the reaction rate was slowed down significantly because C_{14}H_{10}O_{4} is less soluble in toluene than chloroform. Because the reaction rate was slowed, after the C_{14}H_{10}O_{4} reduced the oleylamine on the QD surface, oxygen was able to form the CdO layer and therefore passivate the defect sites on the QD surface. To confirm this theory, additional testing is required. A possible experiment involves treating the QDs with a lower concentration of C_{14}H_{10}O_{4} in chloroform to see if the reaction rate slows enough to allow for the formation of a CdO layer and therefore increased QY.

As mentioned above, treatment of CdSe (oleylamine) QDs with NaBH_{4} resulted in an enhanced QY, while treatment with CaH_{2} decreased the QY of the QDs. We hypothesize that this result can be explained by a difference in the reducing agents reactivity with water. Specifically, we hypothesize that the reducing agents react with the
residual water present in each of the solvents to form hydrogen. The hydrogen then reacts with the surface ligands, causing them to detach from the QD surface, and allowing oxygen from the atmospheric air to diffuse to the exposed cadmium. The resulting CdO layer around the QDs serves to passivate the defect sites located on the QD surface and therefore improves the QY of the QDs. If the reducing agent reacts too fast with the residual water, the QDs will aggregate and the QY will be quenched. In a study by Kong et al., the reaction rate of NaBH₄ with water vapor was found to be ten times slower than that of CaH₂.¹⁶ For this reason, it is hypothesized that CaH₂ reacted very fast with the residual water present in the QD solution, causing the QDs to aggregate, and the QY to be quenched. This aggregation was confirmed by an increase in the measured absorbance. NaBH₄, on the other hand, reacted with the water at a slow enough rate that the hydrogen produced was able to effectively detach ligands on the QD surface and allow for the formation of the CdO layer.

In each of the 10 preceding subsections, a fluorescence peak centered at approximately 450 nm was observed. To account for this peak, fluorescence spectroscopy was performed on solutions consisting of each oleylamine, solvent, and reducing/oxidizing agent combination. Several of these spectra are included in the above section. From these spectra, the peak at 450 nm was consistently found to represent the ligand, solvent, and reducing/oxidizing agent combination, not the QDs. In 8 of the 10 cases summarized above, an increase in this peak centered at 450 nm was observed with time. A possible explanation for this increase is that the solvent evaporated over time, as seen by the decrease in solution volume in the pictures included in the figures above. As
the solvent evaporated, the concentration of the precursor solution increased, and an increase in fluorescence was therefore observed.

### 4.2 CdSe (OA and ODE) Quantum Dot Cores

#### 4.2.1 Treatment with Sodium Borohydride (NaBH₄) in Chloroform

Figure 4.18 displays the absorbance and fluorescence spectra of a CdSe (OA & ODE) QD and sodium borohydride (NaBH₄) solution dissolved in chloroform at a $2.02 \times 10^{-5}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 4.11 below. These values show that the QY of the QDs increased after treatment with NaBH₄ and reached a maximum 5 d after treatment. Additionally, the $E_g$ decreased slightly with time, indicating a minor increase in QD size and slight red-shift in emission color. Figure 4.18d illustrates this increase in QY and red-shift in emission color 5 d after treatment as the treated sample (right) is significantly brighter and slightly more red than the untreated sample (left). Lastly, the FWHM decreased significantly 5 d and 10 d after treatment, indicating a significant narrowing of the QD size distribution.

A possible explanation for the observed red-shift in emission is explained by the measured increase in absorbance 10 d after treatment (see Figure 4.18a). Absorbance is related to the concentration of QDs in solution, therefore an increase in absorbance is indicative of a higher density of particles packed in the QD solution. When the space
between QDs is small, it is possible for the wave function of the electrons in an individual QD to ‘leak out’ and overlap with the wave function of a neighboring QD.\(^7\) This formation of collective electronic states due to electron overlap interactions results in a spectral red-shift of QD emission.\(^7\) In conclusion, treatment of CdSe (OA & ODE) QDs dissolved in chloroform with NaBH\(_4\) resulted in a 170 % increase in the QY of the QDs and a red-shift in emission 5 d after treatment.

Figure 4.18. Absorbance spectra (a) and fluorescence spectra (b) of a 6.43 x 10\(^{-7}\) M solution of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with NaBH\(_4\) (2.02 x 10\(^{-5}\) molar ratio of QDs to NaBH\(_4\)). Photos of untreated QDs (left) and QDs treated with NaBH\(_4\) (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 4.11. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdSe (OA & ODE) QD and NaBH₄ solution dissolved in chloroform at a 2.02 x 10⁻⁵ molar ratio.

<table>
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<th>QY</th>
<th>FWHM (nm)</th>
<th>E_g (eV)</th>
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<td>Untreated</td>
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<td>217</td>
<td>2.23</td>
</tr>
<tr>
<td>Initial</td>
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<td>217</td>
<td>2.23</td>
</tr>
<tr>
<td>1 d</td>
<td>0.061</td>
<td>217</td>
<td>2.23</td>
</tr>
<tr>
<td>5 d</td>
<td>0.162</td>
<td>172</td>
<td>2.18</td>
</tr>
<tr>
<td>10 d</td>
<td>0.130</td>
<td>154</td>
<td>2.20</td>
</tr>
</tbody>
</table>

4.2.2 Treatment with Sodium Borohydride (NaBH₄) in Toluene

Figure 4.19 displays the absorbance and fluorescence spectra of a CdSe (OA & ODE) QD and sodium borohydride (NaBH₄) solution dissolved in toluene at a 9.21 x 10⁻⁵ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 4.12 below. These values show that the QY of the QDs increased slightly after treatment with NaBH₄ before decreasing to below that of the untreated QDs 1 d later. Additionally, the E_g decreased slightly with time, indicating a minor increase in QD size and red-shift in emission color. The pictures included in Figure 4.19 illustrate this decrease in QY and red-shift, as the treated sample (right) is less fluorescent and more red than the untreated sample (left).

Similar to the previous section, a possible explanation for the observed red-shift is explained by the measured increase in absorbance 5 d and 10 d after treatment (see Figure 4.19a). Absorbance is related to the concentration of QDs in solution, therefore an
increase in absorbance is indicative of a higher density of particles packed in the QD solution. When the space between QDs is small, it is possible for the wave function of the electrons in an individual QD to ‘leak out’ and overlap with the wave function of a neighboring QD. This formation of collective electronic states due to electron overlap interactions results in a spectral red-shift of QD emission. In conclusion, treatment of CdSe (OA & ODE) QDs dissolved in toluene with NaBH₄ resulted in a 0.05 % increase in the QY of the QDs immediately after treatment as well as a red-shift in emission.

Figure 4.19. Absorbance spectra (a) and fluorescence spectra (b) of a 2.93 x 10⁻⁶ M solution of CdSe (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with NaBH₄ (9.21 x 10⁻⁵ molar ratio of QDs to NaBH₄). Photos of untreated QDs (left) and QDs treated with NaBH₄ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 4.12. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdSe (OA & ODE) QD and NaBH$_4$ solution dissolved in toluene at a $9.21 \times 10^{-5}$ molar ratio.

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<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
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<tbody>
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<td>2.52</td>
</tr>
<tr>
<td>Initial</td>
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<td>156</td>
<td>2.52</td>
</tr>
<tr>
<td>1 d</td>
<td>0.165</td>
<td>155</td>
<td>2.52</td>
</tr>
<tr>
<td>5 d</td>
<td>0.103</td>
<td>159</td>
<td>2.50</td>
</tr>
<tr>
<td>10 d</td>
<td>0.066</td>
<td>166</td>
<td>2.49</td>
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4.2.3 Treatment with Calcium Hydride (CaH$_2$) in Chloroform

Figure 4.20 displays the absorbance and fluorescence spectra of a CdSe (OA & ODE) QD and calcium hydride (CaH$_2$) solution dissolved in chloroform at a $1.34 \times 10^{-4}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 4.13. These values show that the QY of the QDs reached a maximum 5 d after treatment with CaH$_2$ before decreasing to below that of the untreated QY 10 d later. Additionally, the absorbance value increased significantly between 5 d and 10 d after treatment. In a study by Mandal et al., an increase in absorbance was found to be indicative of aggregation because absorbance measurements are sensitive to scattering from colloidal suspensions that form as QD aggregates grow in size.$^6$ Furthermore, they found that a decrease in QD fluorescence also resulted from aggregation.$^6$ Similar to treatment of CdSe (oleylamine) QDs with CaH$_2$ as described in section 4.1.3 above, the observed
increase in absorbance and flattening of the fluorescence peak (see Figure 4.20) indicates that the QDs began to aggregate 10 d after treatment.

Figure 4.20. Absorbance spectra (a) and fluorescence spectra (b) of a 6.43 x 10^{-7} M solution of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with CaH₂ (1.34 x 10^{-4} molar ratio of QDs to CaH₂). Photos of untreated QDs (left) and QDs treated with CaH₂ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
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<td>156</td>
<td>2.23</td>
</tr>
<tr>
<td>Initial</td>
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<td>218</td>
<td>2.23</td>
</tr>
<tr>
<td>1 d</td>
<td>0.071</td>
<td>163</td>
<td>2.24</td>
</tr>
<tr>
<td>5 d</td>
<td>0.165</td>
<td>155</td>
<td>2.25</td>
</tr>
<tr>
<td>10 d</td>
<td>0.040</td>
<td>163</td>
<td>2.21</td>
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</table>

Table 4.13. Quantum yield (QY) and full-width half-maximum (FWHM) of a CdSe (OA & ODE) QD and CaH₂ solution dissolved in chloroform at a 1.34 x 10^{-4} molar ratio.
From the above results, a slight red-shift in emission was also observed 10 d after treatment as confirmed by the slight red-shift of the fluorescence peak, minor decrease in $E_g$, and in Figure 4.20e where the treated QDs (right) appeared slightly more red than the untreated QDs (left). Several other research groups have reported observing a red-shift in conjunction with aggregation. This red-shift is attributed to the tight packing of the QDs contained in the aggregates. Similar to treatment with NaBH$_4$ as described in the preceding sections, when QDs are tightly packed, the wave function of the electrons in an individual QD is believed to ‘leak out’ and overlap with the wave function of a neighboring QD. This formation of collective electronic states due to electron overlap interactions results in a spectral red shift of QD emission. In conclusion, treatment of CdSe (OA & ODE) QDs dissolved in chloroform with CaH$_2$ resulted in a 136 % increase in the QY of the QDs 5 d after treatment and a red-shift due to aggregation 10 d after treatment.

4.2.4 Treatment with Calcium Hydride (CaH$_2$) in Toluene

Figure 4.21 displays the absorbance and fluorescence spectra of a CdSe (OA & ODE) QD and calcium hydride (CaH$_2$) solution dissolved in toluene at a $6.10 \times 10^{-4}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 4.14 below. These values show that the QY of the QDs steadily decreased with time after treatment with CaH$_2$. Furthermore, a significant increase in absorbance was observed.
10 d after treatment (see Figure 4.21a). As explained in detail in section 4.2.3 above, an increase in absorbance was found to be indicative of aggregation because absorbance measurements are sensitive to scattering from colloidal suspensions that form as QD aggregates grow in size. Furthermore, aggregation also results in a decrease in QD fluorescence. It is therefore hypothesized that the observed increase in absorbance coupled with a decrease in fluorescence 10 d after treatment indicates that the QDs began to aggregate at this time.

In Table 4.1 below, the FWHM was reported to increase and $E_g$ to decrease slightly 5 d and 10 d after treatment, indicating a broadening of the size distribution and slight red-shift in emission color. This red-shift was confirmed in Figure 4.21 where the treated sample (right) is more red than the untreated sample (left) 5 d (d) and 10 d (e) after treatment. Similar to the preceding section, a possible explanation for the observed red-shift in emission is attributed to the tight packing of the QDs contained in the aggregates. When QDs are tightly packed, the wave function of the electrons in an individual QD is believed to ‘leak out’ and overlap with the wave function of a neighboring QD. This formation of collective electronic states due to electron overlap interactions results in a spectral red shift of QD emission. In conclusion, treatment of CdSe (OA & ODE) QDs dissolved in toluene with CaH$_2$ resulted in a decline in the QY of the QDs and a red-shift in emission due to aggregation.
Figure 4.21. Absorbance spectra (a) and fluorescence spectra (b) of a $2.93 \times 10^{-6}$ M solution of CdSe (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with CaH$_2$ ($6.10 \times 10^{-4}$ molar ratio of QDs to CaH$_2$). Photos of untreated QDs (left) and QDs treated with CaH$_2$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.14. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdSe (OA & ODE) QD and CaH$_2$ solution dissolved in chloroform at a $6.10 \times 10^{-4}$ molar ratio.

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<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
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<td>Untreated</td>
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<td>154</td>
<td>2.53</td>
</tr>
<tr>
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<td>2.55</td>
</tr>
<tr>
<td>5 d</td>
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<tr>
<td>10 d</td>
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<td>196</td>
<td>2.50</td>
</tr>
</tbody>
</table>
4.2.5 Treatment with Hydrazine ($N_2H_4$) in Chloroform

Figure 4.22 displays the absorbance and fluorescence spectra of a CdSe (OA & ODE) QD and hydrazine ($N_2H_4$) solution dissolved in chloroform at a $2.03 \times 10^{-6}$ molar ratio. Because the fluorescence of the QDs was quenched immediately after treatment, it was not possible to calculate the quantum yield (QY), full-width half-maximum (FWHM) or bandgap energy ($E_g$) of the QDs. Similar to treatment of CdSe (oleylamine) QDs in chloroform (as described in section 4.1.5 above), the addition of $N_2H_4$ resulted in an emulsion. We hypothesize that OA was able to act as a surfactant and stabilize the hydrazine droplets, as its surface tension (32.5 mN/m$^9$) was in between that of $N_2H_4$ (66.39 mN/m$^9$) and chloroform (27.5 mN/m$^9$). The hydrophilic-lipophilic balance (HLB) of OA was found to be 1$^{20}$, indicating that it is a hydrophobic surfactant.$^{11}$ Chloroform is a hydrophobic solvent, therefore OA was found to be a good surfactant that yielded a stable emulsion with small, evenly dispersed droplets of $N_2H_4$.

Immediately after adding $N_2H_4$ to the chloroform, a small amount of soluble $N_2H_4$ reacted with the QDs and reduced their surface to etch and destroy the QDs thereby quenching the QD fluorescence. The fluorescence spectrum included in Figure 4.22b confirms this quenching of the fluorescence as the peak completely flattened immediately after treatment. The residual OA in the solution then stabilized the remaining $N_2H_4$ into small, evenly dispersed $N_2H_4$ droplets. These droplets scattered the light, causing the solution to appear cloudy in visible light. When a 365 nm UV lamp was used as the incident light, the evenly dispersed droplets of $N_2H_4$ in the QD solution scattered the light causing the solution to appear purple (see pictures in Figure 4.22). In conclusion,
treatment of CdSe (OA & ODE) QDs dissolved in chloroform with N₂H₄ caused the QDs to stop fluorescing immediately after treatment.

Figure 4.22. Absorbance spectra (a) and fluorescence spectra (b) of a 6.43 x 10⁻⁷ M solution of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with N₂H₄ (2.03 x 10⁻⁶ molar ratio of QDs to N₂H₄). Photos of untreated QDs (left) and QDs treated with N₂H₄ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.15. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdSe (OA & ODE) QD and N₂H₄ solution dissolved in toluene at a 2.03 x 10⁻⁶ molar ratio.

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<th>FWHM (nm)</th>
<th>E_g (eV)</th>
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<td>Untreated</td>
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<td>2.23</td>
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<td>Initial</td>
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<td>---</td>
</tr>
<tr>
<td>1 d</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>5 d</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>10 d</td>
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</tbody>
</table>
4.2.6 Treatment with Hydrazine ($N_2H_4$) in Toluene

Figure 4.23 displays the absorbance and fluorescence spectra of a CdSe (OA & ODE) QD and hydrazine ($N_2H_4$) solution dissolved in toluene at a $9.27 \times 10^{-6}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 4.16 below. As illustrated in Figure 4.23b, immediately after treatment with $N_2H_4$, the fluorescence peak centered at 550 nm flattened completely and a peak centered at 460 nm was observed. This peak was found to be representative of the solution of toluene, OA, ODE, and $N_2H_4$, not the QDs (see Figure 4.24 below). We therefore hypothesize that immediately after treatment with $N_2H_4$ the fluorescence of the QD solution was quenched. The blue color observed in the pictures included in Figure 4.23 is therefore representative of the precursor solution, not the QDs. Because $N_2H_4$ is soluble in toluene, the issues explained in section 4.2.5 above are not applicable to this system. In conclusion, treatment of CdSe (OA & ODE) QDs dissolved in toluene with $N_2H_4$ resulted in the quenching of the QD fluorescence immediately after treatment.
Figure 4.23. Absorbance spectra (a) and fluorescence spectra (b) of a $2.93 \times 10^{-6}$ M solution of CdSe (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with N$_2$H$_4$ ($9.27 \times 10^{-6}$ molar ratio of QDs to N$_2$H$_4$). Photos of untreated QDs (left) and QDs treated with N$_2$H$_4$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.16. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdSe (OA & ODE) QD and N$_2$H$_4$ solution dissolved in toluene at a $9.27 \times 10^{-6}$ molar ratio.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.173</td>
<td>155</td>
<td>2.52</td>
</tr>
<tr>
<td>Initial</td>
<td>0.004</td>
<td>133</td>
<td>2.71</td>
</tr>
<tr>
<td>1 d</td>
<td>0.003</td>
<td>121</td>
<td>2.74</td>
</tr>
<tr>
<td>5 d</td>
<td>0.008</td>
<td>121</td>
<td>2.74</td>
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<tr>
<td>10 d</td>
<td>0.006</td>
<td>117</td>
<td>2.83</td>
</tr>
</tbody>
</table>
4.2.7 Treatment with Benzoyl Peroxide ($C_{14}H_{10}O_4$) in Chloroform

Figure 4.25 displays the absorbance and fluorescence spectra of a CdSe (OA & ODE) QD and benzoyl peroxide ($C_{14}H_{10}O_4$) solution dissolved in chloroform at a $1.29 \times 10^{-4}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, which are summarized in Table 4.17 below, show that the QY of the QDs increased significantly after treatment with $C_{14}H_{10}O_4$ and reached a maximum 5 d after treatment before decreasing to slightly below that of the untreated QY 10 d later. Additionally, the FWHM was at a minimum 5 d after treatment, indicating a narrowing of the size distribution. Lastly, the absorbance peak shifted to a slightly higher wavelength 5 d and 10 d after treatment (Figure 4.25a), the fluorescence peak red-shifted slightly (Figure 4.25b), and the $E_g$ decreased slightly, indicating a slight red-shift in emission. Figure 4.25 illustrates this increase in QY and
red-shift, as the treated sample (right) is brighter and slightly more red than the untreated sample (left).

Similar to treatment with CaH₂ and NaBH₄ as described in the preceding sections, a possible explanation for the observed red-shift in emission is explained by the measured increase in absorbance 10 d after treatment. Absorbance is related to the concentration of QDs in solution, therefore an increase in absorbance is indicative of a higher density of particles packed in the QD solution. When the space between QDs is small, it is possible for the wave function of the electrons in an individual QD to ‘leak out’ and overlap with the wave function of a neighboring QD.⁷ This formation of collective electronic states due to electron overlap interactions results in a spectral red-shift of QD emission.⁷ In conclusion, treatment of CdSe (OA & ODE) QDs dissolved in chloroform with C₁₄H₁₀O₄ resulted in an 81.5 % increase in the QY of the QDs 5 d after treatment as well as a red-shift in emission.
Figure 4.25. Absorbance spectra (a) and fluorescence spectra (b) of a 6.43 x 10^{-7} M solution of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with C_{14}H_{10}O_4 (1.29 x 10^{-4} molar ratio of QDs to C_{14}H_{10}O_4). Photos of untreated QDs (left) and QDs treated with 0.025 mmol C_{14}H_{10}O_4 (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.17. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdSe (OA & ODE) QD and C_{14}H_{10}O_4 solution dissolved in chloroform at a 1.29 x 10^{-4} molar ratio.

<table>
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<th>QY</th>
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<th>E_g (eV)</th>
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<tr>
<td>Initial</td>
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<td>176</td>
<td>2.25</td>
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<tr>
<td>1 d</td>
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<td>170</td>
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<tr>
<td>5 d</td>
<td>0.147</td>
<td>156</td>
<td>2.20</td>
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<tr>
<td>10 d</td>
<td>0.074</td>
<td>168</td>
<td>2.20</td>
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4.2.8 Treatment with Benzoyl Peroxide ($C_{14}H_{10}O_4$) in Toluene

Figure 4.26 displays the absorbance and fluorescence spectra of a CdSe (OA & ODE) QD and benzoyl peroxide ($C_{14}H_{10}O_4$) solution dissolved in toluene at a $5.86 \times 10^{-4}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 4.18 below. From these values, it can be seen that the QY of the QDs steadily decreased with time after treatment with $C_{14}H_{10}O_4$. Additionally, the absorbance peak shifted to a higher wavelength 5 d and 10 d after treatment indicating the QDs grew and size and therefore a red-shift in emission is expected. Conversely, the fluorescence peak narrowed and centered at a lower wavelength 5 d and 10 d after treatment indicating a blue-shift in emission. Furthermore, Figure 4.26 illustrates that the QDs fluoresced pink 5 d and 10 d after treatment. An explanation for these conflicting results is not known and it is therefore recommended that this treatment be redone to ensure accuracy. In conclusion, treatment of CdSe (OA & ODE) QDs dissolved in toluene with $C_{14}H_{10}O_4$ resulted in a decrease in the QY of the QDs.
Figure 4.26. Absorbance spectra (a) and fluorescence spectra (b) of a 2.93 x 10^{-7} M solution of CdSe (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with C_{14}H_{10}O_{4} (5.86 x 10^{-4} molar ratio of QDs to C_{14}H_{10}O_{4}). Photos of untreated QDs (left) and QDs treated with C_{14}H_{10}O_{4} (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.18. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdSe (OA & ODE) QD and C_{14}H_{10}O_{4} solution dissolved in toluene at a 5.86 x 10^{-4} molar ratio.

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<th>QY</th>
<th>FWHM (nm)</th>
<th>E_g (eV)</th>
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<tr>
<td>Untreated</td>
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<td>156</td>
<td>2.50</td>
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<tr>
<td>Initial</td>
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<td>156</td>
<td>2.50</td>
</tr>
<tr>
<td>1 d</td>
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<tr>
<td>5 d</td>
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<td>84.6</td>
<td>2.66</td>
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<td>10 d</td>
<td>0.037</td>
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4.2.9 Treatment with tert-Butyl Hydroperoxide (C₄H₁₀O₂) in Chloroform

Figure 4.27 displays the absorbance and fluorescence spectra of a CdSe (OA & ODE) QD and tert-butyl hydroperoxide (C₄H₁₀O₂) solution dissolved in chloroform at a 2.06 x 10⁻⁶ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E₉) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 4.19 below. From these values, it can be seen that the QY of the QDs decreased after treatment with C₄H₁₀O₂. Despite this measured decrease in fluorescence, the solution appeared blue when excited by a 365 nm UV lamp (see pictures in Figure 4.27) because the mixture of residual OA, ODE, and C₄H₁₀O₂ in solution emits light at 450 nm upon excitation (see Figure 4.28). Additionally, the broad fluorescence peak narrowed and centered at a lower wavelength, resulting in a decreased FWHM and increased E₉. In conclusion, treatment of CdSe (OA & ODE) QDs dissolved in chloroform with C₄H₁₀O₂ resulted in a decrease in the QY of the QDs.
Figure 4.27. Absorbance spectra (a) and fluorescence spectra (b) of a $6.43 \times 10^{-7}$ M solution of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with $C_4H_{10}O_2$ ($2.06 \times 10^{-6}$ molar ratio of QDs to $C_4H_{10}O_2$). Photos of untreated QDs (left) and QDs treated with $C_4H_{10}O_2$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.19. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdSe (OA & ODE) QD and $C_4H_{10}O_2$ solution dissolved in toluene at a $2.06 \times 10^{-6}$ molar ratio.

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<th>$E_g$ (eV)</th>
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</tr>
<tr>
<td>Initial</td>
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<td>198</td>
<td>---</td>
</tr>
<tr>
<td>1 d</td>
<td>0.013</td>
<td>158</td>
<td>2.31</td>
</tr>
<tr>
<td>5 d</td>
<td>0.021</td>
<td>124</td>
<td>2.30</td>
</tr>
<tr>
<td>10 d</td>
<td>0.007</td>
<td>---</td>
<td>2.31</td>
</tr>
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</table>
4.2.10 Treatment with tert-Butyl Hydroperoxide (C4H10O2) in Toluene

Figure 4.29 displays the absorbance and fluorescence spectra of a CdSe (OA & ODE) QD and tert-butyl hydroperoxide (C4H10O2) solution dissolved in toluene at a 9.39 x 10^{-6} molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, which are summarized in Table 4.20 below, show that the QY of the QDs decreased after treatment with C4H10O2. This decrease in QY was confirmed by the significant decrease in the fluorescence peak (Figure 4.29b) as well from the pictures in Figure 4.29 where the treated QDs (right) are less bright than the untreated QDs (left). Additionally, the broad fluorescence peak narrowed and centered at a lower wavelength, resulting in a decreased FWHM and increased E_g. These observations suggest an expected blue-shift in emission which was confirmed in Figure 4.29 where the treated QD solution (right) is significantly bluer than
the untreated solution (left). In conclusion, treatment of CdSe (OA & ODE) QDs dissolved in toluene with C₄H₁₀O₂ resulted in a decrease in the QY of the QDs.

Figure 4.29. Absorbance spectra (a) and fluorescence spectra (b) of a 2.93 x 10⁻⁶ M solution of CdSe (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with C₄H₁₀O₂ (9.39 x 10⁻⁶ molar ratio of QDs to C₄H₁₀O₂). Photos of untreated QDs (left) and QDs treated with C₄H₁₀O₂ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.20. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E₉) of a CdSe (OA & ODE) QD and C₄H₁₀O₂ solution dissolved in toluene at a 9.39 x 10⁻⁶ molar ratio.

<table>
<thead>
<tr>
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<th>QY</th>
<th>FWHM (nm)</th>
<th>E₉ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
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<td>156</td>
<td>2.52</td>
</tr>
<tr>
<td>Initial</td>
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<td>198</td>
<td>---</td>
</tr>
<tr>
<td>1 d</td>
<td>0.007</td>
<td>119</td>
<td>2.64</td>
</tr>
<tr>
<td>5 d</td>
<td>0.013</td>
<td>100</td>
<td>2.68</td>
</tr>
<tr>
<td>10 d</td>
<td>0.012</td>
<td>110</td>
<td>2.67</td>
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4.2.11 Summary of CdSe/OA & ODE Treatments

Figure 4.30 compares the effect of treating CdSe (OA & ODE) QDs with various reducing and oxidizing agents in chloroform versus toluene. From these photographs, it can be seen that the QDs dissolved in toluene were visibly brighter than those in chloroform. This observation was confirmed as the QY of the QDs before treatment in chloroform was approximately 0.067 while the QY in toluene was approximately 0.170. Because both sets of QDs came from the same master batch of cores, this difference in QY may be due to the solubility of OA in the various solvents. Thuy et al. have shown that the QY is higher when the capping ligand is less soluble in a given solvent.\textsuperscript{13} From our results, we found that the QY of the QDs was higher in toluene than chloroform therefore implying that OA is less soluble in toluene than chloroform. The literature, however, states that OA is more soluble in toluene than chloroform, therefore disproving this explanation. A possible explanation for this dependence on solvent may therefore be due to the solubility of oxygen in each of the solvents. The $E_g$ of the untreated QDs in chloroform and toluene were 2.23 eV and 2.52 eV, respectively, which suggests that the solvent does have an effect on QD size and color emitted. An explanation for this phenomenon is not readily known, and will be explored via additional characterization methods in the future work of this thesis.
Figure 4.30. Photos of CdSe (OA & ODE) QDs that are from left to right: untreated, treated with NaBH₄, C₁₄H₁₀O₄, CaH₂, N₂H₄, and C₄H₁₀O₂ excited with 365 nm UV light. The QDs in the left column were suspended and treated in chloroform while those in the right column were suspended and treated in toluene. Photos were taken 1 d (top row), 5 d (middle row), and 10 d (bottom row) after treatment.

The overall effect of reducing and oxidizing agents on the overall QY of CdSe (OA & ODE) QDs was found to be independent of solvent for 3 of the 5 treatments. More specifically, it was found that the QY of the QDs improved after treatment with NaBH₄ and worsened after treatment with N₂H₄ and C₄H₁₀O₂ in both chloroform and toluene. Treatment with CaH₂ and C₁₄H₁₀O₄, on the other hand, increased the QY of the QDs when dissolved in chloroform, but not in toluene. Even though the QY of the QDs increased after treatment with NaBH₄ in both chloroform and toluene, the percent increase in QY in chloroform was significantly higher than in toluene, 170 % compared
to 0.05 %, respectively. These results clearly illustrate that the surface treatment of CdSe (OA & ODE) QDs was more effective in chloroform than toluene.

The reason for this dependence on solvent is not known, however, a possible explanation focuses on the solubility of the ligand (OA) in the dispersion solvent. In a study by Bullen et al., it was concluded that desorption of the surface ligands may occur if the ligand is more soluble in a given solvent, therefore resulting in decreased QY. Oleic acid is more soluble in toluene than chloroform as confirmed by comparing Hildebrand solubility parameters. Specifically, the Hildebrand solubility parameter ($\delta$) provides a good estimation of the solubility of two substances as it is a numerical estimate of the degree of interaction between materials. The closer the $\delta$ of two substances, the better the degree of solubility. Furthermore, $\delta_{\text{OA}} = 15.95$, $\delta_{\text{toluene}} = 17.8$, and $\delta_{\text{chloroform}} = 19.0$, therefore confirming that OA is more soluble in toluene than chloroform. For this reason, it can be hypothesized that OA ligands will desorb from the QD surface at a faster rate in toluene than chloroform, thereby explaining why surface treatment is more effective in chloroform than toluene.

A second possible explanation for the observed results focuses on the solubility of the reducing agent in the dispersion solvent. We hypothesize that when a reducing/oxidizing agent it highly soluble in a given solvent, it reacts with the QDs at a rate so fast desorption of the ligands and aggregation occur before forming a stable QD with a CdO layer. The net result is an increase in the UV absorbance and a quenching of the fluorescence resulting in a decrease in QY. As explained above, treatment of QDs
dispersed in toluene resulted in a decreased QY, while treatment in chloroform enhanced the QY. We therefore hypothesize that CaH₂ is more soluble in toluene than chloroform, resulting in a faster reduction rate of the QDs when dissolved and treated in the former solvent. Unfortunately, information is not currently available regarding the solubility of CaH₂ in toluene versus chloroform. For this reason, it is recommended that future work include a solubility study to determine the solubility of CaH₂ in both chloroform and toluene to confirm this theory.

Treatment with C₁₄H₁₀O₄ also resulted in an enhanced QY when the QDs were dispersed and treated in chloroform but not in toluene. This result is opposite of the results obtained in the treatment of CdSe (oleylamine) QDs as detailed in section 4.1.11 above. When dissolved in toluene, treatment with C₁₄H₁₀O₄ resulted in conflicting results. Specifically, the absorbance spectrum showed a red-shift in emission while the fluorescence spectrum showed a blue-shift in emission after treatment. An explanation for these conflicting results is not known and it was therefore recommended that this treatment be redone to ensure accuracy. It is expected that after retreating CdSe (OA & ODE) QDs dissolved in toluene with C₁₄H₁₀O₄, a greater increase in QY will result than the 81.5 % increase observed when the QDs were dissolved in chloroform. This expectation is supported by the fact that C₁₄H₁₀O₄ is more soluble in chloroform than toluene, therefore the rate of reaction will be higher in chloroform than toluene. Because an increase in QY was observed in chloroform, it can therefore be hypothesized that an even greater increase in QY will be observed when the QDs are retreated in toluene.
In Figure 4.30, it can clearly be seen that treatment with N$_2$H$_4$ and C$_4$H$_{10}$O$_2$ had a different effect in chloroform than toluene. Specifically, the QD solutions appeared very bright when dissolved in chloroform but did not fluoresce when in toluene. Although the QY was calculated to decrease after treatment in both solvents, the reason for the observed decrease was very different. In the case of N$_2$H$_4$, as explained in detail in the preceding sections, the reducing agent was nearly insoluble in chloroform and has poor solubility in toluene. For this reason, an emulsion formed when the QDs were treated in chloroform, causing the incident light to scatter, and the QD solution to appear purple. When the QDs were treated in toluene, however, the N$_2$H$_4$ was soluble in toluene therefore no emulsion formed. Instead, the QDs reacted with the reducing agent immediately after treatment resulting in a quenched fluorescence. In the case of C$_4$H$_{10}$O$_2$, when added to QDs dispersed in chloroform, the solution appeared significantly brighter than when added to toluene, even though the QY was calculated to decrease in both cases. A reason for this decrease is not known, however, as explained above, the increased solubility of OA in toluene over chloroform may be a potential reason.

In section 4.1.11 above, a fluorescence peak centered at approximately 450 nm was observed in every measured fluorescence spectra. This peak was not observed in any of the 10 preceding sections. Similar to the case of oleylamine, fluorescence spectroscopy was performed on solutions consisting of each OA, ODE, solvent, and reducing/oxidizing agent combination to account for the potential influence of the various reaction materials on QD fluorescence. In these spectra, a peak at 450 nm was measured and was therefore said to be representative of the reaction materials. Because this peak was not observed in
the above spectra, we hypothesize that there was no residual OA present in the solvents. In other words, if residual OA was present in the solution, we would expect to see a fluorescence peak representing its interaction with the solvent it is dispersed in and added reducing/oxidizing agent.

**4.3 CdSe (OA and TOA) Quantum Dot Cores**

*4.3.1 Treatment with Sodium Borohydride (NaBH₄) in Chloroform*

Figure 4.31 displays the absorbance and fluorescence spectra of a CdSe (OA & TOA) QD and sodium borohydride (NaBH₄) solution dissolved in chloroform at a 5.54 x 10⁻⁵ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E₉) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 4.21 below, show that the QY of the QDs steadily increased after treatment with NaBH₄ until reaching a maximum 10 d after treatment. Figure 4.31e illustrates this increase in QY 10 d after treatment, as the treated sample (right) is brighter than the untreated sample (left). Additionally, no notable change in FWHM or E₉ was observed therefore ruling out a significant broadening of the QD size distribution or shift in QD emission after treatment.

In calculating QY for this sample, the fluorescence peak centered at 620 nm was determined to be representative of the QDs rather than the negative peak centered at 430 nm because the QDs fluoresced red in color (see pictures in Figure 4.31) which
indicates a higher wavelength. To account for the potential influence of the various reaction materials on the negative fluorescence peak, fluorescence spectroscopy was performed on a solution of chloroform, OA, TOA and NaBH₄. The normalized fluorescence spectrum of this solution is included in Figure 4.32. From this spectrum it can be seen that a significant fluorescence peak centered at 450 nm resulted, however, no negative peak was measured. An explanation for this negative peak is therefore not known and will be explored further in future work. In conclusion, treatment of CdSe (OA & TOA) QDs dissolved in chloroform with NaBH₄ resulted in a 133 % increase in the QY of the QDs 10 d after treatment.

Figure 4.31. Absorbance spectra (a) and fluorescence spectra (b) of a 2.88 x 10⁻⁷ M solution of CdSe (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with NaBH₄ (5.54 x 10⁻⁵ molar ratio of QDs to NaBH₄). Photos of untreated QDs (left) and QDs treated with NaBH₄ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 4.21. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdSe (OA & TOA) QD and NaBH₄ solution dissolved in chloroform at a 5.54 x 10⁻⁵ molar ratio.

<table>
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<td>1.91</td>
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<tr>
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<td>0.004</td>
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<td>53.3</td>
<td>1.93</td>
</tr>
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Figure 4.32. Normalized fluorescence spectrum of a solution composed of chloroform, OA, TOA and NaBH₄.

4.3.2 Treatment with Sodium Borohydride (NaBH₄) in Toluene

Figure 4.33 displays the absorbance and fluorescence spectra of a CdSe (OA & TOA) QD and sodium borohydride (NaBH₄) solution dissolved in toluene at a 5.83 x 10⁻⁵ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 4.22 below, show that the QY of the QDs steadily decreased with time after treatment.
with NaBH₄. From the pictures in Figure 4.33, however, an increase in the QY was observed as the treated QDs (right) appeared more bright than the untreated QDs (left). In fact, the untreated QD solution appeared to decrease in brightness with time. This result leads to the hypothesis that CdSe (OA & TOA) QDs are not stable with time. Furthermore, this decrease in the QY of the untreated QDs over time may explain why the QY calculated after treatment with NaBH₄ decreased with time even though an increase in brightness was observed. Lastly, no noticeable change in FWHM or Eₓ was observed, therefore ruling out a significant change in the size distribution or size of the QDs. In conclusion, treatment of CdSe (OA & TOA) QDs dissolved in toluene with NaBH₄ resulted in an increase in the QY of the QDs.
Figure 4.33. Absorbance spectra (a) and fluorescence spectra (b) of a $3.03 \times 10^{-7} \text{ M}$ solution of CdSe (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with NaBH$_4$ ($5.83 \times 10^{-5}$ molar ratio of QDs to NaBH$_4$). Photos of untreated QDs (left) and QDs treated with NaBH$_4$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.22. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdSe (OA & TOA) QD and NaBH$_4$ solution dissolved in toluene at a $5.83 \times 10^{-5}$ molar ratio.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.073</td>
<td>61.1</td>
<td>1.92</td>
</tr>
<tr>
<td>Initial</td>
<td>0.072</td>
<td>60.7</td>
<td>1.92</td>
</tr>
<tr>
<td>1 d</td>
<td>0.040</td>
<td>55.2</td>
<td>1.93</td>
</tr>
<tr>
<td>5 d</td>
<td>0.040</td>
<td>56.1</td>
<td>1.93</td>
</tr>
<tr>
<td>10 d</td>
<td>0.038</td>
<td>56.7</td>
<td>1.93</td>
</tr>
</tbody>
</table>
4.3.3 Treatment with Calcium Hydride (CaH$_2$) in Chloroform

Figure 4.34 displays the absorbance and fluorescence spectra of a CdSe (OA & TOA) QD and calcium hydride (CaH$_2$) solution dissolved in chloroform at a 6.00 x 10$^{-5}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 4.23 below, show that the QY of the QDs decreased immediately after treatment with CaH$_2$ and the QDs stopped fluorescing 5 d after treatment. Additionally, the absorbance value increased after treatment. In a study by Mandal et al., an increase in absorbance was found to be indicative of aggregation because absorbance measurements are sensitive to scattering from colloidal suspensions that form as QD aggregates grow in size.$^6$ Furthermore, they found that a decrease in QD fluorescence also resulted from aggregation.$^6$ Similar to treatment of CdSe (OA & ODE) QDs with CaH$_2$ as described in section 4.2.3 above, the observed increase in absorbance and flattening of the fluorescence peak (see Figure 4.34) therefore indicate that the QDs began to aggregate 5 d after treatment. In Figure 4.34d, a decrease in the QY was observed as the treated QDs (right) are less bright than the untreated QDs (left).

The absorbance continued to increase 10 d after treatment (see purple line in Figure 4.34a) which indicates that the QD aggregates continued to grow between 5 d and 10 d after treatment. Furthermore, because in Figure 4.34e the fluorescence of the treated QDs solution is quenched, it can be hypothesized that the aggregates grew large enough that the QDs precipitated out of solution at this time.$^7$ Lastly, as explained in section
4.3.1, a reason for the observed negative peak centered at 430 nm is not readily known and will be explored further in future work. In conclusion, treatment of CdSe (OA & TOA) QDs dissolved in chloroform with CaH₂ resulted in a quenching of the QD fluorescence 10 d after treatment due to aggregation.

Figure 4.34. Absorbance spectra (a) and fluorescence spectra (b) of a 2.88 x 10⁻⁷ M solution of CdSe (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with CaH₂ (6.00 x 10⁻⁵ molar ratio of QDs to CaH₂). Photos of untreated QDs (left) and QDs treated with CaH₂ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 4.23. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E\textsubscript{g}) of a CdSe (OA & TOA) QD and CaH\textsubscript{2} solution dissolved in chloroform at a 6.00 x 10\textsuperscript{-5} molar ratio.

<table>
<thead>
<tr>
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<th>QY</th>
<th>FWHM (nm)</th>
<th>E\textsubscript{g} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
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<td>53.5</td>
<td>1.92</td>
</tr>
<tr>
<td>Initial</td>
<td>0.002</td>
<td>56.7</td>
<td>1.90</td>
</tr>
<tr>
<td>1 d</td>
<td>0.002</td>
<td>54.0</td>
<td>1.91</td>
</tr>
<tr>
<td>5 d</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>10 d</td>
<td>---</td>
<td>---</td>
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</tr>
</tbody>
</table>

4.3.4 Treatment with Calcium Hydride (CaH\textsubscript{2}) in Toluene

Figure 4.35 displays the absorbance and fluorescence spectra of a CdSe (OA & TOA) QD and calcium hydride (CaH\textsubscript{2}) solution dissolved in toluene at a 6.31 x 10\textsuperscript{-5} molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E\textsubscript{g}) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 4.24 below, show that the QY of the QDs steadily decreased with time after treatment with CaH\textsubscript{2}. This decrease in QY after treatment was confirmed by both the flattening of the fluorescence peak and pictures included in Figure 4.35 where the treated QDs (right) appeared less bright than the untreated QDs (left). Additionally, a slightly broader fluorescence peak, increased FWHM, and less refined absorption peak indicate broadening of the QD size distribution after treatment. In conclusion, treatment of CdSe (OA & TOA) QDs dissolved in toluene with CaH\textsubscript{2} resulted in a decrease in the QY of the QDs.
Figure 4.35. Absorbance spectra (a) and fluorescence spectra (b) of a $3.03 \times 10^{-7}$ M solution of CdSe (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with CaH$_2$ ($6.31 \times 10^{-5}$ molar ratio of QDs to CaH$_2$). Photos of untreated QDs (left) and QDs treated with CaH$_2$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.24. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdSe (OA & TOA) QD and CaH$_2$ solution dissolved in toluene at a $6.31 \times 10^{-5}$ molar ratio.

<table>
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<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
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<td>Initial</td>
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<td>1.91</td>
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<tr>
<td>1 d</td>
<td>0.038</td>
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<td>5 d</td>
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<td>10 d</td>
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<td>75.3</td>
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4.3.5 Treatment with Hydrazine (N$_2$H$_4$) in Chloroform

Figure 4.36 displays the absorbance and fluorescence spectra of a CdSe (OA & TOA) QD and hydrazine (N$_2$H$_4$) solution dissolved in chloroform at a $3.04 \times 10^{-7}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 4.25 below. Similar to treatment of CdSe (OA & ODE) QDs in chloroform (as described in section 4.2.5 above), treatment of CdSe (OA & TOA) QDs with N$_2$H$_4$ resulted in an emulsion due to the near insolubility of N$_2$H$_4$ in chloroform. Although it was previously concluded that OA was a good surfactant in chloroform due to its low HLB value, large, poorly dispersed droplets of N$_2$H$_4$ formed in the treatment of CdSe (OA & TOA) QDs in chloroform (see pictures in Figure 4.36).

Octadecene does not have surfactant-like properties because it does not contain both polar and non-polar groups, therefore it was not a factor in the emulsion described in section 4.2.5. Tricoctylamine, on the other hand, does contain polar and non-polar groups and was therefore a factor in the emulsion. More specifically, the nitrogen in TOA forms three bonds, leaving a single lone pair of electrons. We hypothesize that this lone pair of electrons is repelled by the lone pair of electrons of N$_2$H$_4$, preventing all of the reducing agent from reacting with the QDs. Instead, immediately after adding N$_2$H$_4$ to the chloroform, a small amount of soluble N$_2$H$_4$ reacted with the QDs and reduced their surface to etch and destroy the QDs thereby quenching the QD fluorescence. The fluorescence spectrum included in Figure 4.36b confirms this quenching of the
fluorescence as the peak completely flattened immediately after treatment. The remainder of the N$_2$H$_4$ formed large, unevenly dispersed N$_2$H$_4$ droplets stabilized by the residual OA and TOA. The solution appeared blue-green when excited by a 365 nm UV lamp because the mixture of chloroform, OA, and TOA emits light at 450 nm upon excitation (see Figure 4.37). After 10 d a visible layer formed at the top of the chloroform solution, presumably due to instability of the emulsion (see Figure 4.36e). This result is consistent with the result of treating CdSe (oleylamine) QDs in chloroform with N$_2$H$_4$ as explained in section 4.1.5 above.

Figure 4.36. Absorbance spectra (a) and fluorescence spectra (b) of a 2.88 x 10$^{-7}$ M solution of CdSe (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with N$_2$H$_4$ (3.04 x 10$^{-7}$ molar ratio of QDs to N$_2$H$_4$). Photos of untreated QDs (left) and QDs treated with N$_2$H$_4$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 4.25. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdSe (OA & TOA) QD and N₂H₄ solution dissolved in chloroform at a 3.04 x 10⁻⁷ molar ratio.

<table>
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<th>$E_g$ (eV)</th>
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<tbody>
<tr>
<td>Untreated</td>
<td>0.003</td>
<td>53.5</td>
<td>1.92</td>
</tr>
<tr>
<td>Initial</td>
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<tr>
<td>1 d</td>
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<td>101</td>
<td>2.33</td>
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<tr>
<td>10 d</td>
<td>---</td>
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</table>

Figure 4.37. Normalized fluorescence spectrum of a solution composed of chloroform, OA, TOA, and N₂H₄.

It is unclear why the fluorescence spectrum of the QDs 5 d after treatment is not similar to that of the 10 d spectrum. A possible explanation is that the cuvette in which the fluorescence was measured was contaminated. Lastly, as explained in section 4.3.1, a reason for the observed negative peak centered at 430 nm is not readily known and will be explored further in future work. Figure 4.36b shows a second negative peak centered at 650 nm that appeared 10 d after treatment. This too will be explored in future work.
conclusion, treatment of CdSe (OA & TOA) QDs dissolved in chloroform with N\textsubscript{2}H\textsubscript{4} resulted in a quenching of the QD fluorescence.

4.3.6 Treatment with Hydrazine (N\textsubscript{2}H\textsubscript{4}) in Toluene

Figure 4.38 displays the absorbance and fluorescence spectra of a CdSe (OA & TOA) QD and hydrazine (N\textsubscript{2}H\textsubscript{4}) solution dissolved in toluene at a 3.20 x 10\textsuperscript{-7} molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E\textsubscript{g}) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 4.26 below, show that the QY of the QDs decreased immediately after treatment with N\textsubscript{2}H\textsubscript{4}. Although N\textsubscript{2}H\textsubscript{4} is soluble in toluene, residual TOA in the QD solution prevented all of the reducing agent from reacting with the QDs, similar to treatment in chloroform as described in section 4.2.5 above. Instead, immediately after adding N\textsubscript{2}H\textsubscript{4} to the toluene, a small amount of N\textsubscript{2}H\textsubscript{4} reacted with the QDs and reduced their surface to etch and destroy the QDs thereby quenching the QD fluorescence. The fluorescence spectrum included in Figure 4.38b confirms this quenching of the fluorescence as the peak completely flattened immediately after treatment. The remainder of the N\textsubscript{2}H\textsubscript{4} formed large, unevenly dispersed N\textsubscript{2}H\textsubscript{4} droplets stabilized by the residual OA and TOA. The solution appeared blue-green when excited by a 365 nm UV lamp because the mixture of toluene, OA, and TOA emits light at 450 nm upon excitation (see Figure 4.39). After 10 d, unreacted N\textsubscript{2}H\textsubscript{4} would visibly be seen in the toluene solution (see Figure 4.38e). A distinct N\textsubscript{2}H\textsubscript{4} layer did not form in this
case because \( \text{N}_2\text{H}_4 \) is more dense than toluene. In conclusion, treatment of CdSe (OA & TOA) QDs dissolved in toluene with \( \text{N}_2\text{H}_4 \) resulted in a quenching of the QD fluorescence.

Figure 4.38. Absorbance spectra (a) and fluorescence spectra (b) of a \( 3.03 \times 10^{-7} \) M solution of CdSe (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with \( \text{N}_2\text{H}_4 \) (3.20 \( \times 10^{-7} \) molar ratio of QDs to \( \text{N}_2\text{H}_4 \)). Photos of untreated QDs (left) and QDs treated with \( \text{N}_2\text{H}_4 \) (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 4.26. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdSe (OA & TOA) QD and N$_2$H$_4$ solution dissolved in toluene at a 3.20 x 10$^{-7}$ molar ratio.

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<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
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<td>1.92</td>
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<tr>
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<td>1 d</td>
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</tr>
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<td>5 d</td>
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<td>2.43</td>
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<tr>
<td>10 d</td>
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<td>151</td>
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Figure 4.39. Normalized fluorescence spectrum of a solution composed of toluene, OA, TOA, and N$_2$H$_4$.

4.3.7 Treatment with Benzoyl Peroxide (C$_{14}$H$_{10}$O$_4$) in Chloroform

Figure 4.40 displays the absorbance and fluorescence spectra of a CdSe (OA & TOA) QD and benzoyl peroxide (C$_{14}$H$_{10}$O$_4$) solution dissolved in chloroform at a 1.20 x 10$^{-4}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 4.27 below, show that the QY of the QDs increased slightly 1 d after treatment with C$_{14}$H$_{10}$O$_4$ before decreasing to below that of the untreated QY 10 d later. Additionally, no
notable change in FWHM or $E_g$ was observed therefore ruling out a significant broadening of the QD size distribution or change in QD size after treatment. Furthermore, as explained in section 4.3.1, a reason for the observed negative peak centered at 430 nm is not readily known and will be explored further in future work. In conclusion, treatment of CdSe (OA & TOA) QDs dissolved in chloroform with $\text{C}_{14}\text{H}_{10}\text{O}_4$ resulted in a 66.7% increase in the QY of the QDs 1 d after treatment.

Figure 4.40. Absorbance spectra (a) and fluorescence spectra (b) of a $2.88 \times 10^{-7}$ M solution of CdSe (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with $\text{C}_{14}\text{H}_{10}\text{O}_4$ (1.20 $\times 10^{-5}$ molar ratio of QDs to $\text{C}_{14}\text{H}_{10}\text{O}_4$). Photos of untreated QDs (left) and QDs treated with $\text{C}_{14}\text{H}_{10}\text{O}_4$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 4.27. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E\textsubscript{g}) of a CdSe (OA & TOA) QD and C\textsubscript{14}H\textsubscript{10}O\textsubscript{4} solution dissolved in chloroform at a 1.20 x 10\textsuperscript{-4} molar ratio.

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<th>FWHM (nm)</th>
<th>E\textsubscript{g} (eV)</th>
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</thead>
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<tr>
<td>Untreated</td>
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<td>53.5</td>
<td>1.92</td>
</tr>
<tr>
<td>Initial</td>
<td>0.003</td>
<td>54.3</td>
<td>1.93</td>
</tr>
<tr>
<td>1 d</td>
<td>0.005</td>
<td>52.8</td>
<td>1.93</td>
</tr>
<tr>
<td>5 d</td>
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<tr>
<td>10 d</td>
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4.3.8 Treatment with Benzoyl Peroxide (C\textsubscript{14}H\textsubscript{10}O\textsubscript{4}) in Toluene

Figure 4.41 displays the absorbance and fluorescence spectra of a CdSe (OA & TOA) QD and benzoyl peroxide (C\textsubscript{14}H\textsubscript{10}O\textsubscript{4}) solution dissolved in toluene at a 1.26 x 10\textsuperscript{-4} molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E\textsubscript{g}) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 4.28 below, show that the QY of the QDs steadily decreased with time after treatment with C\textsubscript{14}H\textsubscript{10}O\textsubscript{4}. This decrease in QY after treatment was confirmed by the flattening of the fluorescence peak and by the pictures in Figure 4.41 where the treated QDs (right) were less bright than the untreated QDs (left). Additionally, no notable change in FWHM or E\textsubscript{g} was observed therefore ruling out a significant broadening of the QD size distribution or change in QD size after treatment. In conclusion, treatment of CdSe (OA & TOA) QDs dissolved in toluene with C\textsubscript{14}H\textsubscript{10}O\textsubscript{4} resulted in a decrease in the QY of the QDs.
Figure 4.41. Absorbance spectra (a) and fluorescence spectra (b) of a $3.03 \times 10^{-7}$ M solution of CdSe (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with C$_{14}$H$_{10}$O$_{4}$ (1.26 $\times 10^{-4}$ molar ratio of QDs to C$_{14}$H$_{10}$O$_{4}$). Photos of untreated QDs (left) and QDs treated with C$_{14}$H$_{10}$O$_{4}$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.28. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdSe (OA & TOA) QD and C$_{14}$H$_{10}$O$_{4}$ solution dissolved in toluene at a 1.26 $\times 10^{-4}$ molar ratio.

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<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
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<td>63.3</td>
<td>1.92</td>
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<tr>
<td>1 d</td>
<td>0.029</td>
<td>61.3</td>
<td>1.92</td>
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<tr>
<td>5 d</td>
<td>0.004</td>
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<td>1.93</td>
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<tr>
<td>10 d</td>
<td>0.001</td>
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<td>1.95</td>
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4.3.9 Treatment with tert-Butyl Hydroperoxide (C₄H₁₀O₂) in Chloroform

Figure 4.42 displays the absorbance and fluorescence spectra of a CdSe (OA & TOA) QD and tert-Butyl Hydroperoxide (C₄H₁₀O₂) solution dissolved in chloroform at a 1.38 x 10⁻⁶ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 4.29 below, show that the QY of the QDs decreased immediately after treatment with C₄H₁₀O₂. In fact, the QDs stopped fluorescing 5 d after treatment as confirmed by both the flattening of the fluorescence spectrum and Figure 4.42 where the treated QDs (right) no longer fluoresced. Furthermore, as seen in the fluorescence spectra of each of the treatments completed in chloroform, a negative peak centered at 430 nm was measured. A second negative peak centered at 650 nm was also measured 10 d after treatment with N₂H₄ as mentioned in section 4.3.5 above. As seen in Figure 4.42b below, both of these negative peaks were observed after treatment with C₄H₁₀O₂. An explanation for these negative peaks is not readily known and will be explored further in future work. In conclusion, treatment of CdSe (OA & TOA) QDs dissolved in chloroform with C₄H₁₀O₂ resulted in a quenching of the QD fluorescence.
Figure 4.42. Absorbance spectra (a) and fluorescence spectra (b) of a 2.88 x 10^{-7} M solution of CdSe (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with C_4H_{10}O_2 (1.38 x 10^{-6} molar ratio of QDs to C_4H_{10}O_2). Photos of untreated QDs (left) and QDs treated with C_4H_{10}O_2 (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.29. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdSe (OA & TOA) QD and C_4H_{10}O_2 solution dissolved in chloroform at a 1.38 x 10^{-6} molar ratio.

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<th>E_g (eV)</th>
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<td>1.92</td>
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<tr>
<td>Initial</td>
<td>0.001</td>
<td>56.1</td>
<td>1.92</td>
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<tr>
<td>1 d</td>
<td>0.001</td>
<td>65.0</td>
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<tr>
<td>5 d</td>
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</tr>
<tr>
<td>10 d</td>
<td>---</td>
<td>---</td>
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</tr>
</tbody>
</table>
4.3.10 Treatment with tert-Butyl Hydroperoxide (C₄H₁₀O₂) in Toluene

Figure 4.43 displays the absorbance and fluorescence spectra of a CdSe (OA & TOA) QD and tert-Butyl Hydroperoxide (C₄H₁₀O₂) solution dissolved in toluene at a 1.46 x 10⁻⁶ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E₉) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 4.30 below, show that the QY of the QDs decreased immediately after treatment with C₄H₁₀O₂. A significant increase in absorbance was also observed immediately after treatment (see orange line in Figure 4.43a). In a study by Mandal et al., an increase in absorbance was found to be indicative of aggregation because absorbance measurements are sensitive to scattering from colloidal suspensions that form as QD aggregates grow in size. Furthermore, they found that a significant decrease in QD fluorescence also resulted from aggregation. It can therefore be concluded that the flattening of the fluorescence peak coupled with the significant increase in absorbance observed immediately after treatment with C₄H₁₀O₂, indicates that the QDs began to aggregate at this time. Eventually, the aggregates grew to a size that allowed them to be clearly visible in the solution, causing the solution to appear cloudy in visible light. When excited with a 365 nm UV light, as seen in the pictures in Figure 4.43, the aggregates scattered the incident light and caused the solution to appear pink. As time progressed, the aggregates continued to grow until the QDs precipitated out of solution 5 d after treatment as seen by the quenching of the QD fluorescence in Figure 4.43d.
Figure 4.43. Absorbance spectra (a) and fluorescence spectra (b) of a $3.03 \times 10^{-7}$ M solution of CdSe (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with C$_4$H$_{10}$O$_2$ ($1.46 \times 10^{-6}$ molar ratio of QDs to C$_4$H$_{10}$O$_2$). Photos of untreated QDs (left) and QDs treated with C$_4$H$_{10}$O$_2$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 4.30. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdSe (OA & TOA) QD and C$_4$H$_{10}$O$_2$ solution dissolved in toluene at a $1.46 \times 10^{-6}$ molar ratio.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.029</td>
<td>64.1</td>
<td>1.92</td>
</tr>
<tr>
<td>Initial</td>
<td>---</td>
<td>---</td>
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<tr>
<td>1 d</td>
<td>0.002</td>
<td>62.4</td>
<td>1.90</td>
</tr>
<tr>
<td>5 d</td>
<td>0.002</td>
<td>71.5</td>
<td>2.46</td>
</tr>
<tr>
<td>10 d</td>
<td>0.010</td>
<td>69.5</td>
<td>2.44</td>
</tr>
</tbody>
</table>
Similar to treatment of CdSe (oleylamine) QDs with C4H10O2 in chloroform (as described in section 4.1.9 above), the fluorescence peak centered at 600 nm in Figure 4.43 represents the emission of the QDs. The peak measured 10 d (purple) after treatment, on the other hand, is centered at 450 nm and is therefore representative of the mixture of toluene, OA, TOA, and C4H10O2, not the QDs (see Figure 4.44 below). For this reason, it can be confirmed that the fluorescence of the QDs died 5 d after treatment. In conclusion, treatment of CdSe (OA & TOA) QDs dissolved in toluene with C4H10O2 resulted in a decrease in the QY of the QDs due to aggregation.

Figure 4.44. Normalized fluorescence spectrum of a solution composed of toluene, OA, TOA, and C4H10O2.

4.3.11 Summary of CdSe/OA & TOA Treatments

Figure 4.45 compares the effect of treating CdSe (OA & TOA) QDs with various reducing and oxidizing agents in chloroform versus toluene. The quality of this batch of QDs was significantly less than that of the previous 2 batches described above, as seen from these photographs. The QY of the QDs before treatment in chloroform was approximately 0.003 while the QY in toluene was approximately 0.049. Because both
sets of QDs came from the same master batch of cores, this difference in QY may be due to the solubility of OA in the various solvents. Thuy et al. have shown that the QY is higher when the capping ligand is less soluble in a given solvent. From our results, we found that the QY of the QDs was higher in toluene than chloroform therefore implying that OA is less soluble in toluene than chloroform. The literature, however, states that OA is more soluble in toluene than chloroform, therefore disproving this explanation. A possible explanation for this dependence on solvent may therefore be due to the solubility of oxygen in each of the solvents. This hypothesis is consistent with the results summarized in section 4.2.11. The $E_g$ of the untreated QDs in chloroform and toluene were both 1.92 eV, which suggests that the solvent does not have an effect on QD size and color emitted.
Figure 4.45. Photos of CdSe (OA & TOA) QDs that are from left to right: untreated, treated with NaBH₄, C₁₄H₁₀O₄, CaH₂, N₂H₄, and C₄H₁₀O₂ excited with 365 nm UV light. The QDs in the left column were suspended and treated in chloroform while those in the right column were suspended and treated in toluene. Photos were taken 1 d (top row), 5 d (middle row), and 10 d (bottom row) after treatment.

The overall effect of reducing and oxidizing agents on the QY of CdSe (OA & TOA) QDs was found to be independent of solvent for 4 of the 5 treatments. More specifically, it was found that the quality of the QDs worsened after treatment with CaH₂, N₂H₄, and C₄H₁₀O₂ and improved after treatment with NaBH₄ in both chloroform and toluene. Treatment with C₁₄H₁₀O₄, on the other hand, increased the quality of the QDs when dissolved in chloroform, but not in toluene. Even though the QY of the QDs increased after treatment with NaBH₄ in both chloroform and toluene, in chloroform a 133 % increase was calculated whereas the increased QY was only qualitative in toluene.
Similar to treatment of CdSe (OA & ODE) QDs, as discussed in section 4.2.11 above, these results clearly illustrate that the surface treatment of CdSe (OA & ODE) QDs was more effective in chloroform than toluene.

The reason for this dependence on solvent is not known, however, the two possible explanations discussed in detail in section 4.2.11 above can be applied to this system because the capping ligand is still OA. The first explanation focuses on the solubility of the ligand (OA) in the dispersion solvent. Specifically, it is hypothesized that because OA is more soluble in toluene than chloroform, OA ligands will desorb from the QD surface at a faster rate in toluene than chloroform. As the ligands continue to detach from the QD surface, the QDs are unable to remain dispersed in the solvent and the QY decreases. The second explanation focuses on the solubility of the reducing agent in the dispersion solvent. Specifically, if a given reducing/oxidizing agent is more soluble is a particular solvent, it will react at a much faster rate than when the treatment occurs in a solvent to which it is less soluble. If the reaction happens too fast, the ligands will detach from the QD surface before oxygen is able to diffuse to the QD surface to form a CdO layer and therefore will not be able to passivate the surface defect sites. To confirm either of these explanations, future work is required.

As mentioned above, treatment of CdS (OA & TOA) QDs with NaBH₄ resulted in an enhanced QY, while treatment with CaH₂ decreased the QY of the QDs. This same result was observed in the treatment of CdSe (oleylamine QDs). As explained in section 4.1.11 above, we hypothesize that this result can be explained by a difference in the
reducing agents reactivity with water. Specifically, we hypothesize that the reducing agents react with the residual water present in each of the solvents to form hydrogen. The hydrogen then reacts with the surface ligands, causing them to detach from the QD surface, and allowing oxygen from the atmospheric air to diffuse to the exposed cadmium. The resulting CdO layer around the QDs serves to passivate the defect sites located on the QD surface and therefore improves the QY of the QDs. If the reducing agent reacts too fast with the residual water, the QDs will aggregate and the QY will be quenched. In a study by Kong et al., the reaction rate of NaBH₄ with water vapor was found to be ten times slower than that of CaH₂.¹⁶ For this reason, it is hypothesized that CaH₂ reacted very fast with the residual water present in the QD solution, causing the QDs to aggregate, and the QY to be quenched. This aggregation was confirmed by an increase in the measured absorbance. NaBH₄, on the other hand, reacted with the water at a slow enough rate that the hydrogen produced was able to effectively detach ligands on the QD surface and allow for the formation of the CdO layer.

In the previous summary sections, the observation of a fluorescence peak centered at approximately 450 nm was discussed. Fluorescence spectroscopy was performed on solutions consisting of each ligand, solvent, and reducing/oxidizing agent combination to confirm that this peak was not representative of the QDs. In the case of CdSe (oleylamine) QDs, this peak was observed in each of the 10 treatments, however it was only observed in 2 of the 10 treatments in the case of CdSe (OA & ODE) QDs. Specifically, this peak was seen in the treatment of the QDs in toluene with N₂H₄ and C₄H₁₀O₂. Although it is not clear why this peak was only measured for 2 of the 5
treatments performed in toluene, the trend was consistent with the theory provided above. In both of these cases, the peak increased with time which further supports that the reaction solution evaporated with time.

From the spectra seen in the above 10 sections representing CdSe (OA & TOA) QDs, a negative peak centered at approximately 450 nm was measured when the QDs were dissolved in chloroform. Fluorescence spectroscopy was performed on solutions consisting of OA, TOA, chloroform, and each reducing/oxidizing agent to account for this negative peak, however, these combinations yielded positive fluorescence peaks centered at 450 nm, similar to those included in the previous sections. An explanation for this negative peak is therefore not known. Munro et al. reported that chloroform contains impurities which may explain this unusual result, however because it was not observed in all chloroform solutions, no conclusions can be made. It is therefore recommended that in future work of this thesis, additional batches of CdSe (OA & TOA) QDs dissolved in chloroform be tested to see if a negative fluorescence peak results. If the negative peak is observed in these new batches, it is recommended that further characterizations be performed to determine its cause.
4.4 References


(23) Munro, A. M.; Jen-La Plante, I.; Ng, M. S.; Ginger, D. S. **2007**.

Chapter 5. Results and Discussion: CdS

Chapter 5 will present and discuss the results of the experimental work performed on CdS QDs. This chapter will be divided into three sections: (1) CdS QDs synthesized with oleylamine, (2) CdS QDs synthesized with oleic acid (OA) and octadecene (ODE), and (3) CdS QDs synthesized with OA and trioctylamine (TOA). Following the same model as Chapter 4, each section will summarize the effect of treating the surface of the various QD batches with three reducing and two oxidizing agents. More specifically, the effect of each treatment on the quantum yield (QY), size distribution, and bandgap energy ($E_g$) of the QDs will be evaluated. The reducing agents to be investigated include: sodium borohydride (NaBH$_4$), calcium hydride (CaH$_2$), and hydrazine (N$_2$H$_4$), while the oxidizing agents include: benzoil peroxide (C$_{14}$H$_{10}$O$_4$) and tert-butyl hydroperoxide (C$_4$H$_{10}$O$_2$).

5.1 CdS (Oleylamine) Quantum Dot Cores

5.1.1 Treatment with Sodium Borohydride (NaBH$_4$) in Chloroform

Figure 5.1 displays the absorbance and fluorescence spectra of a CdS (oleylamine) QD and sodium borohydride (NaBH$_4$) solution dissolved in chloroform at a 6.11 x $10^{-6}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.1 below, show that the QY of the QDs reached a maximum 10 d after treatment with
NaBH₄. Additionally, the $E_g$ decreased and fluorescence peak shifted to a lower wavelength 5 d and 10 d after treatment indicating a blue-shift in emission. This increase in QY and blue-shift in emission are illustrated in Figure 5.1e as the treated solution (right) is brighter and more blue than the untreated solution (left). Lastly, the FWHM decreased slightly 5 d and 10 d after treatment, indicating a narrowing of the QD size distribution. In conclusion, treatment of CdS (oleylamine) QDs dissolved in chloroform with NaBH₄ resulted in a 3.85 % increase in the QY of the QDs 10 d after treatment.

Figure 5.1. Absorbance spectra (a) and fluorescence spectra (b) of a $9.65 \times 10^{-8}$ M solution of CdS (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with NaBH₄ ($6.11 \times 10^{-6}$ molar ratio of QDs to NaBH₄). Photos of untreated QDs (left) and QDs treated with NaBH₄ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 5.1. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdS (oleylamine) QD and NaBH₄ solution dissolved in chloroform at a 6.11 x 10⁻⁶ molar ratio.

<table>
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<th>QY</th>
<th>FWHM (nm)</th>
<th>E_g (eV)</th>
</tr>
</thead>
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<td>Untreated</td>
<td>0.078</td>
<td>194</td>
<td>2.42</td>
</tr>
<tr>
<td>Initial</td>
<td>0.076</td>
<td>195</td>
<td>2.42</td>
</tr>
<tr>
<td>1 d</td>
<td>0.076</td>
<td>194</td>
<td>2.42</td>
</tr>
<tr>
<td>5 d</td>
<td>0.074</td>
<td>146</td>
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<tr>
<td>10 d</td>
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<td>134</td>
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5.1.2 Treatment with Sodium Borohydride (NaBH₄) in Toluene

Figure 5.2 displays the absorbance and fluorescence spectra of a CdS (oleylamine) QD and sodium borohydride (NaBH₄) solution dissolved in toluene at a 4.18 x 10⁻⁶ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.2 below, show that the QY of the QDs reached a maximum 5 d after treatment with NaBH₄ before decreasing to below that of the untreated QY 10 d later. This increase in QY 5 d after treatment is illustrated in Figure 5.2d as the treated sample (right) is brighter than the untreated sample (left). In Figure 5.2e, however, the treated sample (right) is less bright than the untreated sample (left) confirming the QY calculations. Additionally, the FWHM decreased slightly 5 d and 10 d after treatment, indicating a narrowing of the QD size distribution. In conclusion, treatment of CdS (oleylamine) QDs dissolved in toluene with NaBH₄ resulted in a 23.4 % increase in QY of the QDs 5 d after treatment.
Figure 5.2. Absorbance spectra (a) and fluorescence spectra (b) of a $6.60 \times 10^{-8}$ M solution of CdS (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with NaBH$_4$ ($4.18 \times 10^{-6}$ molar ratio of QDs to NaBH$_4$). Photos of untreated QDs (left) and QDs treated with NaBH$_4$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.2. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdS (oleylamine) QD and NaBH$_4$ solution dissolved in toluene at a $4.18 \times 10^{-6}$ molar ratio.

<table>
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<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.448</td>
<td>174</td>
<td>2.40</td>
</tr>
<tr>
<td>Initial</td>
<td>0.440</td>
<td>175</td>
<td>2.40</td>
</tr>
<tr>
<td>1 d</td>
<td>0.450</td>
<td>174</td>
<td>2.40</td>
</tr>
<tr>
<td>5 d</td>
<td>0.553</td>
<td>158</td>
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<td>10 d</td>
<td>0.391</td>
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<td>2.50</td>
</tr>
</tbody>
</table>
5.1.3 Treatment with Calcium Hydride (CaH$_2$) in Chloroform

Figure 5.3 displays the absorbance and fluorescence spectra of a CdS (oleylamine) QD and calcium hydride (CaH$_2$) solution dissolved in chloroform at a 2.01 x 10$^{-5}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.3 below, show that the QY of the QDs decreased after treatment with CaH$_2$. The spectra in Figure 5.3 illustrate that the fluorescence peak flattened and the absorbance increased immediately after treatment. In a study by Mandal et al., an increase in absorbance was found to be indicative of aggregation because absorbance measurements are sensitive to scattering from colloidal suspensions that form as QD aggregates grow in size.$^{1}$ Furthermore, they found that a significant decrease in QD fluorescence also resulted from aggregation.$^{1}$ It can therefore be hypothesized that the flattening of the fluorescence peak coupled with the significant increase in absorbance observed immediately after treatment with CaH$_2$, indicates that the QDs began to aggregate at this time.

Figure 5.3d shows that 5 d after treatment, a slight red-shift was observed as the treated QDs (right) appear more red than the untreated QDs (left). This red-shift is attributed to the tight packing of the QDs contained in the aggregates. When the QDs are tightly packed, the wave function of the electrons in an individual QD is believed to ‘leak out’ and overlap with the wave function of a neighboring QD.$^{2}$ This formation of collective electronic states due to electron overlap interactions results in a spectral red shift of QD emission.$^{2}$ Between 5 d and 10 d after treatment, the aggregates continued to
grow until the QDs precipitated out of solution, as seen in Figure 5.3e where the QD solution no longer fluoresced. Rather than confirming this quenching of the QY by completely flattening, the fluorescence peak blue-shifted to a wavelength of 450 nm (see purple peak in Figure 5.3).

As seen in the CdSe (oleylamine) treatments, the same peak was observed at 450 nm (see section 4.2). After performing fluorescence spectroscopy on a solution of each oleylamine, chloroform, and reducing/oxidizing agent combination, the peak was determined to represent the precursor solution, not the QDs. To verify that the peak measured 10 d after treatment of CdS (oleylamine) QDs with CaH₂ was also representative of the precursor solution, fluorescence spectroscopy was performed on a solution consisting of oleylamine, chloroform, and CaH₂. This normalized fluorescence spectrum can be seen in Figure 5.4 below. A peak centered at 450 nm was clearly measured, therefore confirming that the blue fluorescence peak centered at 510 nm was representative of the QDs. For this reason, it can be confirmed that the CdS (oleylamine) QDs stopped fluorescing 10 d after treatment with CaH₂ due to precipitation of the QDs.
Figure 5.3. Absorbance spectra (a) and fluorescence spectra (b) of a $9.65 \times 10^{-8}$ M solution of CdS (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with CaH$_2$ ($2.01 \times 10^{-5}$ molar ratio of QDs to CaH$_2$). Photos of untreated QDs (left) and QDs treated with CaH$_2$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.3. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdS (oleylamine) QD and CaH$_2$ solution dissolved in chloroform at a $2.01 \times 10^{-5}$ molar ratio.

<table>
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<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
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<tr>
<td>Untreated</td>
<td>0.087</td>
<td>197</td>
<td>2.42</td>
</tr>
<tr>
<td>Initial</td>
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<td>2.41</td>
</tr>
<tr>
<td>1 d</td>
<td>0.032</td>
<td>158</td>
<td>2.42</td>
</tr>
<tr>
<td>5 d</td>
<td>0.049</td>
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<td>2.43</td>
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<tr>
<td>10 d</td>
<td>0.037</td>
<td>63.9</td>
<td>2.51</td>
</tr>
</tbody>
</table>
5.1.4 Treatment with Calcium Hydride (CaH\textsubscript{2}) in Toluene

Figure 5.5 displays the absorbance and fluorescence spectra of a CdS (oleylamine) QD and calcium hydride (CaH\textsubscript{2}) solution dissolved in toluene at a 1.38 \times 10^{-5} molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E\textsubscript{g}) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.4 below, show that the QY of the QDs decreased after treatment with CaH\textsubscript{2}. This decrease in QY was confirmed by both the fluorescence spectrum and pictures included in Figure 5.5 as the treated sample (right) is less bright than the untreated sample (left). Additionally, no notable change in FWHM or E\textsubscript{g} was observed therefore ruling out a significant broadening of the QD size distribution or change in QD size after treatment. In conclusion, treatment of CdS (oleylamine) QDs dissolved in toluene with CaH\textsubscript{2} resulted in a decrease in the QY of the QDs.
Figure 5.5. Absorbance spectra (a) and fluorescence spectra (b) of a $6.60 \times 10^{-8}$ M solution of CdS (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with CaH$_2$ ($1.38 \times 10^{-5}$ molar ratio of QDs to CaH$_2$). Photos of untreated QDs (left) and QDs treated with CaH$_2$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.4. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdS (oleylamine) QD and CaH$_2$ solution dissolved in toluene at a $1.38 \times 10^{-5}$ molar ratio.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
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<tbody>
<tr>
<td>Untreated</td>
<td>0.471</td>
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<td>2.40</td>
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<tr>
<td>Initial</td>
<td>0.193</td>
<td>174</td>
<td>2.42</td>
</tr>
<tr>
<td>1 d</td>
<td>0.210</td>
<td>170</td>
<td>2.42</td>
</tr>
<tr>
<td>5 d</td>
<td>0.442</td>
<td>183</td>
<td>2.40</td>
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<tr>
<td>10 d</td>
<td>0.212</td>
<td>187</td>
<td>2.41</td>
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</tbody>
</table>
5.1.5 Treatment with Hydrazine (N\textsubscript{2}H\textsubscript{4}) in Chloroform

Figure 5.6 displays the absorbance and fluorescence spectra of a CdS (oleylamine) QD and hydrazine (N\textsubscript{2}H\textsubscript{4}) solution dissolved in chloroform at a 1.02 x 10\textsuperscript{-7} molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E\textsubscript{g}) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 5.5 below. From these values, it can be seen that the QY of the QDs decreased after treatment with N\textsubscript{2}H\textsubscript{4}. Similar to treatment of CdSe (oleylamine) QDs in chloroform (as described in section 4.1.5), the addition of N\textsubscript{2}H\textsubscript{4} resulted in an emulsion. Oleylamine was again identified as the surfactant, as its surface tension (31.4 mN/m\textsuperscript{3}) was in between that of N\textsubscript{2}H\textsubscript{4} (66.39 mN/m\textsuperscript{3}) and chloroform (27.5 mN/m\textsuperscript{3}).

Immediately after treatment, a small amount of soluble N\textsubscript{2}H\textsubscript{4} reacted with the QDs and reduced their surface to etch and destroy the QDs thereby quenching the QD fluorescence. The remainder of the N\textsubscript{2}H\textsubscript{4} formed large, unevenly dispersed N\textsubscript{2}H\textsubscript{4} droplets stabilized by the residual oleylamine. Because the large droplets could clearly be seen in the solution, similar to the corresponding CdSe case, I shook the solution. Agitation enabled the large N\textsubscript{2}H\textsubscript{4} droplets to break up and disperse in the solution temporarily, thereby scattering the 365 nm UV light and causing the solution to appear purple (see Figure 5.6c). Five days after treatment, the N\textsubscript{2}H\textsubscript{4} droplets returned to their original size and again were clearly separated from the chloroform. Figure 5.6d confirms this observation as large, poorly dispersed N\textsubscript{2}H\textsubscript{4} droplets were again visible. After 10 d a visible layer formed at the top of the chloroform solution, presumably due to instability.
of the emulsion (see Figure 5.6e). The solution appeared blue-green when excited by a 365 nm UV lamp because the oleylamine emits light at 450 nm upon excitation (see Figure 4.6 in Chapter 4). In conclusion, the fluorescence of CdS (oleylamine) QDs dissolved in chloroform died immediately after treatment with N$_2$H$_4$.

![Absorbance spectra and fluorescence spectra](image)

Figure 5.6. Absorbance spectra (a) and fluorescence spectra (b) of a $9.65 \times 10^{-8}$ M solution of CdS (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with N$_2$H$_4$ (1.02 x $10^{-7}$ molar ratio of QDs to N$_2$H$_4$). Photos of untreated QDs (left) and QDs treated with N$_2$H$_4$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 5.5. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdS (oleylamine) QD and N_2H_4 solution dissolved in chloroform at a 1.02 x 10^{-7} molar ratio.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.071</td>
<td>197</td>
<td>2.42</td>
</tr>
<tr>
<td>Initial</td>
<td>0.008</td>
<td>---</td>
<td>2.55</td>
</tr>
<tr>
<td>1 d</td>
<td>0.005</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>5 d</td>
<td>0.011</td>
<td>75.0</td>
<td>2.56</td>
</tr>
<tr>
<td>10 d</td>
<td>0.029</td>
<td>66.2</td>
<td>2.57</td>
</tr>
</tbody>
</table>

5.1.6 Treatment with Hydrazine (N_2H_4) in Toluene

Figure 5.7 displays the absorbance and fluorescence spectra of a CdS (oleylamine) QD and hydrazine (N_2H_4) solution dissolved in toluene at a 6.96 x 10^{-8} molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.6 below, show that the QY of the QDs was quenched immediately after treatment with N_2H_4. This decrease in QY was confirmed by the pictures included in Figure 5.3 as the treated sample (right) is less bright than the untreated sample (left). Similar to several of the treatments described previously, the fluorescence peak centered at 510 nm in Figure 5.7b represents the emission of the QDs. The peaks measured 5 d (green) and 10 d (purple) after treatment, on the other hand, are centered at approximately 440 nm and are therefore representative of the mixture of toluene, oleylamine, and N_2H_4, not the QDs (see Figure 5.8 below). Focusing on the peak representing the QDs, it can therefore be seen that the fluorescence of the QDs was quenched immediately after treatment. Hydrazine is soluble in toluene, therefore it was assumed that all of the reducing agent
reacted with the QDs immediately after treatment and the concerns discussed in section 5.1.5 above were not applicable. In conclusion, treatment of CdS (oleylamine) QDs dissolved in toluene with N₂H₄ resulted in a quenching of the fluorescence of the QDs.

Figure 5.7. Absorbance spectra (a) and fluorescence spectra (b) of a 6.60 x 10⁻⁸ M solution of CdS (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with N₂H₄ (6.96 x 10⁻⁸ molar ratio of QDs to N₂H₄). Photos of untreated QDs (left) and QDs treated with N₂H₄ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 5.6. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdS (oleylamine) QD and N$_2$H$_4$ solution dissolved in toluene at a 6.96 x 10$^{-8}$ molar ratio.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.458</td>
<td>174</td>
<td>2.40</td>
</tr>
<tr>
<td>Initial</td>
<td>0.026</td>
<td>150</td>
<td>---</td>
</tr>
<tr>
<td>1 d</td>
<td>0.003</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>5 d</td>
<td>0.082</td>
<td>90.0</td>
<td>2.57</td>
</tr>
<tr>
<td>10 d</td>
<td>0.074</td>
<td>96.0</td>
<td>2.57</td>
</tr>
</tbody>
</table>

Figure 5.8. Normalized fluorescence spectrum of a solution composed of toluene, oleylamine, and N$_2$H$_4$.

5.1.7 Treatment with Benzoyl Peroxide ($C_{14}H_{10}O_4$) in Chloroform

Figure 5.9 displays the absorbance and fluorescence spectra of a CdS (oleylamine) QD and benzoyl peroxide ($C_{14}H_{10}O_4$) solution dissolved in chloroform at a 1.21 x 10$^{-4}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 5.7 below. From these values, it can be seen that the QY of the QDs steadily decreased with time after treatment with $C_{14}H_{10}O_4$. Additionally, the $E_g$ increased 5 d and 10 d after treatment.
treatment, indicating a blue-shift in emission. Rather than confirming this expected blue-shift, however, pictures d and e in Figure 5.9 illustrate that the QDs fluoresced pink after treatment.

A possible explanation for these conflicting results may be explained by a change in the QD size distribution after treatment. More specifically, prior to treatment, the solution of QDs contained a very broad size distribution as illustrated by the wide fluorescence peak (blue) centered at 510 nm (see Figure 5.9b) as well as the high FWHM value. Five (green) and ten (purple) days after treatment, however, the fluorescence peaks transformed from a wide peak to a bimodal peak. This bimodal peak indicates that the QD solution was comprised of two distinct populations of QDs: one set of smaller QDs centered at 440 nm and one larger set of QDs centered at 650 nm. Additionally, 5 d and 10 d after treatment, a slight increase in absorbance was observed representing an increase in concentration. In a study by Kagan et al.⁴, it was concluded that in a system composed of small and large QDs, electronic energy transfer from the small to the large QDs is observed as fluorescence quenching of the small dots, and fluorescence enhancement of the large QDs. In other words, electronic energy transfer in close-packed QD systems arises from dipole-dipole interactions between proximal QDs resulting in an observed red-shift in emission.⁴ In conclusion, treatment of CdS (oleylamine) QDs dissolved in chloroform with C₁₄H₁₀O₄ resulted in a red-shift in emission as well as a decrease in the QY of the QDs.
Figure 5.9. Absorbance spectra (a) and fluorescence spectra (b) of a $9.65 \times 10^{-8}$ M solution of CdS (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with $C_{14}H_{10}O_4$ (1.21 x $10^{-4}$ molar ratio of QDs to $C_{14}H_{10}O_4$). Photos of untreated QDs (left) and QDs treated with $C_{14}H_{10}O_4$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.7. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdS (oleylamine) QD and $C_{14}H_{10}O_4$ solution dissolved in chloroform at a 1.21 x $10^{-4}$ molar ratio.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Untreated</strong></td>
<td>0.075</td>
<td>197</td>
<td>2.40</td>
</tr>
<tr>
<td><strong>Initial</strong></td>
<td>0.063</td>
<td>201</td>
<td>2.42</td>
</tr>
<tr>
<td><strong>1 d</strong></td>
<td>0.058</td>
<td>196</td>
<td>2.42</td>
</tr>
<tr>
<td><strong>5 d</strong></td>
<td>0.041</td>
<td>75.7</td>
<td>2.52</td>
</tr>
<tr>
<td><strong>10 d</strong></td>
<td>0.043</td>
<td>80.9</td>
<td>2.51</td>
</tr>
</tbody>
</table>
5.1.8 Treatment with Benzoyl Peroxide \((C_{14}H_{10}O_4)\) in Toluene

Figure 5.10 displays the absorbance and fluorescence spectra of a CdS (oleylamine) QD and benzoyl peroxide \((C_{14}H_{10}O_4)\) solution dissolved in toluene at an 8.25 \times 10^{-5} \text{ molar ratio}. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy \((E_g)\) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.8 below, show that the QY of the QDs decreased immediately after treatment with \(C_{14}H_{10}O_4\) before increasing to above that of the untreated QY 10 d later. This increase in QY 10 d after treatment is illustrated in Figure 5.10e where the treated QDs (right) are brighter than the untreated cores (left). Additionally, the FWHM decreased and \(E_g\) increased 10 d after treatment, indicating a narrowing of the size distribution and blue-shift in emission. In conclusion, treatment of CdS (oleylamine) QDs dissolved in toluene with \(C_{14}H_{10}O_4\) resulted in a 25.0 \% increase in the QY of the QDs 10 d after treatment.
Figure 5.10. Absorbance spectra (a) and fluorescence spectra (b) of a 6.60 x 10^{-8} M solution of CdS (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with C_{14}H_{10}O_{4} (8.25 x 10^{-5} molar ratio of QDs to C_{14}H_{10}O_{4}). Photos of untreated QDs (left) and QDs treated with C_{14}H_{10}O_{4} (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.8. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdS (oleylamine) QD and C_{14}H_{10}O_{4} solution dissolved in toluene at a 8.25 x 10^{-5} molar ratio.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.404</td>
<td>174</td>
<td>2.42</td>
</tr>
<tr>
<td>Initial</td>
<td>0.338</td>
<td>194</td>
<td>2.41</td>
</tr>
<tr>
<td>1 d</td>
<td>0.078</td>
<td>98.5</td>
<td>2.54</td>
</tr>
<tr>
<td>5 d</td>
<td>0.293</td>
<td>99.1</td>
<td>2.50</td>
</tr>
<tr>
<td>10 d</td>
<td>0.505</td>
<td>71.0</td>
<td>2.49</td>
</tr>
</tbody>
</table>
5.1.9 Treatment with tert-Butyl Hydroperoxide (C₄H₁₀O₂) in Chloroform

Figure 5.11 displays the absorbance and fluorescence spectra of a CdS (oleylamine) QD and tert-butyl hydroperoxide (C₄H₁₀O₂) solution dissolved in chloroform at a 3.09 x 10⁻⁷ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E₉) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 5.9 below. From these values, it can be seen that the QY of the QDs decreased immediately after treatment with C₄H₁₀O₂ before ceasing to fluoresce 1 d later. This quenching of the QD fluorescence was confirmed by the pictures in Figure 5.11 where the treated QDs (right) were not fluorescent. Similar to treatment of CdSe (oleylamine) QDs in chloroform with C₄H₁₀O₂ (as described in section 4.1.9), the wide fluorescence peak centered at 540 nm in Figure 5.11 represents the emission of the QDs. The peaks measured after treatment, on the other hand, are centered at 450 nm and are therefore representative of the mixture of chloroform, oleylamine, and C₄H₁₀O₂, not the QDs. For this reason, the quenching of the fluorescence of the QDs 1 d after treatment was confirmed. In conclusion, treatment of CdS (oleylamine) QDs dissolved in chloroform with C₄H₁₀O₂ resulted in a quenching of the QD fluorescence 1 d after treatment.
Figure 5.11. Absorbance spectra (a) and fluorescence spectra (b) of a $9.65 \times 10^{-8}$ M solution of CdS (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with $C_4H_{10}O_2$ ($3.09 \times 10^{-7}$ molar ratio) of QDs to $C_4H_{10}O_2$). Photos of untreated QDs (left) and QDs treated with $C_4H_{10}O_2$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.9. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdS (oleylamine) QD and $C_4H_{10}O_2$ solution dissolved in chloroform at a $3.09 \times 10^{-7}$ molar ratio.

<table>
<thead>
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<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.085</td>
<td>188</td>
<td>2.42</td>
</tr>
<tr>
<td>Initial</td>
<td>0.037</td>
<td>140</td>
<td>2.52</td>
</tr>
<tr>
<td>1 d</td>
<td>0.021</td>
<td>97.8</td>
<td>2.53</td>
</tr>
<tr>
<td>5 d</td>
<td>0.079</td>
<td>50.8</td>
<td>2.56</td>
</tr>
<tr>
<td>10 d</td>
<td>0.024</td>
<td>68.1</td>
<td>2.54</td>
</tr>
</tbody>
</table>
5.1.10 Treatment with tert-Butyl Hydroperoxide (C₄H₁₀O₂) in Toluene

Figure 5.12 displays the absorbance and fluorescence spectra of a CdS (oleylamine) QD and tert-butyl hydroperoxide (C₄H₁₀O₂) solution dissolved in toluene at a 2.12 x 10⁻⁷ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E₉) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.10 below, show that the QY of the QDs decreased immediately after treatment with C₄H₁₀O₂. This decrease in QY was confirmed by the pictures included in Figure 5.12 as the treated sample (right) is less bright than the untreated sample (left). Similar to treatment in chloroform, as explained in the previous section, the fluorescence peaks measured after treatment were centered at 440 nm and were therefore representative of the mixture of toluene, oleylamine, and C₄H₁₀O₂, not the QDs (see Figure 4.15 in Chapter 4). For this reason, the quenching of the fluorescence of the QDs immediately after treatment was confirmed. In conclusion, treatment of CdS (oleylamine) QDs dissolved in toluene with C₄H₁₀O₂ resulted in a quenching of the QD fluorescence immediately after treatment.
Figure 5.12. Absorbance spectra (a) and fluorescence spectra (b) of a 6.60 x 10^{-8} M solution of CdS (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with C_4H_{10}O_2 \ (2.12 \times 10^{-7} \text{ molar ratio of QDs to } C_4H_{10}O_2). Photos of untreated QDs (left) and QDs treated with C_4H_{10}O_2 (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.10. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdS (oleylamine) QD and C_4H_{10}O_2 solution dissolved in toluene at a 2.12 x 10^{-7} molar ratio.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.384</td>
<td>162</td>
<td>2.40</td>
</tr>
<tr>
<td>Initial</td>
<td>0.030</td>
<td>91.0</td>
<td>2.55</td>
</tr>
<tr>
<td>1 d</td>
<td>0.019</td>
<td>98.2</td>
<td>2.55</td>
</tr>
<tr>
<td>5 d</td>
<td>0.104</td>
<td>96.6</td>
<td>2.53</td>
</tr>
<tr>
<td>10 d</td>
<td>0.064</td>
<td>89.9</td>
<td>2.54</td>
</tr>
</tbody>
</table>
5.1.11 Summary of CdS/Oleylamine Treatments

Figure 5.13 compares the effect of treating CdS (oleylamine) QDs with various reducing and oxidizing agents in chloroform versus toluene. From these photographs, it can be seen that the QDs dissolved in toluene were visibly brighter than those in chloroform. This observation was confirmed as the QY of the QDs before treatment in chloroform was approximately 0.085 while the QY in toluene was approximately 0.475. Because both sets of QDs came from the same master batch of cores, this difference in QY may be due to the solubility of oleylamine in the various solvents. Thuy et al. have shown that the QY is higher when the capping ligand is less soluble in a given solvent.\textsuperscript{13} Because the QY was higher in toluene than chloroform, we therefore hypothesize that oleylamine is less soluble in toluene than chloroform. This result is consistent with the results summarized in section 4.1.11 regarding the QY of CdSe (oleylamine) QDs in each solvent. The $E_g$ of the untreated QDs in chloroform and toluene were 2.42 eV and 2.40 eV, respectively, which suggests the solvent does not have an effect on QD size and therefore color emitted.
The effect of reducing and oxidizing agents on the QY of CdS (oleylamine) QDs was found to be independent of solvent for 4 of the 5 treatments. More specifically, it was found that the QY of the QDs declined after treatment with CaH₂, N₂H₄, and C₄H₁₀O₂ and improved after treatment with NaBH₄ in both chloroform and toluene. Treatment with C₁₄H₁₀O₄, on the other hand, increased the QY of the QDs when dissolved in toluene, but not in chloroform. These exact trends were observed when treating CdSe (oleylamine) QDs as discussed in detail in section 4.1. For this reason, we hypothesize that the effect of treating QDs capped with oleylamine with various reducing/oxidizing agents is
independent of chalcogenide (Se or S). Furthermore, the theory proposed to explain the
dependence on solvent is applicable to this batch of QDs as well.

Treatment of QDs with a reducing/oxidizing agent is expected to reduce the
surface ligands thereby causing them to lose their coordinating properties and detach
from the QD surface.\textsuperscript{6} Oxygen from atmospheric air is then able to diffuse to the exposed
cadmium on the QD surface to form a cadmium oxide (CdO) layer around the QDs.\textsuperscript{6} This
CdO layer serves to passivate defects on the QD surface, thereby enhancing the QY of
the QDs.\textsuperscript{6} A possible explanation for the observed decrease of the QY after treatment
with \textit{C}_{14}\textit{H}_{10}\textit{O}_{4} in chloroform is that the oxidizing agent reacted with the QDs at a rate so
fast that oxygen was not able to diffuse to the QD surface and form a CdO layer. Instead,
\textit{C}_{14}\textit{H}_{10}\textit{O}_{4} caused the oleylamine ligands to quickly detach from the QD surface and
therefore caused aggregation in chloroform (as measured by the increase in absorbance),
and resulted in a quenched QY.\textsuperscript{2} In toluene, however, the reaction rate was slowed down
significantly because \textit{C}_{14}\textit{H}_{10}\textit{O}_{4} is less soluble in toluene than chloroform.\textsuperscript{7} Because the
reaction rate was slowed, after the \textit{C}_{14}\textit{H}_{10}\textit{O}_{4} reduced the oleylamine on the QD surface,
oxygen was able to form the CdO layer and therefore passivate the defect sites on the QD
surface. To confirm this theory, additional testing is required. A possible experiment
involves treating the QDs with a lower concentration of \textit{C}_{14}\textit{H}_{10}\textit{O}_{4} in chloroform to see if
the reaction rate slows enough to allow for the formation of a CdO layer and therefore
increased QY.
As mentioned above, treatment of CdS (oleylamine) QDs with NaBH₄ resulted in an enhanced QY, while treatment with CaH₂ decreased the QY of the QDs. We hypothesize that this result can be explained by a difference in the reducing agents reactivity with water. Specifically, we hypothesize that the reducing agents react with the residual water present in each of the solvents to form hydrogen. The hydrogen then reacts with the surface ligands, causing them to detach from the QD surface, and allowing oxygen from the atmospheric air to diffuse to the exposed cadmium. The resulting CdO layer around the QDs serves to passivate the defect sites located on the QD surface and therefore improves the QY of the QDs. If the reducing agent reacts too fast with the residual water, the QDs will aggregate and the QY will be quenched. In a study by Kong et al., the reaction rate of NaBH₄ with water vapor was found to be ten times slower than that of CaH₂. For this reason, it is hypothesized that CaH₂ reacted very fast with the residual water present in the QD solution, causing the QDs to aggregate, and the QY to be quenched. This aggregation was confirmed by an increase in the measured absorbance.

NaBH₄, on the other hand, reacted with the water at a slow enough rate that the hydrogen produced was able to effectively detach ligands on the QD surface and allow for the formation of the CdO layer.

In several of the 10 preceding subsections, a fluorescence peak centered at approximately 440 nm was observed. To account for this peak, fluorescence spectroscopy was performed on solutions consisting of each oleylamine, solvent, and reducing/oxidizing agent combination. Several of these spectra are included in the above section. From these spectra, the peak at 440 nm was consistently found to represent the
ligand, solvent, and reducing/oxidizing agent combination, not the QDs. Often, an increase in this peak was observed with time. A possible explanation for this increase is that the solvent evaporated over time, as seen by the decrease in solution volume in the pictures included in the figures above. As the solvent evaporated, the concentration of the precursor solution increased, and an increase in fluorescence was therefore observed. This observation is consistent with the results obtained for the treatment of CdSe (oleylamine) QDs.

5.2 CdS (OA and ODE) Quantum Dot Cores

The following 11 sections discuss the effect of treating CdS (OA & ODE) QDs with each of the investigated reducing/oxidizing agents. This batch of QDs was different from the previous 4 batches of QDs in two ways: (1) the untreated QDs yielded a bimodal fluorescence peak in both solvents, and (2) a different batch of QDs was used in chloroform than toluene. These two differences make this set of results unique and help to explain the results obtained.

A bimodal fluorescence peak indicates that either there are two separate size populations of QDs in the solution or that the peaks represent multiple things present in the QD solution. For example, if there is residual ligand present in the solution, one peak may correspond to the combination of solvent and ligand while the other represents the QDs. Similar to in previous sections, fluorescence spectroscopy was performed on solutions of each ligand, solvent, and reducing/oxidizing agent combination to account
for their influence on the measured fluorescence spectra. Figure 5.14 below illustrates the fluorescence spectra of the combination of OA, ODE, and chloroform as well as the combination of OA, ODE, and toluene. From these fluorescence spectra, it can clearly be seen that a peak centered at 450 nm was measured in both solvents that represents the mixture of the ligand, non-coordinating solvent, and dispersion solvent. We therefore hypothesize that because the bimodal fluorescence peaks representing the untreated QD solution contain one peak centered at 450 nm and one centered at approximately 620 nm, the latter peak is representative of the QDs. For this reason, the 620 nm peak will be the focus of the following sections to evaluate the effect of each surface treatment. Furthermore, the QYs calculated for each treatment only accounted for the area under the peak corresponding to the QDs. The reported $E_g$ and FWHM values are also only representative of the QD peak.

Figure 5.14. Normalized fluorescence spectrum of a solution composed of chloroform, OA, and ODE (solid) and a solution composed of toluene, OA, and ODE (dashed).
5.2.1 Treatment with Sodium Borohydride (NaBH₄) in Chloroform

Figure 5.15 displays the absorbance and fluorescence spectra of a CdS (OA & ODE) QD and sodium borohydride (NaBH₄) solution dissolved in chloroform at a 5.62 x 10⁻⁶ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.11 below, show that the QY of the QDs increased slightly after treatment with NaBH₄ and reached a maximum 1 d after treatment before decreasing to below that of the untreated QY 5 d later. Additionally, the absorbance value increased significantly 5 d and 10 d after treatment. In a study by Mandal et al., an increase in absorbance was found to be indicative of aggregation because absorbance measurements are sensitive to scattering from colloidal suspensions that form as QD aggregates grow in size. Furthermore, they found that a decrease in QD fluorescence also resulted from aggregation. The observed increase in absorbance and decrease of the fluorescence peak measured 5 d and 10 d after treatment therefore imply that the QDs began to aggregate 5 d after treatment. Lastly, no notable change in FWHM or E_g was observed therefore ruling out a significant broadening of the QD size distribution or change in QD size after treatment. In conclusion, treatment of CdS (OA & ODE) QDs dissolved in chloroform with NaBH₄ resulted in a 45.8 % increase in QY of the QDs 1 d after treatment.
Figure 5.15. Absorbance spectra (a) and fluorescence spectra (b) of a $8.99 \times 10^{-8}$ M solution of CdS (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with NaBH$_4$ ($5.62 \times 10^{-6}$ molar ratio of QDs to NaBH$_4$). Photos of untreated QDs (left) and QDs treated with NaBH$_4$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.11. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdS (OA & ODE) QD and NaBH$_4$ solution dissolved in chloroform at a $5.62 \times 10^{-5}$ molar ratio.

<table>
<thead>
<tr>
<th></th>
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<tr>
<td>10 d</td>
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<td>188</td>
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5.2.2 Treatment with Sodium Borohydride (NaBH₄) in Toluene

Figure 5.16 displays the absorbance and fluorescence spectra of a CdS (OA & ODE) QD and sodium borohydride (NaBH₄) solution dissolved in toluene at a $7.69 \times 10^{-6}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.12 below, show that the QY of the QDs decreased after treatment with NaBH₄. Furthermore, 5 d and 10 d after treatment, the peak centered at 450 nm that was representative of the combination of OA, ODE, toluene, and NaBH₄ increased significantly. The normalized fluorescence peak of this solution as well as a picture of the solution excited by a 365 nm UV light is shown in Figure 5.17 below. As seen in the picture, this solution fluoresces bright blue. Because the fluorescence of the QD solution decreased and the fluorescence of the precursor solution increased, a blue-shift in emission is expected. Figure 5.16d and e illustrate this expected blue-shift as the treated QDs (right) appear more blue than the untreated QDs (left). In conclusion, treatment of CdS (OA & ODE) QDs dissolved in toluene with NaBH₄ resulted in a decrease in the QY of the QDs.
Figure 5.16. Absorbance spectra (a) and fluorescence spectra (b) of a 1.23 x 10^-7 M solution of CdS (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with NaBH₄ (7.69 x 10^-6 molar ratio of QDs to NaBH₄). Photos of untreated QDs (left) and QDs treated with NaBH₄ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.12. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdS (OA & ODE) QD and NaBH₄ solution dissolved in toluene at a 7.69 x 10^-6 molar ratio.

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<tr>
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5.2.3 Treatment with Calcium Hydride (CaH$_2$) in Chloroform

Figure 5.18 displays the absorbance and fluorescence spectra of a CdS (OA & ODE) QD and calcium hydride (CaH$_2$) solution dissolved in chloroform at a 1.87 x 10$^{-5}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.13 below, show that the QY of the QDs decreased immediately after treatment with CaH$_2$. An increase in absorbance was also observed after treatment (see Figure 5.18a). In a study by Mandal et al., an increase in absorbance was found to be indicative of aggregation because absorbance measurements are sensitive to scattering from colloidal suspensions that form as QD aggregates grow in size. Furthermore, they found that a significant decrease in QD fluorescence also resulted from aggregation. It can therefore be concluded that the flattening of the fluorescence peak coupled with the significant increase in absorbance observed immediately after treatment with CaH$_2$, indicates that the
QDs began to aggregate at this time. The aggregates grew to a size that allowed them to be clearly visible in the solution, causing the solution to appear cloudy in visible light. When excited with a 365 nm UV light, as seen in the pictures in Figure 5.18, the aggregates scattered the incident light and caused the solution to appear pink. With time, the aggregates continued to grow which explains why the absorbance continued to increase and fluorescence peak continued to flatten with time. In conclusion, treatment of CdS (OA & ODE) QDs dissolved in chloroform with CaH₂ resulted in aggregation and a decrease in the QY of the QDs.

Figure 5.18. Absorbance spectra (a) and fluorescence spectra (b) of a 8.99 x 10⁻⁸ M solution of CdS (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with CaH₂ (1.87 x 10⁻⁵ molar ratio of QDs to CaH₂). Photos of untreated QDs (left) and QDs treated with CaH₂ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 5.13. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdS (OA & ODE) QD and CaH_2 solution dissolved in chloroform at a 1.87 x 10^{-5} molar ratio.

<table>
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<th>E_g (eV)</th>
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5.2.4 Treatment with Calcium Hydride (CaH_2) in Toluene

Figure 5.19 displays the absorbance and fluorescence spectra of a CdS (OA & ODE) QD and calcium hydride (CaH_2) solution dissolved in toluene at a 2.56 x 10^{-5} molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.14 below, show that the QY of the QDs decreased after treatment with CaH_2. Furthermore, 5 d and 10 d after treatment, the peak centered at 450 nm that was representative of the combination of OA, ODE, toluene, and CaH_2 increased significantly. The normalized fluorescence peak of this solution as well as a picture of the solution excited by a 365 nm UV light is shown in Figure 5.20 below. As seen in the picture, this solution fluoresces bright blue. Because the fluorescence of the QD solution decreased and the fluorescence of the precursor solution increased, a blue-shift in emission is expected. Figure 5.19d and e illustrate this expected blue-shift as the treated QDs (right) appear more blue than the untreated QDs (left). This same result was
observed after treatment with NaBH₄, as detailed in section 5.2.2 above. In conclusion, treatment of CdS (OA & ODE) QDs dissolved in toluene with CaH₂ resulted in a decrease in the QY of the QDs.

Figure 5.19. Absorbance spectra (a) and fluorescence spectra (b) of a 1.23 x 10⁻⁷ M solution of CdS (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with CaH₂ (2.56 x 10⁻⁵ molar ratio of QDs to CaH₂). Photos of untreated QDs (left) and QDs treated with CaH₂ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 5.14. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdS (OA & ODE) QD and CaH_2 solution dissolved in toluene at a 2.56 x 10^{-5} molar ratio.

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<tr>
<td>10 d</td>
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Figure 5.20. Normalized fluorescence spectrum and picture (inset) of a solution composed of chloroform, OA, ODE, and CaH_2.

5.2.5 Treatment with Hydrazine (N_2H_4) in Chloroform

Figure 5.21 displays the absorbance and fluorescence spectra of a CdS (OA & ODE) QD and hydrazine (N_2H_4) solution dissolved in chloroform at a 2.84 x 10^{-7} molar ratio. Because the fluorescence of the QDs was quenched immediately after treatment, it was not possible to calculate the quantum yield (QY), full-width half-maximum (FWHM) or bandgap energy (E_g) of the QDs. Similar to treatment of CdSe (OA & ODE) QDs in chloroform (as described in section 4.2.5), the addition of N_2H_4 resulted in an emulsion. We hypothesize that OA was able to act as a surfactant and stabilize the hydrazine
droplets, as its surface tension (32.5 mN/m$^3$) was in between that of N$_2$H$_4$ (66.39 mN/m$^3$) and chloroform (27.5 mN/m$^3$). The hydrophilic-lipophilic balance (HLB) of OA was found to be 1.9, indicating that it is a hydrophobic surfactant. Chloroform is a hydrophobic solvent, therefore OA was found to be a good surfactant that yielded a stable emulsion with small, evenly dispersed droplets of N$_2$H$_4$.

Immediately after adding N$_2$H$_4$ to the chloroform, a small amount of soluble N$_2$H$_4$ reacted with the QDs and reduced their surface to etch and destroy the QDs thereby quenching the QD fluorescence. The fluorescence spectrum included in Figure 5.21b confirms this quenching of the fluorescence as the peak completely flattened immediately after treatment. The residual OA in the solution then stabilized the remaining N$_2$H$_4$ into small, evenly dispersed N$_2$H$_4$ droplets. These droplets scattered the light, causing the solution to appear cloudy in visible light. When a 365 nm UV lamp was used as the incident light, the evenly dispersed droplets of N$_2$H$_4$ in the QD solution scattered the light causing the solution to appear purple (see pictures in Figure 5.21). In conclusion, treatment of CdS (OA & ODE) QDs dissolved in chloroform with N$_2$H$_4$ caused the QDs to stop fluorescing immediately after treatment.
Figure 5.21. Absorbance spectra (a) and fluorescence spectra (b) of a 8.99 x 10^{-8} M solution of CdS (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with N_2H_4 (2.84 x 10^{-7} molar ratio of QDs to N_2H_4). Photos of untreated QDs (left) and QDs treated with N_2H_4 (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.15. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdS (OA & ODE) QD and N_2H_4 solution dissolved in chloroform at a 2.84 x 10^{-7} molar ratio.

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</tr>
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5.2.6 Treatment with Hydrazine (N₂H₄) in Toluene

Figure 5.22 displays the absorbance and fluorescence spectra of a CdS (OA & ODE) QD and hydrazine (N₂H₄) solution dissolved in toluene at a 3.89 x 10⁻⁷ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results are summarized in Table 5.16 below. As illustrated in Figure 5.22b, immediately after treatment with N₂H₄, the fluorescence peak corresponding to the QDs flattened completely. The peak corresponding to the solution of toluene, OA, ODE, and N₂H₄, on the other hand, was still measured. We therefore hypothesize that immediately after treatment the fluorescence of the QD solution was quenched. The blue color observed in the pictures included in Figure 5.22 is therefore representative of the precursor solution, not the QDs. Because N₂H₄ is soluble in toluene, the issues explained in section 5.2.5 above are not applicable to this system. Lastly, these results are consistent with those observed in the treatment of CdSe (OA & ODE) QDs with N₂H₄ as detailed in section 4.2.6. In conclusion, treatment of CdS (OA & ODE) QDs dissolved in toluene with N₂H₄ resulted in the quenching of the QD fluorescence immediately after treatment.
Figure 5.22. Absorbance spectra (a) and fluorescence spectra (b) of a 1.23 x 10^{-7} M solution of CdS (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with N_2H_4 (3.89 x 10^{-7} molar ratio of QDs to N_2H_4). Photos of untreated QDs (left) and QDs treated with N_2H_4 (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.16. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdS (OA & ODE) QD and N_2H_4 solution dissolved in toluene at a 3.89 x 10^{-7} molar ratio.

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</tr>
<tr>
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5.2.7 Treatment with Benzoyl Peroxide (C$_{14}$H$_{10}$O$_{4}$) in Chloroform

Figure 5.23 displays the absorbance and fluorescence spectra of a CdS (OA & ODE) QD and benzoyl peroxide (C$_{14}$H$_{10}$O$_{4}$) solution dissolved in chloroform at a 3.75 x 10$^{-5}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.17 below, show that the QY of the QDs increased after treatment with C$_{14}$H$_{10}$O$_{4}$ and reached a maximum 10 d after treatment. Figure 5.23e illustrates this increase in QY 10 d after treatment as the treated sample (right) is significantly brighter than the untreated sample (left). Additionally, the FWHM decreased slightly and the absorbance peak became more sharp (see Figure 5.23a) 10 d after treatment, indicating a significant narrowing of the QD size distribution. In conclusion, treatment of CdS (OA & ODE) QDs dissolved in chloroform with C$_{14}$H$_{10}$O$_{4}$ resulted in a 62.5 % increase in the QY of the QDs 10 d after treatment.
Figure 5.23. Absorbance spectra (a) and fluorescence spectra (b) of a $8.99 \times 10^{-8}$ M solution of CdS (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with $\text{C}_{14}\text{H}_{10}\text{O}_4$ ($3.75 \times 10^{-5}$ molar ratio of QDs to $\text{C}_{14}\text{H}_{10}\text{O}_4$). Photos of untreated QDs (left) and QDs treated with $\text{C}_{14}\text{H}_{10}\text{O}_4$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.17. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdS (OA & ODE) QD and $\text{C}_{14}\text{H}_{10}\text{O}_4$ solution dissolved in chloroform at a $3.75 \times 10^{-5}$ molar ratio.

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5.2.8 Treatment with Benzoyl Peroxide (C_{14}H_{10}O_{4}) in Toluene

Figure 5.24 displays the absorbance and fluorescence spectra of a CdS (OA & ODE) QD and benzoyl peroxide (C_{14}H_{10}O_{4}) solution dissolved in toluene at a 5.13 \times 10^{-5} molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.18 below, show that the QY of the QDs reached a maximum 10 d after treatment with C_{14}H_{10}O_{4}. Figure 5.24e illustrates this increase in QY 10 d after treatment as the treated sample (right) is significantly brighter than the untreated sample (left). In conclusion, treatment of CdS (OA & ODE) QDs dissolved in toluene with C_{14}H_{10}O_{4} resulted in a 6.84 % increase in the QY of the QDs 10 d after treatment.
Figure 5.24. Absorbance spectra (a) and fluorescence spectra (b) of a $1.23 \times 10^{-7}$ M solution of CdS (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with $C_{14}H_{10}O_4$ ($5.13 \times 10^{-5}$ molar ratio of QDs to $C_{14}H_{10}O_4$). Photos of untreated QDs (left) and QDs treated with $C_{14}H_{10}O_4$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.18. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdS (OA & ODE) QD and $C_{14}H_{10}O_4$ solution dissolved in toluene at a $5.13 \times 10^{-5}$ molar ratio.

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5.2.9 Treatment with tert-Butyl Hydroperoxide ($C_4H_{10}O_2$) in Chloroform

Figure 5.25 displays the absorbance and fluorescence spectra of a CdS (OA & ODE) QD and tert-butyl hydroperoxide ($C_4H_{10}O_2$) solution dissolved in chloroform at a 4.32 x $10^{-7}$ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.19 below, show that the QY of the QDs decreased immediately after treatment with $C_4H_{10}O_2$. An increase in absorbance was also observed immediately after treatment (see Figure 5.25a). In a study by Mandal et al., an increase in absorbance was found to be indicative of aggregation because absorbance measurements are sensitive to scattering from colloidal suspensions that form as QD aggregates grow in size. Furthermore, they found that a significant decrease in QD fluorescence also resulted from aggregation. It can therefore be concluded that the flattening of the fluorescence peak coupled with the significant increase in absorbance observed immediately after treatment with $C_4H_{10}O_2$, indicates that the QDs began to aggregate at this time. One day after treatment, the aggregates grew to a size that allowed them to be clearly visible in the solution, causing the solution to appear cloudy in visible light. When excited with a 365 nm UV light, as seen in Figure 5.25c, the aggregates scattered the incident light and caused the solution to appear pink.

In previous cases of aggregation, the aggregates grew to a large enough size that they precipitated out of solution and caused the fluorescence of the QD solution to quench. In this case, however, a fluorescence peak centered at 510 nm increased 5 d and
10 d after treatment. Additionally, the QDs blue-shifted in color and increased in brightness, as illustrated in Figure 5.25d and e. These observations are unlike any of the others and have no obvious explanation.

Figure 5.25. Absorbance spectra (a) and fluorescence spectra (b) of a 8.99 x 10^{-8} M solution of CdS (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with C_{4}H_{10}O_{2} (4.32 x 10^{-7} molar ratio of QDs to C_{4}H_{10}O_{2}). Photos of untreated QDs (left) and QDs treated with C_{4}H_{10}O_{2} (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 5.19. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdS (OA & ODE) QD and C$_4$H$_{10}$O$_2$ solution dissolved in chloroform at a 4.32 x 10^{-7} molar ratio.

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</table>

5.2.10 Treatment with tert-Butyl Hydroperoxide (C$_4$H$_{10}$O$_2$) in Toluene

Figure 5.26 displays the absorbance and fluorescence spectra of a CdS (OA & ODE) QD and tert-butyl hydroperoxide (C$_4$H$_{10}$O$_2$) solution dissolved in toluene at a 5.91 x 10^{-7} molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.20 below, show that the QY of the QDs decreased after treatment with C$_4$H$_{10}$O$_2$. This decrease in QY was confirmed as the fluorescence peak corresponding to the QDs decreased after treatment. Furthermore, the pictures in Figure 5.26 illustrate that the treated sample (right) is less bright than the untreated sample (left). In conclusion, treatment of CdS (OA & ODE) QDs dissolved in toluene with C$_4$H$_{10}$O$_2$ resulted in a decline in the QY of the QDs.
Figure 5.26. Absorbance spectra (a) and fluorescence spectra (b) of a 1.23 x 10^{-7} M solution of CdS (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with C\textsubscript{4}H\textsubscript{10}O\textsubscript{2} (5.91 x 10^{-7} molar ratio of QDs to C\textsubscript{4}H\textsubscript{10}O\textsubscript{2}). Photos of untreated QDs (left) and QDs treated with N\textsubscript{2}H\textsubscript{4} (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.20. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E\textsubscript{g}) of a CdS (OA & ODE) QD and N\textsubscript{2}H\textsubscript{4} solution dissolved in toluene at a 5.91 x 10^{-7} molar ratio.

<table>
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<th>FWHM (nm)</th>
<th>E\textsubscript{g} (eV)</th>
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</tr>
<tr>
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<td>---</td>
<td>2.61</td>
</tr>
<tr>
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<td>---</td>
<td>2.61</td>
</tr>
<tr>
<td>5 d</td>
<td>0.021</td>
<td>---</td>
<td>2.61</td>
</tr>
<tr>
<td>10 d</td>
<td>0.028</td>
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<td>2.60</td>
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</table>
5.2.11 Summary of CdS/OA & ODE Treatments

Figure 5.27 compares the effect of treating CdS (OA & ODE) QDs with various reducing and oxidizing agents in chloroform and toluene. From these photographs, it can be seen that the QDs dissolved in toluene were visibly brighter than those in chloroform. This observation was confirmed as the QY of the QDs before treatment in chloroform was approximately 0.024 while the QY in toluene was approximately 0.085. A different batch of QDs was used for treatments in chloroform than toluene due to low yield therefore it is unclear if this difference in QY is attributed to differences in the batch quality or to QD solubility in each solvent. In each of the other 2 batches of QDs capped with OA, it was hypothesized that the QDs exhibited a higher QY in toluene over chloroform because of the difference in dissolved oxygen concentration in each solvent. The $E_g$ of the untreated QDs in chloroform and toluene were 2.65 eV and 2.60 eV, respectively, which suggests the solvent does not have a significant effect on QD size and therefore color emitted.
Figure 5.27. Photos of CdS (OA & ODE) QDs that are from left to right: untreated, treated with NaBH₄, C₁₄H₁₀O₄, CaH₂, N₂H₄, and C₄H₁₀O₂ excited with 365 nm UV light. The QDs in the left column were suspended and treated in chloroform while those in the right column were suspended and treated in toluene. Photos were taken 1 d (top row), 5 d (middle row), and 10 d (bottom row) after treatment.

The effect of reducing and oxidizing agents on the QY of CdS (OA & ODE) QDs was found to be independent of solvent for 3 of the 5 treatments. More specifically, it was found that the quality of the QDs worsened after treatment with N₂H₄ and CaH₂, and improved after treatment with C₁₄H₁₀O₄ in both chloroform and toluene. Treatment with NaBH₄ and C₄H₁₀O₂, on the other hand, increased the quality of the QDs when dissolved in chloroform, but not toluene. Even though the QY of the QDs increased after treatment with C₁₄H₁₀O₄ in both chloroform and toluene, the percent increase in QY in chloroform was significantly higher than in toluene, 62.5 % compared to 6.84 %, respectively. These
results clearly illustrate that the surface treatment of CdS (OA & ODE) QDs was more effective in chloroform than toluene. This is consistent with the CdSe (OA & ODE) case where surface treatment was also more effective in chloroform than toluene.

The reason for this dependence on solvent is not known, however, a possible explanation focuses on the solubility of the ligand (OA) in the dispersion solvent. In a study by Bullen et al., it was concluded that desorption of the surface ligands may occur if the ligand is more soluble in a given solvent, therefore resulting in decreased QY.\textsuperscript{11} Oleic acid is more soluble in toluene than chloroform as confirmed by comparing Hildebrand solubility parameters. Specifically, the Hildebrand solubility parameter ($\delta$) provides a good estimation of the solubility of two substances as it is a numerical estimate of the degree of interaction between materials. The closer the $\delta$ of two substances, the better the degree of solubility. Furthermore, $\delta_{\text{OA}} = 15.95$, $\delta_{\text{toluene}} = 17.8$, and $\delta_{\text{chloroform}} = 19.0$\textsuperscript{12}, therefore confirming that OA is more soluble in toluene than chloroform. For this reason, it can be hypothesized that OA ligands will desorb from the QD surface at a faster rate in toluene than chloroform, thereby explaining why surface treatment is more effective in chloroform than toluene.

A second possible explanation for the observed results focuses on the solubility of the reducing agent in the dispersion solvent. It is hypothesized that NaBH\textsubscript{4} is more soluble in toluene than chloroform. For this reason, the reducing agent reacts with the QDs at a faster rate when dissolved in toluene than chloroform. It is therefore hypothesized that when dispersed and treated in toluene, oxygen was not able to diffuse
to the QD surface to form a CdO layer and therefore was not able to passivate the surface defect sites. Instead, NaBH$_4$ caused the OA ligands to detach from the QD surface and destroyed the QDs dispersibility in toluene, thereby resulting in a decreased QY.$^2$ Unfortunately, information is not currently available regarding the solubility of NaBH$_4$ in toluene versus chloroform. For this reason, it is recommended that future work include a solubility study to determine the solubility of NaBH$_4$ in both chloroform and toluene to confirm this theory.

Treatment with C$_4$H$_{10}$O$_2$ also resulted in an enhanced QY when the QDs were dispersed and treated in chloroform but not in toluene. As detailed in section 5.2.9 above, the observed increase in QY was unlike any other C$_4$H$_{10}$O$_2$ treatment. Furthermore, the measured fluorescence and absorbance spectra indicate that the QDs aggregated immediately after treatment before increasing significantly in brightness. Due to the uniqueness of this result, it is recommended that the treatment be redone to validate accuracy.

In each of the 10 preceding sections, a bimodal fluorescence peak was measured to represent the untreated QDs. As previously explained, the fluorescence peak centered at 450 nm was believed to be representative of the mixture of OA, ODE, and solvent, whereas the peak centered at 620 nm was representative of the QDs. We hypothesize that measurement of a fluorescence peak at 450 nm indicates that residual ligand is present in the QD solution after washing. As explained in section 4.2.11 where the treatment of CdSe (OA & ODE) QDs is summarized, no peak at 450 nm was measured. It is unclear
why residual OA and ODE were found to be present in the case of CdS QDs but not CdSe QDs. Furthermore, in previous cases where residual ligand was present in solution after washing, a peak centered at 450 nm was only observed after treatment. This leads to another interesting difference between CdS (OA & ODE) QDs and the other batches: a peak representing the precursor solution was measured prior to treatment. A reason for this observation is not readily known.

5.3 CdS (OA and TOA) Quantum Dot Cores

Each of the previous 5 QD batches were treated with various reducing and oxidizing agents at an initial absorbance between 0.08 a.u. and 0.10 a.u.. This starting absorbance value was chosen to ensure accurate QY calculations. CdS (OA & TOA) QD solutions with this same concentration did not fluoresce. Furthermore, treatment of these poor quality QDs with each of the reducing and oxidizing agents failed to improve the quality. Appendix B illustrates these results. Jang et al.\textsuperscript{6} report an increase in QY of CdS (OA & TOA) QDs after treatment with NaBH\textsubscript{4}. For their study, a starting absorbance of 0.35 a.u. was reported. For this reason, the CdS (OA & TOA) QD treatments described in the following section had an initial absorbance of 0.35 a.u..

Similar to CdS (OA & ODE) QDs, the untreated CdS (OA & TOA) QDs yielded a bimodal fluorescence peak in both solvents. As explained in section 5.2 above, we hypothesize that this bimodal fluorescence peak indicates that there is residual ligand present in the solution. Similar to in previous sections, fluorescence spectroscopy was
performed on solutions of each ligand, solvent, and reducing/oxidizing agent combination to account for their influence on the measured fluorescence spectra. Figure 5.28 below illustrates the fluorescence spectra of the combination of OA, TOA, and chloroform as well as the combination of OA, TOA, and toluene. From these fluorescence spectra, it can clearly be seen that a peak centered at 460 nm was measured in both solvents that represents the mixture of the ligand, non-coordinating solvent, and dispersion solvent. We therefore hypothesize that because the bimodal fluorescence peaks representing the untreated QD solution contain one peak centered at 460 nm and one centered at approximately 650 nm, the latter peak is representative of the QDs. For this reason, the 650 nm peak will be the focus of the following sections to evaluate the effect of each surface treatment. Furthermore, the QYs calculated for each treatment only accounted for the area under the peak corresponding to the QDs. The reported $E_g$ and FWHM values are also only representative of the QD peak.

Figure 5.28. Normalized fluorescence spectrum of a solution composed of chloroform, OA, and TOA (solid) and a solution composed of toluene, OA, and TOA (dashed).
5.3.1 Treatment with Sodium Borohydride (NaBH₄) in Chloroform

Figure 5.29 displays the absorbance and fluorescence spectra of a CdS (OA & TOA) QD and sodium borohydride (NaBH₄) solution dissolved in chloroform at a 9.19 x 10⁻⁶ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E₉) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.21 below, show that the QY of the QDs decreased after treatment with NaBH₄. Additionally, the absorbance value increased 1 d after treatment. In a study by Mandal et al., an increase in absorbance was found to be indicative of aggregation because absorbance measurements are sensitive to scattering from colloidal suspensions that form as QD aggregates grow in size.¹ Furthermore, they found that a decrease in QD fluorescence also resulted from aggregation.¹ The observed increase in absorbance and flattening of the fluorescence peak (see Figure 5.29) therefore indicate that the QDs began to aggregate 1 d after treatment.

Similar to in the fluorescence spectra of CdSe (OA & TOA) QDs dissolved in chloroform as described in section 4.3, a negative peak was measured after treatment (see Figure 5.29b). This peak was found to represent the combination of OA, TOA, chloroform, and NaBH₄ (see Figure 4.27 in Chapter 4), however it is unclear why the peak is negative. An explanation for this negative peak is therefore not known and will be explored further in future work. In conclusion, treatment of CdS (OA & TOA) QDs dissolved in chloroform with NaBH₄ resulted in a decrease in the QY of the QDs.
Figure 5.29. Absorbance spectra (a) and fluorescence spectra (b) of a $2.94 \times 10^{-7}$ M solution of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with NaBH₄ ($9.19 \times 10^{-6}$ molar ratio of QDs to NaBH₄). Photos of untreated QDs (left) and QDs treated with NaBH₄ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.21. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdS (OA & TOA) QD and NaBH₄ solution dissolved in chloroform at a $9.19 \times 10^{-6}$ molar ratio.

<table>
<thead>
<tr>
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<th>QY x $10^{-3}$</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
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<td>Untreated</td>
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</tr>
<tr>
<td>Initial</td>
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<td>2.45</td>
</tr>
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</tr>
<tr>
<td>5 d</td>
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<td>---</td>
<td>2.45</td>
</tr>
<tr>
<td>10 d</td>
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<td>195</td>
<td>2.45</td>
</tr>
</tbody>
</table>
5.3.2 Treatment with Sodium Borohydride (NaBH₄) in Toluene

Figure 5.30 displays the absorbance and fluorescence spectra of a CdS (OA & TOA) QD and sodium borohydride (NaBH₄) solution dissolved in toluene at an 8.16 x 10⁻⁶ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (Eₔ) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.22 below, show that the QY of the QDs increased immediately after treatment with NaBH₄. Additionally, a significant increase in the fluorescence peak corresponding to the precursor solution was seen over time (see Figure 5.30b). In conclusion, treatment of CdS (OA & TOA) QDs dissolved in toluene with NaBH₄ resulted in a 200 % increase in the QY of the QDs immediately after treatment.
Figure 5.30. Absorbance spectra (a) and fluorescence spectra (b) of a \(2.61 \times 10^{-7}\) M solution of CdS (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with NaBH\(_4\) (8.16 \times 10^{-6}\) molar ratio of QDs to NaBH\(_4\)). Photos of untreated QDs (left) and QDs treated with NaBH\(_4\) (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.22. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (\(E_g\)) of a CdS (OA & TOA) QD and NaBH\(_4\) solution dissolved in toluene at a 8.16 \times 10^{-5}\) molar ratio.

<table>
<thead>
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<th>QY</th>
<th>FWHM (nm)</th>
<th>(E_g) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
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<td>198</td>
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</tr>
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<td>197</td>
<td>2.47</td>
</tr>
<tr>
<td>5 d</td>
<td>0.001</td>
<td>---</td>
<td>2.47</td>
</tr>
<tr>
<td>10 d</td>
<td>0.003</td>
<td>195</td>
<td>2.47</td>
</tr>
</tbody>
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5.3.3 Treatment with Calcium Hydride (CaH₂) in Chloroform

Figure 5.31 displays the absorbance and fluorescence spectra of a CdS (OA & TOA) QD and calcium hydride (CaH₂) solution dissolved in chloroform at a 2.10 × 10⁻⁵ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.23 below, show that the QY of the QDs decreased after treatment with CaH₂. Additionally, the absorbance value increased after treatment. In a study by Mandal et al., an increase in absorbance was found to be indicative of aggregation because absorbance measurements are sensitive to scattering from colloidal suspensions that form as QD aggregates grow in size.¹ Furthermore, they found that a decrease in QD fluorescence also resulted from aggregation.¹ Similar to treatment of CdSe (OA & TOA) QDs with CaH₂ as described in section 4.3.3, the observed increase in absorbance and flattening of the fluorescence peak (see Figure 5.31) therefore indicate that the QDs began to aggregate after treatment.

The absorbance continued to increase 10 d after treatment (see purple line in Figure 5.31a) which indicates that the QD aggregates continued to grow with time. Ten days after treatment, the aggregates grew to a size that allowed them to be clearly visible in the solution, causing the solution to appear cloudy in visible light. When a 365 nm UV lamp was used as the incident light (as in the case in Figure 5.31e) the QD aggregates scattered the incident light causing the solution to appear pink. In conclusion, treatment
of CdS (OA & TOA) QDs dissolved in chloroform with CaH$_2$ resulted in a decrease in the QY of the QDs due to aggregation.

![Absorbance spectra (a) and fluorescence spectra (b) of a 2.94 x 10^{-7} M solution of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with CaH$_2$ (2.10 x 10^{-5} molar ratio of QDs to CaH$_2$). Photos of untreated QDs (left) and QDs treated with CaH$_2$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.]

![Table 5.23. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdS (OA & TOA) QD and CaH$_2$ solution dissolved in chloroform at a 2.10 x 10^{-5} molar ratio.]

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<td>1 d</td>
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<td>2.45</td>
</tr>
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<td>5 d</td>
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<tr>
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5.4.4 Treatment with Calcium Hydride (CaH₂) in Toluene

Figure 5.32 displays the absorbance and fluorescence spectra of a CdS (OA & TOA) QD and calcium hydride (CaH₂) solution dissolved in toluene at a 1.86 x 10⁻⁵ molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E₉) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.24 below, show that the QY of the QDs decreased after treatment with CaH₂. Additionally, a significant increase in the fluorescence peak corresponding to the precursor solution was seen over time (see Figure 5.32b). In conclusion, treatment of CdS (OA & TOA) QDs dissolved in toluene with CaH₂ resulted in a decrease in the QY of the QDs.
Figure 5.32. Absorbance spectra (a) and fluorescence spectra (b) of a 2.61 x 10^{-7} M solution of CdS (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with CaH₂ (1.86 x 10^{-5} molar ratio of QDs to CaH₂). Photos of untreated QDs (left) and QDs treated with CaH₂ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.24. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdS (OA & TOA) QD and CaH₂ solution dissolved in toluene at a 1.86 x 10^{-5} molar ratio.

<table>
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<th>QY</th>
<th>FWHM (nm)</th>
<th>E_g (eV)</th>
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<tr>
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<td>2.45</td>
</tr>
<tr>
<td>5 d</td>
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<tr>
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</table>
5.3.5 Treatment with Hydrazine (N₂H₄) in Chloroform

Figure 5.33 displays the absorbance and fluorescence spectra of a CdS (OA & TOA) QD and hydrazine (N₂H₄) solution dissolved in chloroform at a 9.30 x 10⁻⁷ molar ratio. Because the fluorescence of the QDs was quenched immediately after treatment, it was not possible to calculate the quantum yield (QY), full-width half-maximum (FWHM) or bandgap energy (E_g) of the QDs. Similar to treatment of CdSe (OA & TOA) QDs with N₂H₄, the fluorescence of the QDs was quenched and an emulsion resulted immediately after treatment due to the near insolubility of N₂H₄ in chloroform. Figure 5.33c illustrates this emulsion 1 d after treatment as an uneven distribution of N₂H₄ droplets can clearly be seen in the solution. Immediately after adding N₂H₄ to the chloroform, a small amount of N₂H₄ reacted with the QDs and reduced their surface to etch and destroy the QDs thereby quenching the QD fluorescence. The fluorescence spectrum included in Figure 5.33b confirms this quenching of the fluorescence as the peak completely flattened immediately after treatment. The remainder of the N₂H₄ formed large, unevenly dispersed N₂H₄ droplets stabilized by the residual OA and TOA. The solution appeared blue-green when excited by a 365 nm UV lamp because the mixture of toluene, OA, and TOA emits light at 450 nm upon excitation (see Figure 4.36 in Chapter 4). By 10 d after treatment, two distinct layers were clearly visible presumably due to instability of the emulsion, so I shook the vial. Agitation enabled the N₂H₄ layer to break up and disperse in the solution temporarily, thereby causing the solution to appear bright (see Figure 5.33e) even though the fluorescence of the QDs had been quenched prior.
Similar to in the fluorescence spectra of the same batch of QDs dissolved in chloroform after treatment with NaBH₄, the peak fell negative at 450 nm. This peak was found to represent the combination of OA, TOA, chloroform, and N₂H₄ (see Figure 4.36 in Chapter 4), however it is unclear why the peak is negative. An explanation for this negative peak is therefore not known and will be explored further in future work. In conclusion, the fluorescence of CdS (OA & TOA) QDs dissolved in chloroform died immediately after treatment with N₂H₄.

Figure 5.33. Absorbance spectra (a) and fluorescence spectra (b) of a 2.94 x 10⁻⁷ M solution of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with N₂H₄ (9.30 x 10⁻⁷ molar ratio of QDs to N₂H₄). Photos of untreated QDs (left) and QDs treated with N₂H₄ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 5.25. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdS (OA & TOA) QD and N_2H_4 solution dissolved in chloroform at a 9.30 x 10^{-7} molar ratio.

<table>
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<th>QY x 10^{-3}</th>
<th>FWHM (nm)</th>
<th>E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>1.00</td>
<td>195</td>
<td>2.45</td>
</tr>
<tr>
<td>Initial</td>
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</tr>
<tr>
<td>1 d</td>
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</tr>
<tr>
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</tr>
<tr>
<td>10 d</td>
<td>---</td>
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5.3.6 Treatment with Hydrazine (N_2H_4) in Toluene

Figure 5.34 displays the absorbance and fluorescence spectra of a CdS (OA & TOA) QD and hydrazine (N_2H_4) solution dissolved in toluene at an 8.26 x 10^{-7} molar ratio. Because the fluorescence of the QDs was quenched immediately after treatment, it was not possible to calculate the quantum yield (QY), full-width half-maximum (FWHM) or bandgap energy (E_g) of the QDs. Although N_2H_4 is soluble in toluene, residual TOA in the QD solution prevented all of the reducing agent from reacting immediately with the QDs, similar to treatment in chloroform, as detailed in section 5.3.5 above. Instead, immediately after adding N_2H_4 to the toluene, a small amount of N_2H_4 reacted with the QDs and reduced their surface to etch and destroy the QDs thereby quenching the QD fluorescence. The fluorescence spectrum included in Figure 5.34b confirms this quenching of the fluorescence as the peak corresponded to the QDs completely flattened immediately after treatment. The remainder of the N_2H_4 formed two clearly separate phases in the solution stabilized by the residual OA and TOA (see pictures in Figure 5.34). The solution appeared blue-green when excited by a 365 nm UV lamp because the mixture of toluene, OA, and TOA emits light at 450 nm upon excitation (see Figure 4.38...
in Chapter 4). In conclusion, the fluorescence of CdS (OA & TOA) QDs dissolved in toluene died immediately after treatment with N₂H₄.

![Figure 5.34. Absorbance spectra (a) and fluorescence spectra (b) of a 2.61 x 10⁻⁷ M solution of CdS (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with N₂H₄ (8.26 x 10⁻⁷ molar ratio of QDs to N₂H₄). Photos of untreated QDs (left) and QDs treated with N₂H₄ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.](image)

Table 5.26. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdS (OA & TOA) QD and N₂H₄ solution dissolved in toluene at a 8.26 x 10⁻⁷ molar ratio.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>E_g (eV)</th>
</tr>
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<tbody>
<tr>
<td>Untreated</td>
<td>0.006</td>
<td>195</td>
<td>2.45</td>
</tr>
<tr>
<td>Initial</td>
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<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1 d</td>
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<td>5 d</td>
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</tr>
<tr>
<td>10 d</td>
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</table>
5.3.7 Treatment with Benzoyl Peroxide (C\textsubscript{14}H\textsubscript{10}O\textsubscript{4}) in Chloroform

Figure 5.35 displays the absorbance and fluorescence spectra of a CdS (OA & TOA) QD and benzoyl peroxide (C\textsubscript{14}H\textsubscript{10}O\textsubscript{4}) solution dissolved in chloroform at a 3.68 x 10\textsuperscript{-4} molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E\textsubscript{g}) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.27 below, show that the QY of the QDs decreased after treatment with C\textsubscript{14}H\textsubscript{10}O\textsubscript{4}. Additionally, the fluorescence peak corresponding to the QDs (centered at 650 nm) flattened completely 5 d and 10 d after treatment, indicating that the fluorescence of the QDs was quenched at this time. Furthermore, the absorbance value increased 5 d and 10 d after treatment. In a study by Mandal et al., an increase in absorbance was found to be indicative of aggregation because absorbance measurements are sensitive to scattering from colloidal suspensions that form as QD aggregates grow in size.\textsuperscript{1} Furthermore, they found that a decrease in QD fluorescence also resulted from aggregation.\textsuperscript{1} The observed increase in absorbance and flattening of the fluorescence peak (see Figure 5.35) therefore indicate that the QDs began to aggregate 5 d after treatment.

The absorbance continued to increase 10 d after treatment (see purple line in Figure 5.35a) which indicates that the QD aggregates continued to grow with time. Ten days after treatment, the aggregates grew to a size that allowed them to be clearly visible in the solution, causing the solution to appear cloudy in visible light. When a 365 nm UV lamp was used as the incident light (as in the case in Figure 5.35e) the QD aggregates scattered the incident light causing the solution to appear pink. Lastly, 5 d and 10 d after
treatment, a measurable fluorescence peak centered at 450 nm was observed. This peak was found to represent the combination of OA, TOA, chloroform, and $C_{14}H_{10}O_4$ (see Figure 5.36 below). In conclusion, treatment of CdS (OA & TOA) QDs dissolved in chloroform with $C_{14}H_{10}O_4$ resulted in a quenching of the fluorescence of the QDs 5 d after treatment.

Figure 5.35. Absorbance spectra (a) and fluorescence spectra (b) of a $2.94 \times 10^{-7}$ M solution of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with $C_{14}H_{10}O_4$ (3.68 $\times 10^{-4}$ molar ratio of QDs to $C_{14}H_{10}O_4$). Photos of untreated QDs (left) and QDs treated with $C_{14}H_{10}O_4$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 5.27. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdS (OA & TOA) QD and C_{14}H_{10}O_4 solution dissolved in chloroform at a 3.68 x 10^{-4} molar ratio.

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<th>QY x 10^{-3}</th>
<th>FWHM (nm)</th>
<th>E_g (eV)</th>
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<td>1.00</td>
<td>198</td>
<td>2.45</td>
</tr>
<tr>
<td>Initial</td>
<td>0.90</td>
<td>198</td>
<td>2.45</td>
</tr>
<tr>
<td>1 d</td>
<td>0.90</td>
<td>198</td>
<td>2.45</td>
</tr>
<tr>
<td>5 d</td>
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<tr>
<td>10 d</td>
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</table>

Figure 5.36. Normalized fluorescence spectrum of a solution composed of chloroform, OA, TOA, and C_{14}H_{10}O_4.

5.3.8 Treatment with Benzoyl Peroxide (C_{14}H_{10}O_4) in Toluene

Figure 5.37 displays the absorbance and fluorescence spectra of a CdS (OA & TOA) QD and benzoyl peroxide (C_{14}H_{10}O_4) solution dissolved in toluene at a 3.26 x 10^{-4} molar ratio. From these spectra, quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) were calculated before treatment, as well as immediately, 1 d, 5 d, and 10 d after treatment. These results, as summarized in Table 5.28 below, show that the QY of the QDs decreased immediately after treatment with
C_{14}H_{10}O_4. The peak corresponding to the QDs (centered at 650nm) flattened completely 1 d after treatment, indicating that the fluorescence of the QDs was quenched at this time (see Figure 5.37b). Additionally, a significant increase in the fluorescence peak corresponding to the precursor solution was seen over time (centered at 450 nm). In conclusion, treatment of CdS (OA & TOA) QDs dissolved in toluene with C_{14}H_{10}O_4 resulted in a quenching of the QD fluorescence 1 d after treatment.

Figure 5.37. Absorbance spectra (a) and fluorescence spectra (b) of a 2.61 x 10^{-7} M solution of CdS (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with C_{14}H_{10}O_4 (3.26 x 10^{-7} molar ratio of QDs to C_{14}H_{10}O_4). Photos of untreated QDs (left) and QDs treated with C_{14}H_{10}O_4 (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
Table 5.28. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdS (OA & TOA) QD and C_{14}H_{10}O_{4} solution dissolved in toluene at a 3.26 x 10^{-4} molar ratio.

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<th>QY</th>
<th>FWHM (nm)</th>
<th>E_g (eV)</th>
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<tbody>
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<td>Untreated</td>
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<td>198</td>
<td>2.45</td>
</tr>
<tr>
<td>Initial</td>
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<td>197</td>
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<td>1 d</td>
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<td>10 d</td>
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5.3.9 Treatment with tert-Butyl Hydroperoxide (C_{4}H_{10}O_{2}) in Chloroform

Figure 5.38 displays the absorbance and fluorescence spectra of a CdS (OA & TOA) QD and tert-butyl hydroperoxide (C_{4}H_{10}O_{2}) solution dissolved in chloroform at a 1.41 x 10^{-6} molar ratio. Because the fluorescence of the QDs was quenched immediately after treatment, it was not possible to calculate the quantum yield (QY), full-width half-maximum (FWHM) or bandgap energy (E_g) of the QDs. The fluorescence peak corresponding to the QDs (centered at 650 nm) flattened immediately after treatment, indicating that the fluorescence of the QDs was quenched at this time (see Figure 5.38b). The fluorescence peak corresponding to the precursor solution (centered at 450 nm), on the other hand, increased significantly 5 d and 10 d after treatment. In conclusion, treatment of CdS (OA & TOA) QDs dissolved in chloroform with C_{4}H_{10}O_{2} resulted in a quenching of the QD fluorescence immediately after treatment.
Figure 5.38. Absorbance spectra (a) and fluorescence spectra (b) of a 2.94 x 10^{-7} M solution of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with C_4H_{10}O_2 (1.41 x 10^{-6} molar ratio of QDs to C_4H_{10}O_2). Photos of untreated QDs (left) and QDs treated with C_4H_{10}O_2 (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.29. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy (E_g) of a CdS (OA & TOA) QD and C_4H_{10}O_2 solution dissolved in chloroform at a 1.41 x 10^{-6} molar ratio.

<table>
<thead>
<tr>
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<th>E_g (eV)</th>
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</thead>
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<td>198</td>
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5.3.10 Treatment with tert-Butyl Hydroperoxide (C₄H₁₀O₂) in Toluene

Figure 5.39 displays the absorbance and fluorescence spectra of a CdS (OA & TOA) QD and tert-butyl hydroperoxide (C₄H₁₀O₂) solution dissolved in toluene at a 1.25 x 10⁻⁶ molar ratio. Because the fluorescence of the QDs was quenched immediately after treatment, it was not possible to calculate the quantum yield (QY), full-width half-maximum (FWHM) or bandgap energy (E₉) of the QDs. The fluorescence peak corresponding to the QDs (centered at 650 nm) flattened immediately after treatment, indicating that the fluorescence of the QDs was quenched at this time (see Figure 5.39b). The fluorescence peak corresponding to the precursor solution (centered at 450 nm), on the other hand, increased significantly 5 d and 10 d after treatment. In conclusion, treatment of CdS (OA & TOA) QDs dissolved in toluene with C₄H₁₀O₂ resulted in a quenching of the QD fluorescence immediately after treatment.
Figure 5.39. Absorbance spectra (a) and fluorescence spectra (b) of a $2.61 \times 10^{-7}$ M solution of CdS (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with $\text{C}_4\text{H}_{10}\text{O}_2$ ($1.25 \times 10^{-6}$ molar ratio of QDs to $\text{C}_4\text{H}_{10}\text{O}_2$). Photos of untreated QDs (left) and QDs treated with $\text{C}_4\text{H}_{10}\text{O}_2$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.

Table 5.30. Quantum yield (QY), full-width half-maximum (FWHM), and bandgap energy ($E_g$) of a CdS (OA & TOA) QD and C$_4$H$_{10}$O$_2$ solution dissolved in toluene at a $1.25 \times 10^{-6}$ molar ratio.

<table>
<thead>
<tr>
<th></th>
<th>QY</th>
<th>FWHM (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
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<tbody>
<tr>
<td>Untreated</td>
<td>0.005</td>
<td>198</td>
<td>2.45</td>
</tr>
<tr>
<td>Initial</td>
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<tr>
<td>10 d</td>
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5.3.11 Summary of CdS/OA & TOA Treatments

Figure 5.40 compares the effect of treating CdS (OA & TOA) QDs with various reducing and oxidizing agents in chloroform and toluene. From these photographs, it can be seen that the initial quality of these QDs were not as high as the other batches described in the preceding sections. This observation was confirmed as the QY of the QDs before treatment was only 0.001 in chloroform and 0.005 in toluene. This batch, therefore, did not have a strong dependence on solvent as seen in the other QD batches. The $E_g$ of the untreated QDs in chloroform and toluene were both 2.45 eV, which suggests the solvent does not have a significant effect on QD size and therefore color emitted.
Figure 5.40. Photos of CdS (OA & TOA) QDs that are from left to right: untreated, treated with NaBH₄, C₁₄H₁₀O₄, CaH₂, N₂H₄, and C₄H₁₀O₂ excited with 365 nm UV light. The QDs in the left column were suspended and treated in chloroform while those in the right column were suspended and treated in toluene. Photos were taken 1 d (top row), 5 d (middle row), and 10 d (bottom row) after treatment.

The effect of reducing and oxidizing agents on the QY of CdS (OA & TOA) QDs was found to be independent of solvent for 4 of the 5 treatments. More specifically, the QY of the QDs decreased after treatment with CaH₂, N₂H₄, C₁₄H₁₀O₄, and C₄H₁₀O₂ in both chloroform and toluene. The latter three treatments resulted in a quenched fluorescence after treatment. Sodium borohydride, on the other hand, resulted in an increased QY immediately after treatment in toluene, however the QY decreased after treatment in chloroform. Although treatment with NaBH₄ seems to have a dependence on solvent, the initial quality of the QDs was so poor that it is difficult to form a concrete
conclusion to explain these results. Furthermore, due to the difference in starting concentration for this set of treatments, laterally comparing these results to the other 5 systems is not consistent. For these reasons, a recommendation for the future work of this thesis is to develop a more robust procedure to synthesize higher quality CdS (OA & TOA) QDs. Once this procedure is developed, it is recommended that the QDs be treated with each of the reducing/oxidizing agents discussed in this thesis.

An important result stemming from the above results is consistent with the CdS (OA & ODE) QD results (see section 5.2.11 above). Specifically, in each of the 10 preceding sections, a bimodal fluorescence peak was measured to represent the untreated QDs. As previously explained, the fluorescence peak centered at 450 nm was believed to be representative of the mixture of OA, TOA, and solvent, whereas the peak centered at 650 nm was representative of the QDs. We hypothesize that measurement of a fluorescence peak at 450 nm indicates that residual ligand is present in the QD solution after washing. A reason for this observation is not readily known.
5.4 References


Chapter 6. Results and Discussion: Concentration Dependence on QY

The previous 2 chapters thoroughly present and discuss the effect of various reducing/oxidizing agents on the optical properties of QDs after treatment. Treatment of QDs with a reducing/oxidizing agent is expected to reduce the surface ligands thereby causing them to lose their coordinating properties and detach from the QD surface. Oxygen from atmospheric air is then able to diffuse to the exposed cadmium on the QD surface to form a cadmium oxide (CdO) layer around the QDs. This CdO layer serves to passivate defects on the QD surface, thereby enhancing the QY of the QDs. As explained in the previous results chapters, however, only 18 of the 50 investigated treatments resulted in an enhanced QY of the QDs. Two possible explanations for the observed decrease of the QY after the majority of the surface treatments involve the reaction rate. Specifically, we hypothesize that when a reducing/oxidizing agent it too soluble in a given solvent, it will lead to the formation of QD aggregates and an eventual decrease in the QY of the QDs. Instead, the reducing/oxidizing agent will cause the ligands to quickly detach from the QD surface and destroy the QDs dispersibility in the solvent, and result in a quenched QY.

A second possible hypothesis to explain the observed decrease in QY of the QDs after several treatments also focuses on the reaction rate. Specifically, we hypothesize that the reducing/oxidizing agents react with the residual water present in each of the solvents to form hydrogen. The hydrogen then reacts with the surface ligands, causing them to detach from the QD surface, and allowing oxygen from the atmospheric air to diffuse to the exposed cadmium. The resulting CdO layer around the QDs serves to
passivate the defect sites located on the QD surface and therefore improves the QY of the QDs. If the reducing/oxidizing agents react too fast with the residual water, the QDs will aggregate and the QY will be quenched. Based on this hypothesis, the amount of water present in each of the solvents may be responsible for the dependence of solvent on the effectiveness of the various surface treatments.

These theories can also be applied to explain why specific treatments were successful in improving the QY of the QDs. For example, 10 of the 18 observed increases in QY resulted after surface treatment with sodium borohydride (NaBH₄). Consistent with the theory presented above, it is believed that NaBH₄ was effective as a reducing agent because it is only slightly soluble in the two dispersion solvents. Because NaBH₄ is only slightly soluble in chloroform and toluene, we hypothesize that the reducing agent diffused through the solvent to react with the QDs at a slow enough reaction rate that the QDs surface was effectively reduced. In the case of reducing/oxidizing agents that were completely soluble in the dispersion solvents, the reaction often happened so fast that the QDs aggregated and the fluorescence of the QD solution was completely quenched. A second possible explanation involves the reactivity of NaBH₄ with water. In a study by Kong et al., the reaction rate of NaBH₄ with water vapor was found to be ten times slower than that of CaH₂.³ For this reason, we hypothesize that NaBH₄ reacted with the residual water in each solvent at a slow enough rate that the hydrogen produced was able to effectively detach ligands on the QD surface and allow for the formation of the CdO layer.
Unlike NaBH₄, surface treatment with tert-butyl hydroperoxide (C₄H₁₀O₂) resulted in a decline in the QY of the QDs in 11 of the 12 treatments. Eight of those treatments led to a total quenching of the QD fluorescence. It is hypothesized that because C₄H₁₀O₂ is a liquid that was miscible in both solvents, all of the oxidizing agent was able to react with each batch of QDs immediately after addition. Consistent with the theory explained above, we hypothesize that because all of the C₄H₁₀O₂ was able to react with the QDs, the reaction rate was too fast for the formation of the CdO layer due to either its solubility in the solvents or its reactivity with water. Regardless of explanation, the fast reaction rate led to a decrease in QY. To test this theory, an additional set of experiments was performed to investigate whether treatment with a lower concentration of C₄H₁₀O₂ would slow the reaction rate down enough to allow for proper passivation of surface defects and therefore enhancement of the QY.

6.1 Effect of tert-Butyl Hydroperoxide (C₄H₁₀O₂) Concentration on QY of QDs

Appendix C contains the results from treating each of the 6 batches of QDs with lower concentrations of C₄H₁₀O₂ in both chloroform and toluene. The new concentrations investigated were: 0.006 M, 0.010 M, and 0.015 M. It is important to note that these concentrations were significantly lower than those evaluated in determining the optimum reducing/oxidizing agent concentration (as summarized in Appendix A). In Appendix A, results for treatment with 0.104 M, 0.208 M, and 0.312 M C₄H₁₀O₂ are presented.
From these results, a clear dependence on C₄H₁₀O₂ concentration was observed on the QY of the QDs. Specifically, the fluorescence of the QDs was never quenched immediately after treatment with lower concentrations of C₄H₁₀O₂, as was seen after treatment with higher concentrations. Instead, the fluorescence often decreased gradually over the 10 d period, indicating a significantly slower reaction rate. Figure 6.1 below illustrates this dependence on concentration as the fluorescence of the CdSe (oleylamine) QDs dissolved in chloroform was quenched immediately after treatment with 0.1038 M C₄H₁₀O₂ (6.14 x 10⁻⁶ molar ratio of QDs to C₄H₁₀O₂), but not after treatment with 0.0062 M C₄H₁₀O₂ (1.37 x 10⁻⁴ molar ratio of QDs to C₄H₁₀O₂). The same trend was observed when the QDs were dispersed and treated in toluene, as illustrated in Figure 6.2. Each of the photos was taken 1 d after the respective treatments.

![Figure 6.1. Photos of a (a) 6.39 x 10⁻⁷ M solution of CdSe (oleylamine) QDs dissolved in chloroform before treatment (left) and 1 d after treatment with C₄H₁₀O₂ (6.14 x 10⁻⁶ molar ratio of QDs to C₄H₁₀O₂) (right), and (b) 8.51 x 10⁻⁷ M solution of CdSe (oleylamine) QDs dissolved in chloroform before treatment (left) and 1 d after treatment with C₄H₁₀O₂ (1.37 x 10⁻⁴ molar ratio of QDs to C₄H₁₀O₂) (right).]
Figure 6.2. Photos of a (a) $1.04 \times 10^{-6}$ M solution of CdSe (oleylamine) QDs dissolved in toluene before treatment (left) and 1 d after treatment with $C_4H_{10}O_2$ ($1.00 \times 10^{-7}$ molar ratio of QDs to $C_4H_{10}O_2$) (right), and (b) $1.04 \times 10^{-6}$ M solution of CdSe (oleylamine) QDs dissolved in toluene before treatment (left) and 1 d after treatment with $C_4H_{10}O_2$ ($1.68 \times 10^{-4}$ molar ratio of QDs to $C_4H_{10}O_2$) (right).

Although only 1 of the 5 reducing/oxidizing agents investigated in this thesis was evaluated as a function of concentration, it is expected that the lower the concentration of reducing/oxidizing agent, the slower the rate of reaction and therefore the better the treatment. Future work based on this thesis will investigate the effect of concentration of the other 4 reducing/oxidizing agents on the QY of the QDs after treatment.
6.2 References


Chapter 7. Conclusions

Quantum dots are nanoscale semiconductors that exhibit fascinating optical and electrical properties not observed in bulk semiconductors. Specifically, the size and shape of QDs can be tuned by varying reaction conditions therefore making QDs advantageous for a variety of applications ranging from electronics to the medical field.

This thesis focused on producing QDs with a high quantum yield (QY) by investigating the effect of treating QDs with either reducing or oxidizing agents to enhance the QY. The reducing agents investigated include: sodium borohydride (NaBH₄), calcium hydride (CaH₂), and hydrazine (N₂H₄); and the oxidizing agents investigated are: benzoyl peroxide (C₁₄H₁₀O₄) and tert-butylhydroperoxide (C₄H₁₀O₂). To correlate what effect the reducing and oxidizing agents were having on the optical properties of the QDs, we investigated these treatments on the following factors: chalcogenide (Se vs. S), ligand (oleylamine vs. OA), coordinating solvent (ODE vs. TOA), and dispersant solvent (chloroform vs. toluene) on the overall optical properties of the QDs. The main conclusions from the work of this thesis are presented below.

- The ability of the various reducing/oxidizing agents to enhance the QY of the QDs was independent of the chalcogenide. No clear trend was observed to indicate that the surface treatments were more effective in treating CdSe QDs versus CdS QDs. In fact, the exact same results were obtained when oleylamine was used as the capping ligand. The initial QY of CdSe QDs, however, was higher than that of CdS
QDs when capped with oleylamine. Conversely, the initial QY of CdS QDs was higher than that of CdSe QDs when capped with oleic acid (regardless of non-coordinating solvent used). A reason for this difference is not known, however, we hypothesize that a possible explanation involves the coverage of ligands on the surface of the QDs. To estimate ligand surface coverage, thermogravimetric analysis (TGA) data coupled with data regarding the geometry of the QD can be used. Specifically, TGA measures the weight change of a sample as it is heated to the temperature at which it degrades. After performing TGA on the QD samples, it is believed that the mass remaining after heating is that of the metal core without the ligands. TGA was performed on each batch of QDs used in this thesis (see Appendix D). Coupling this TGA data with information regarding the size and shape of the QDs would allow for the estimate of ligand surface coverage and therefore provide an explanation as to why the QY of the untreated QDs was higher when CdSe QDs were capped with oleylamine and CdS QDs were capped with OA. To estimate the size and shape of the QDs, it is recommended that transmission electron microscopy (TEM) or dynamic light scattering (DLS) be performed in the future work of this thesis.

- **The QY of the QDs was calculated to be higher when octadecene (ODE) was used as the non-coordinating solvent versus trioctylamine (TOA).** The QY of the QDs synthesized with OA as the ligand and ODE as the non-coordinating solvent were visibly brighter and yielded a higher QY than those with TOA as the non-coordinating solvent. This was observed regardless of chalcogenide or dispersion
solvent. The primary difference between the two investigated solvents is that ODE is a non-coordinating solvent whereas TOA is a weakly-coordinated solvent. Because TOA has both polar and non-polar groups, it may have coordinated to the QD surface and interfered with the OA coverage of the QD surface, therefore leading to a reduced QY. Further characterization of the QDs is required before a definitive conclusion can be made.

In terms of surface treatment, the QY of the QDs was enhanced after treatment with the various reducing/oxidizing agents more often when ODE was used as the non-coordinating solvent than TOA. More specifically, 8 of the 20 treatments performed on QDs with ODE as the non-coordinating solvent resulted in an increased QY, whereas only 4 of the 20 treatments increased in the presence of TOA. Similar to the effect of the chalcogenide, it is believed that the difference in coverage of the ligands on the QD surface is responsible for this observation. As mentioned above, it is possible that the TOA may have interfered with the OA coverage of the QD surface, therefore preventing the reducing/oxidizing agents from effectively passivating the surface defects on the QDs surface. To determine the effect the non-coordinating solvent has on the ability of OA to bind to the QD surface, it is recommended that further characterization techniques be performed. Specifically, TEM or DLS should be performed to determine the size and shape of the QDs. Coupling this geometry data with the TGA data summarized in Appendix D of this thesis would allow for the estimate of OA coverage in the presence of the 2 non-coordinating solvents. Furthermore, this data would provide an explanation about
why the surface treatment of the QDs was more effective at increasing the QY of the QDs when ODE was used instead of TOA.

- **The QY of the QDs was calculated to be higher when the QDs were dispersed in toluene versus chloroform.** Regardless of chalcogenide, ligand, non-coordinating solvent, or treatment, QDs were visibly brighter and yielded a higher QY when dissolved in toluene than chloroform. This result is consistent with the work of Bullen et al. who concluded that when capping ligands are very soluble in a solvent, the ligands detach from the QD surface, therefore resulting in a quenched QY.¹ Conversely, if the ligands are less soluble in a solvent, they will tend to adsorb onto the surface of the QDs from solution which may enhance the QY even further.¹ Because oleylamine is more soluble in chloroform than toluene, the higher QY of QDs capped with oleylamine in toluene than chloroform was therefore justified. Oleic acid, on the other hand, is more soluble in toluene than chloroform therefore the dependence of solvent is hypothesized to be due to the difference in dissolved oxygen concentration in each solvent.

In terms of surface treatment, the QY of the QDs capped with OA was enhanced after treatment with the various reducing/oxidizing agents more often when the QDs were dispersed and treated in chloroform than toluene. When oleylamine was used as the capping ligand, no difference in solvent was observed. To explain the dependence on solvent in the presence of OA, we present 2 possible explanations. First, we
hypothesize that if the reducing/oxidizing agent is more soluble in a given solvent it will react at a significantly faster rate than in a poor solvent. If the reaction happens too fast, the QDs will begin to aggregate, and the QY will be quenched. To test this theory, a solubility study to determine the solubility of each reducing/oxidizing agent in both chloroform and toluene should be conducted. Based on the results presented in this thesis, we expect that the reducing/oxidizing agents will be more soluble in toluene than chloroform, therefore explaining our results.

A second possible explanation for the observed results also focuses on the reaction rate. Specifically, we hypothesize that the reducing/oxidizing agents react with the residual water present in each of the solvents to form hydrogen. The hydrogen then reacts with the surface ligands, causing them to detach from the QD surface, and allowing oxygen from the atmospheric air to diffuse to the exposed cadmium. The resulting CdO layer around the QDs serves to passivate the defect sites located on the QD surface and therefore improves the QY of the QDs. If the reducing/oxidizing agents react too fast with the residual water, the QDs will aggregate and the QY will be quenched. Based on this hypothesis, the amount of water present in each of the solvents may be responsible for the dependence of solvent on the effectiveness of the various surface treatments. To test this theory, the hydrogen concentration emitted from the reaction of each reducing/oxidizing agent with both chloroform and toluene should be measured and compared.
Surface treatment of QDs with sodium borohydride (NaBH₄) resulted in an enhanced QY in 10 of the 12 treatments. Sodium borohydride (NaBH₄) was found to be the most effective reducing agent at improving the QY of the as-synthesized QDs. Of the 12 batches of QDs investigated, NaBH₄ effectively improved the QY of all but 2 after treatment (including CdS (OA & TOA) in chloroform, and CdS (OA & ODE) in toluene). One potential explanation for the success of NaBH₄ in enhancing the QY of the QDs is due to the slight solubility of NaBH₄ in the two dispersion solvents. Because NaBH₄ is only slightly soluble in chloroform and toluene, we hypothesize that the reducing agent diffused through the solvent to react with the QDs at a slow enough reaction rate that the QDs surface was effectively reduced. In the case of reducing/oxidizing agents that were completely soluble in the dispersion solvents, the reaction often happened so fast that the QDs aggregated and the fluorescence of the QD solution was completely quenched.

A second possible explanation involves the reactivity of NaBH₄ with water. In a study by Kong et al., the reaction rate of NaBH₄ with water vapor was found to be ten times slower than that of CaH₂. For this reason, we hypothesize that NaBH₄ reacted with the residual water in each solvent at a slow enough rate that the hydrogen produced was able to effectively detach ligands on the QD surface and allow for the formation of the CdO layer. As explained above, if a reducing/oxidizing agent reacts too fast with the residual water, the QDs will aggregate and the QY will be quenched. It is therefore hypothesized that CaH₂ reacted with the residual water at too fast a rate, therefore explaining the observed aggregation and decrease in QY.
- Surface treatment of QDs with hydrazine (N$_2$H$_4$) in chloroform resulted in poor dispersion of the hydrazine which quenched the QY. Hydrazine is a liquid that is nearly insoluble in chloroform. When hydrazine was added to the QD solution an emulsion formed. We hypothesize that OA and oleylamine were able to act as surfactants and stabilize the N$_2$H$_4$ droplets in their respective emulsions. In the presence of oleylamine, large, poorly dispersed droplets of N$_2$H$_4$ formed, indicating that oleylamine is not a good surfactant for N$_2$H$_4$ in chloroform. However, OA seemed to be a better surfactant for N$_2$H$_4$ in chloroform because small, evenly dispersed droplets of N$_2$H$_4$ could be seen in the chloroform. Figure 7.2 illustrates this difference in droplet suspension when oleylamine was used as opposed to OA.

We hypothesized the emulsions had two effects on the QD solutions. For the oleylamine QDs, a small amount of soluble N$_2$H$_4$ reacts with the QDs and reduces their surface to etch and destroy the QDs thereby quenching the QD fluorescence. The remainder of the N$_2$H$_4$ forms large, unevenly dispersed N$_2$H$_4$ droplets stabilized by the residual oleylamine. The solution appears blue-green when excited by a 365 nm UV lamp because the oleylamine emits light at 450 nm upon excitation. After 10 days a visible layer forms at the top of the chloroform solution, presumably due to instability of the emulsion. A similar effect was observed with the OA/TOA QDs presumably because residual TOA is a poor surfactant for N$_2$H$_4$ in chloroform.

In the case of the OA QDs, when the N$_2$H$_4$ is added to the chloroform a small amount of soluble N$_2$H$_4$ reacts with the QDs and reduces their surface to etch and destroy the QDs thereby quenching the QD fluorescence. The residual OA then
stabilized the remaining \( \text{N}_2\text{H}_4 \) into small, evenly dispersed \( \text{N}_2\text{H}_4 \) droplets. These droplets scatter light, causing the solution to appear cloudy in visible light. When a 365 nm UV lamp was used as the incident light, the evenly dispersed droplets of \( \text{N}_2\text{H}_4 \) in the QD solution scattered the light causing the solution to appear purple (see Figure 7.1).

![Figure 7.1](image)

Figure 7.1. Schematic illustrating effect of ligand on \( \text{N}_2\text{H}_4 \) dispersion in chloroform.

Regardless of ligand, the fluorescence of the OA/TOA QDs was quenched immediately after treatment with \( \text{N}_2\text{H}_4 \).

- **The effectiveness of QD surface treatment with various reducing/oxidizing agents is dependent on concentration.** As explained above, often the reduction/oxidation of the QD surface happened so fast that the fluorescence of the QD solution was quenched after treatment. We hypothesize that when a reducing/oxidizing agent it highly soluble in a given solvent or very reactive with water, it reacts with the QDs at a rate so fast desorption of the ligands and
aggregation occur before forming a stable QD with a CdO layer. The net result is an increase in the UV absorbance and a quenching of the fluorescence resulting in a decrease in QY. This theory was investigated by treating each of the 6 batches of QDs with tert-butylhydroperoxide (C₄H₁₀O₂) in both chloroform and toluene at several concentrations. From this set of treatments, a clear dependence on the oxidizing agent’s concentration was observed. Specifically, at lower concentrations of the oxidizing agent, the reaction rate slowed significantly, and the fluorescence was not quenched. Although this theory was only tested for 1 of the 5 reducing/oxidizing agents, it is expected the concentration dependence on the reactivity effect the other 4 treatments as well.
7.1 References


Chapter 8. Future Work

The work detailed in this thesis was aimed at surveying the effect of oxidizing and reducing agents on the quantum yield of CdSe and CdS QDs. Future work focuses on expanding on these results to include additional characterization methods to gather more information about the effect of the reducing and oxidizing agents on the structure of the QDs. Additional future work involves investigating the solubility and reactivity of each reducing/oxidizing agent to support the conclusion that the effectiveness of each agent was dependent on reaction rate. Specific recommendations for future work of this thesis are presented below.

- **Characterization methods should be performed to quantify the size and shape of the QDs.** Specifically, transmission electron microscopy (TEM), atomic force microscopy (AFM) or dynamic light scattering (DLS) should be performed to measure the size and shape of the QDs before and after treatment. Knowledge of the morphology of the QDs would help to quantitatively determine what effect the oxidizing and reducing agents have on the size of the QDs due to etching or aggregation. For example, increases in absorbance and flattening of the fluorescence peak seem to indicate aggregation had occurred after treating several of the QD batches with calcium hydride (CaH₂). Information regarding the size of the QDs before treatment and at each time interval after treatment with CaH₂ could quantify what fraction of the QDs aggregated with time. TEM images would also provide
information about the shape of the QDs. The size and shape of the QDs could be used in conjunction with thermogravitational analysis (TGA) results to determine the ligand surface coverage of the various QD batches. The ligand surface coverage could be used to determine if there is a correlation between coverage of the ligands on the QDs surface and effectiveness of a reducing/oxidizing agent.

- **The dependence of concentration on the effectiveness of QD surface treatment should be investigated for each reducing/oxidizing agent.** One of the main conclusions of this thesis is that the effectiveness of QD surface treatments on the QY of the QDs is dependent on concentration. This conclusion was explored by retreating each of the 6 batches of QDs with a lower concentration of tert-butylhydroperoxide ($\text{C}_4\text{H}_{10}\text{O}_2$) in both chloroform and toluene. From this set of treatments, a clear dependence on the oxidizing agent’s concentration was observed. Specifically, lower oxidizing agent concentrations resulted in slower reaction rates and greater increases in QY. Given these results, the concentration dependence of the remaining surface treatments (sodium borohydride ($\text{NaBH}_4$), hydrazine ($\text{N}_2\text{H}_4$), calcium hydride ($\text{CaH}_2$), and benzoyl peroxide ($\text{C}_{14}\text{H}_{10}\text{O}_2$)) on the QY should be explored.

- **A solubility study should be performed to determine the solubility of each reducing/oxidizing agent in chloroform and toluene.** As explained in the results sections of this thesis, little information is available regarding the solubility of each reducing/oxidizing agent in toluene versus chloroform. We hypothesize that if a given
reducing/oxidizing agent is more soluble is a particular solvent, it will react at a much faster rate than in a poor solvent. The result of the faster reaction rate leads to the ligands detaching from the QD surface at a rate that favors aggregation of the QDs. For this reason, information concerning the solubility of each agent in the dispersion solvents is crucial to confirming this hypothesis. It is therefore recommended that a solubility study be conducted on each of the 5 reducing/oxidizing agents in both toluene and chloroform.

- **Additional testing should be performed to test the hypothesis that water contained in the solvents reacted with each reducing/oxidizing agent to reduce/oxidize the QD surface.** As explained in Chapter 7, we hypothesize that water contained in the solvents reacted with each reducing/oxidizing agent to produce hydrogen. This hydrogen then reacted with the surface ligands, causing them to detach from the QD surface, and allowing oxygen from the atmospheric air to diffuse to the exposed cadmium. The resulting CdO layer around the QDs served to passivate the defect sites located on the QD surface and resulted in an enhanced QY. To test this hypothesis, it is recommended that each of the QDs be dispersed and treated in dried chloroform and toluene. If our hypothesis is correct, the QDs will not be reduced/oxidized and no change in the QY of the QDs will be observed.

This hypothesis was also applied as a possible explanation as to why NaBH₄ was an effective reducing agent but CaH₂ was not. Specifically, CaH₂ reacts with water vapor at a significantly faster rate (10 X) than NaBH₄.¹ For this reason, it is
believed that because the reduction of the QDs happened so fast when treated with CaH₂, the QDs often aggregated, resulting in reduced QY. To further test this hypothesis, the hydrogen concentration emitted from the reaction of each solvent, ligand, and CaH₂ reaction can be compared to that of each solvent, ligand, and NaBH₄ reaction. If our hypothesis is correct, the amount of hydrogen produced from the reaction with CaH₂ will be significantly higher than the amount produced from the NaBH₄ reaction.

- **It is recommended that techniques to synthesize better quality CdS (OA & TOA) QDs be investigated.** Of the 6 batches of QDs synthesized in the work of this thesis, CdS (OA & TOA) QDs had the lowest initial QY. It is therefore recommended that techniques to synthesize better quality CdS (OA & TOA) QDs be investigated. A potential modification to the existing procedure involves heating the precursor solution to a higher temperature prior to injection into the reaction solution. Currently, the precursor solution is heated to 120 °C prior to injection into the reaction solution which is then heated to 175 °C. It is recommended that the precursor solution be preheated to temperatures between 120 °C and 175 °C to determine the influence, if any, that this temperature has on the QY of the synthesized QDs. Another potential modification involves exploring other cadmium sources. In this thesis, cadmium acetate was used as the cadmium source for each of the batches, however, several research groups report the use of cadmium oxide (CdO) to produce high quality CdS QDs.² It is therefore recommended that CdO be investigated.
• **Methods to quench the QD synthesis reaction should be explored.** The procedure followed to synthesize QDs in this thesis involved heating the reaction mixture in a microwave to a specific temperature. After the reaction was complete, the reaction solution slowly cooled to room temperature. As seen from the fluorescence spectra included in the results of this thesis, the as-synthesized QDs yielded a broad fluorescence peak indicating a wide size distribution of particles. Specifically, an average full-width half-maximum (FWHM) of 90 nm was reported for CdSe QDs and 170 nm for CdS QDs. The literature, on the other hand, reports CdSe FWHM values as low as 25 nm\(^3,4\), and CdS values of 18 nm.\(^3\) A recommendation for future work involves quenching the reaction immediately after heating to prevent any further reaction. It is expected that by quenching the reaction, a more uniform size distribution of particles will be achieved. A possible technique to explore involves adding a small amount of ethanol to the reaction solution immediately after the reaction is complete.\(^5\)

• **It is recommended that the negative fluorescence peak observed in the fluorescence spectra of CdSe (OA & TOA) and CdS (OA & TOA) QDs dissolved in chloroform be investigated further.** Fluorescence spectroscopy was performed on solutions consisting of each ligand, non-coordinating solvent, dispersion solvent, and reducing/oxidizing agent combination to account for the potential influence of the various reaction materials on QD fluorescence. Each spectra yielded a similar peak at 450 nm, therefore this peak was said to be representative of the reaction materials.
Although this peak was observed in several of the QD batches, in the case of both CdSe (OA & TOA) and CdS (OA & TOA) QDs dissolved in chloroform, this fluorescence peak was negative. Because a positive peak centered at 450 nm was observed in the fluorescence spectra of OA, TOA, and chloroform (no negative peak), it is unclear why this negative peak was seen. The final recommendation for future work of this thesis is that additional batches of CdSe (OA & TOA) and CdS (OA & TOA) QDs dissolved in chloroform be tested to confirm this result. If the negative peak is observed in these new batches, it is recommended that further characterizations be performed to determine its cause.

- **A method to purify the QDs after treatment should be explored.** As explained in Chapter 4, the measured absorbance and fluorescence spectra presented in this thesis (and therefore calculated quantum yield values) were representative of the QD mixture, not just the QDs. For this reason, it is unclear what led to the quenching of the QD solutions. Developing a method to purify the QDs after treatment may remove the quenching agent and enable us to measure the absorbance and fluorescence of just the QDs. Furthermore, if the quenching is reversible, purification may allow for the restoration of the QD fluorescence after quenching. For example, if excess free ligand led to the quenching of the fluorescence, purifying the QDs would remove the residual ligand, and, if the quenching is reversible, restore the fluorescence. Future work should also focus on determining the specific effect of the ligands on QD quenching as well as determining the extinction coefficient of the QD mixture.
8.1 References


Appendix A. Determining the Optimum Concentration of Reducing/Oxidizing Agents for Experiments

Included in this appendix are plots and pictures that led to the determination of the optimal concentration of each of the 5 reducing/oxidizing agents used in this thesis. The agents investigated include: (1) sodium borohydride (NaBH₄), (2) calcium hydride (CaH₂), (3) hydrazine (N₂H₄), (4) benzoyl peroxide (C₁₄H₁₀O₄), and (5) tert-butyl hydroperoxide (C₄H₁₀O₂). Preliminary results showed that QDs fluoresced brighter in chloroform than toluene, therefore, chloroform was used as the solvent when determining each reducing/oxidizing agent concentration.

A.1 CdSe Quantum Dot Cores Synthesized with Oleylamine

A.1.1 Sodium Borohydride (NaBH₄)

Cadmium selenide QD cores synthesized with oleylamine were treated with 0.001 g (0.026 mmol), 0.003 g (0.079 mmol), and 0.006 g (0.159 mmol) NaBH₄ to determine which concentration yielded the highest fluorescence peak. Figure A1 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of NaBH₄ for this batch type was found to be 0.006 g (0.159 mmol) as represented by the green line.
Figure A.1. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdSe (oleylamine) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g NaBH₄. (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g NaBH₄ excited with 365 nm UV light.

A.1.2 Calcium Hydride (CaH₂)

Cadmium selenide QD cores synthesized with oleylamine were treated with 0.001 g (0.024 mmol), 0.003 g (0.071 mmol), and 0.006 g (0.143 mmol) CaH₂ to determine
which concentration yielded the highest fluorescence peak. Figure A2 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of CaH$_2$ for this batch type was found to be 0.001 g (0.024 mmol) as represented by the orange line.

Figure A.2. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdSe (oleylamine) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g CaH$_2$. (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g CaH$_2$ excited with 365 nm UV light.
A.1.3 Hydrazine (N\textsubscript{2}H\textsubscript{4})

Cadmium selenide QD cores synthesized with oleylamine were treated with 0.05 mL (1.58 mmol), 0.10 mL (3.16 mmol), and 0.15 mL (4.74 mmol) N\textsubscript{2}H\textsubscript{4} to determine which concentration yielded the highest fluorescence peak. Figure A3 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of N\textsubscript{2}H\textsubscript{4} for this batch type was found to be 0.15 mL (4.74 mmol) as represented by the green line.

Figure A.3. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdSe (oleylamine) QDs dissolved in chloroform before treatment (blue), after treatment with 0.05 mL (orange), 0.10 mL (red), and 0.15 mL N\textsubscript{2}H\textsubscript{4}. (c) Photo of QDs that are from left to right, untreated, treated with 0.05 mL, 0.10 mL, and 0.15 mL N\textsubscript{2}H\textsubscript{4} excited with 365 nm UV light.
A.1.4 Benzoyl Peroxide (C$_{14}$H$_{10}$O$_4$)

Cadmium selenide QD cores synthesized with oleylamine were treated with 0.001 g (0.004 mmol), 0.003 g (0.012 mmol), and 0.006 g (0.025 mmol) C$_{14}$H$_{10}$O$_4$ to determine which concentration yielded the highest fluorescence peak. Figure A4 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of C$_{14}$H$_{10}$O$_4$ for this batch type was found to be 0.001 g (0.004 mmol) as represented by the orange line.

![Absorbance and Fluorescence Spectra](image)

Figure A.4. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdSe (oleylamine) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g C$_{14}$H$_{10}$O$_4$. (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g C$_{14}$H$_{10}$O$_4$ excited with 365 nm UV light.
A.1.5 tert-Butyl Hydroperoxide (C₄H₁₀O₂)

Cadmium selenide QD cores synthesized with oleylamine were treated with 0.05 mL (0.519 mmol), 0.10 mL (1.04 mmol), and 0.15 mL (1.56 mmol) C₄H₁₀O₂ to determine which concentration yielded the highest fluorescence peak. Figure A5 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. Although the QDs stopped fluorescing after the addition of C₄H₁₀O₂ as seen in Figure A5c, the optimal concentration of C₄H₁₀O₂ for this batch type was assumed to be 0.05 mL (orange line).

![Absorbance and Fluorescence Spectra](image)

Figure A.5. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdSe (oleylamine) QDs dissolved in chloroform before treatment (blue), after treatment with 0.05 mL (orange), 0.10 mL (red), and 0.15 mL C₄H₁₀O₂. (c) Photo of QDs that are from left to right, untreated, treated with 0.05 mL, 0.10 mL, and 0.15 mL C₄H₁₀O₂ excited with 365 nm UV light.
A.2 CdSe Quantum Dot Cores Synthesized with Oleic Acid and ODE

A.2.1 Sodium Borohydride (NaBH₄)

Cadmium selenide QD cores synthesized with oleic acid and ODE were treated with 0.001 g (0.026 mmol), 0.003 g (0.079 mmol), and 0.006 g (0.159 mmol) NaBH₄ to determine which concentration yielded the highest fluorescence peak. Figure A6 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of NaBH₄ for this batch type was found to be 0.006 g (0.159 mmol) as represented by the green line.
Figure A.6. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g NaBH₄. (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g NaBH₄ excited with 365 nm UV light.

A.2.2 Calcium Hydride (CaH₂)

Cadmium selenide QD cores synthesized with oleic acid and ODE were treated with 0.001 g (0.024 mmol), 0.003 g (0.071 mmol), and 0.006 g (0.143 mmol) CaH₂ to determine which concentration yielded the highest fluorescence peak. Figure A7 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples.
The optimal concentration of CaH$_2$ for this batch type was found to be 0.001 g (0.024 mmol) as represented by the orange line.

Figure A.7. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g CaH$_2$. (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g CaH$_2$ excited with 365 nm UV light.
A.2.3 Hydrazine ($N_2H_4$)

Cadmium selenide QD cores synthesized with oleic acid and ODE were treated with 0.05 mL (1.58 mmol), 0.10 mL (3.16 mmol), and 0.15 mL (4.74 mmol) $N_2H_4$ to determine which concentration yielded the highest fluorescence peak. Figure A8 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. Although the QDs stopped fluorescing after the addition of $N_2H_4$, the optimal concentration of $N_2H_4$ for this batch type was assumed to be 0.05 mL (orange line).

![Absorbance and fluorescence spectra](image)

**Figure A.8.** Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), after treatment with 0.05 mL (orange), 0.10 mL (red), and 0.15 mL $N_2H_4$. (c) Photo of QDs that are from left to right, untreated, treated with 0.05 mL, 0.10 mL, and 0.15 mL $N_2H_4$ excited with 365 nm UV light.
A.2.4 Benzoyl Peroxide ($C_{14}H_{10}O_4$)

Cadmium selenide QD cores synthesized with oleic acid and ODE were treated with 0.001 g (0.004 mmol), 0.003 g (0.012 mmol), and 0.006 g (0.025 mmol) $C_{14}H_{10}O_4$ to determine which concentration yielded the highest fluorescence peak. Figure A9 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of $C_{14}H_{10}O_4$ for this batch type was found to be 0.006 g (0.025 mmol) as represented by the green line.

Figure A.9. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g $C_{14}H_{10}O_4$. (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g $C_{14}H_{10}O_4$ excited with 365 nm UV light.
A.2.5 tert-Butyl Hydroperoxide (C₄H₁₀O₂)

Cadmium selenide QD cores synthesized with oleic acid and ODE were treated with 0.05 mL (0.519 mmol), 0.10 mL (1.04 mmol), and 0.15 mL (1.56 mmol) C₄H₁₀O₂ to determine which concentration yielded the highest fluorescence peak. Figure A10 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of C₄H₁₀O₂ for this batch type was found to be 0.15 mL (1.56 mmol) as represented by the green line.

Figure A.10. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), after treatment with 0.05 mL (orange), 0.10 mL (red), and 0.15 mL C₄H₁₀O₂. (c) Photo of QDs that are from left to right, untreated, treated with 0.05 mL, 0.10 mL, and 0.15 mL C₄H₁₀O₂ excited with 365 nm UV light.
A.3 CdSe Quantum Dot Cores Synthesized with Oleic Acid and TOA

A.3.1 Sodium Borohydride (NaBH₄)

Cadmium selenide QD cores synthesized with oleic acid and TOA were treated with 0.001 g (0.026 mmol), 0.003 g (0.079 mmol), and 0.006 g (0.159 mmol) NaBH₄ to determine which concentration yielded the highest fluorescence peak. Figure A11 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of NaBH₄ for this batch type was found to be 0.001 g (0.026 mmol) as represented by the orange line.
Figure A.11. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdSe (OA & TOA) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g NaBH₄. (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g NaBH₄ excited with 365 nm UV light.

A.3.2 Calcium Hydride (CaH₂)

Cadmium selenide QD cores synthesized with oleic acid and TOA were treated with 0.001 g (0.024 mmol), 0.003 g (0.071 mmol), and 0.006 g (0.143 mmol) CaH₂ to determine which concentration yielded the highest fluorescence peak. Figure A12 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples.
The optimal concentration of \( \text{CaH}_2 \) for this batch type was found to be 0.001 g (0.024 mmol) as represented by the orange line.

Figure A.12. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdSe (OA & TOA) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g CaH\(_2\). (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g CaH\(_2\) excited with 365 nm UV light.
A.3.3 Hydrazine ($N_2H_4$)

Cadmium selenide QD cores synthesized with oleic acid and TOA were treated with 0.05 mL (1.58 mmol), 0.10 mL (3.16 mmol), and 0.15 mL (4.74 mmol) $N_2H_4$ to determine which concentration yielded the highest fluorescence peak. Figure A13 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. Although the QDs stopped fluorescing after the addition of $N_2H_4$, the optimal concentration of $N_2H_4$ for this batch type was assumed to be 0.15 mL (green line).

Figure A.13. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdSe (OA & TOA) QDs dissolved in chloroform before treatment (blue), after treatment with 0.05 mL (orange), 0.10 mL (red), and 0.15 mL $N_2H_4$. (c) Photo of QDs that are from left to right, untreated, treated with 0.05 mL, 0.10 mL, and 0.15 mL $N_2H_4$ excited with 365 nm UV light.
A.3.4 Benzoyl Peroxide \((C_{14}H_{10}O_4)\)

Cadmium selenide QD cores synthesized with oleic acid and TOA were treated with 0.001 g (0.004 mmol), 0.003 g (0.012 mmol), and 0.006 g (0.025 mmol) \(C_{14}H_{10}O_4\) to determine which concentration yielded the highest fluorescence peak. Figure A14 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of \(C_{14}H_{10}O_4\) for this batch type was found to be 0.003 g (0.012 mmol) as represented by the red line.

![Absorbance and Fluorescence Spectra](image)

Figure A.14. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdSe (OA & TOA) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g \(C_{14}H_{10}O_4\). (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g \(C_{14}H_{10}O_4\) excited with 365 nm UV light.
A.3.5 tert-Butyl Hydroperoxide (C₄H₁₀O₂)

Cadmium selenide QD cores synthesized with oleic acid and TOA were treated with 0.05 mL (0.519 mmol), 0.10 mL (1.04 mmol), and 0.15 mL (1.56 mmol) C₄H₁₀O₂ to determine which concentration yielded the highest fluorescence peak. Figure A15 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of C₄H₁₀O₂ for this batch type was found to be 0.10 mL (1.04 mmol) as represented by the red line.

![Absorbance and Fluorescence Spectra](image)

Figure A.15. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdSe (OA & TOA) QDs dissolved in chloroform before treatment (blue), after treatment with 0.05 mL (orange), 0.10 mL (red), and 0.15 mL C₄H₁₀O₂. (c) Photo of QDs that are from left to right, untreated, treated with 0.05 mL, 0.10 mL, and 0.15 mL C₄H₁₀O₂ excited with 365 nm UV light.
A.4 CdS Quantum Dot Cores Synthesized with Oleylamine

A.4.1 Sodium Borohydride (NaBH₄)

Cadmium sulfide QD cores synthesized with oleylamine were treated with 0.001 g (0.026 mmol), 0.003 g (0.079 mmol), and 0.006 g (0.159 mmol) NaBH₄ to determine which concentration yielded the highest fluorescence peak. Figure A16 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of NaBH₄ for this batch type was found to be 0.003 g (0.079 mmol) as represented by the red line.
Figure A.16. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdS (oleylamine) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g NaBH₄. (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g NaBH₄ excited with 365 nm UV light.

A.4.2 Calcium Hydride (CaH₂)

Cadmium sulfide QD cores synthesized with oleylamine were treated with 0.001 g (0.024 mmol), 0.003 g (0.071 mmol), and 0.006 g (0.143 mmol) CaH₂ to determine
which concentration yielded the highest fluorescence peak. Figure A17 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of CaH$_2$ for this batch type was found to be 0.001 g (0.024 mmol) as represented by the orange line.

Figure A.17. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdS (oleylamine) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g CaH$_2$. (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g CaH$_2$ excited with 365 nm UV light.
A.4.3 Hydrazine (N$_2$H$_4$)

Cadmium sulfide QD cores synthesized with oleylamine were treated with 0.05 mL (1.58 mmol), 0.10 mL (3.16 mmol), and 0.15 mL (4.74 mmol) N$_2$H$_4$ to determine which concentration yielded the highest fluorescence peak. Figure A52 below shows the absorbance spectrum, Figure A53 shows the fluorescence spectrum, and Figure A54 includes a picture of the samples. The optimal concentration of N$_2$H$_4$ for this batch type was found to be 0.15 mL (4.74 mmol) in Figure A53 (green line).

Figure A.18. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdS (oleylamine) QDs dissolved in chloroform before treatment (blue), after treatment with 0.05 mL (orange), 0.10 mL (red), and 0.15 mL N$_2$H$_4$. (c) Photo of QDs that are from left to right, untreated, treated with 0.05 mL, 0.10 mL, and 0.15 mL N$_2$H$_4$ excited with 365 nm UV light.
A.4.4 Benzoyl Peroxide ($C_{14}H_{10}O_4$)

Cadmium sulfide QD cores synthesized with oleylamine were treated with 0.001 g (0.004 mmol), 0.003 g (0.012 mmol), and 0.006 g (0.025 mmol) $C_{14}H_{10}O_4$ to determine which concentration yielded the highest fluorescence peak. Figure A19 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of $C_{14}H_{10}O_4$ for this batch type was found to be 0.001 g (0.004 mmol) as represented by the orange line.

Figure A.19. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdS (oleylamine) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g $C_{14}H_{10}O_4$. (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g $C_{14}H_{10}O_4$ excited with 365 nm UV light.
A.4.5 tert-Butyl Hydroperoxide ($C_{4}H_{10}O_{2}$)

Cadmium sulfide QD cores synthesized with oleylamine were treated with 0.05 mL (0.519 mmol), 0.10 mL (1.04 mmol), and 0.15 mL (1.56 mmol) $C_{4}H_{10}O_{2}$ to determine which concentration yielded the highest fluorescence peak. Figure A20 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of $C_{4}H_{10}O_{2}$ for this batch type was found to be 0.15 mL (1.56 mmol) as represented by the green line.

![Absorbance and Fluorescence Spectra](image-url)

Figure A.20. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdS (oleylamine) QDs dissolved in chloroform before treatment (blue), after treatment with 0.05 mL (orange), 0.10 mL (red), and 0.15 mL $C_{4}H_{10}O_{2}$. (c) Photo of QDs that are from left to right, untreated, treated with 0.05 mL, 0.10 mL, and 0.15 mL $C_{4}H_{10}O_{2}$ excited with 365 nm UV light.
A.5 CdSe Quantum Dot Cores Synthesized with Oleic Acid and ODE

A.5.1 Sodium Borohydride (NaBH₄)

Cadmium sulfide QD cores synthesized with oleic acid and ODE were treated with 0.001 g (0.026 mmol), 0.003 g (0.079 mmol), and 0.006 g (0.159 mmol) NaBH₄ to determine which concentration yielded the highest fluorescence peak. Figure A21 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of NaBH₄ for this batch type was found to be 0.003 g (0.079 mmol) as represented by the red line.
A.5.2 Calcium Hydride (CaH$_2$)

Cadmium sulfide QD cores synthesized with oleic acid and ODE were treated with 0.001 g (0.024 mmol), 0.003 g (0.071 mmol), and 0.006 g (0.143 mmol) CaH$_2$ to determine which concentration yielded the highest fluorescence peak. Figure A22 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples.

Figure A.21. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdS (OA & ODE) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g NaBH$_4$. (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g NaBH$_4$ excited with 365 nm UV light.
The optimal concentration of CaH$_2$ for this batch type was found to be 0.001 g (0.024 mmol) as represented by the orange line.

Figure A.22. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdS (OA & ODE) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g CaH$_2$. (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g CaH$_2$ excited with 365 nm UV light.
A.5.3 Hydrazine (N\textsubscript{2}H\textsubscript{4})

Cadmium sulfide QD cores synthesized with oleic acid and ODE were treated with 0.05 mL (1.58 mmol), 0.10 mL (3.16 mmol), and 0.15 mL (4.74 mmol) N\textsubscript{2}H\textsubscript{4} to determine which concentration yielded the highest fluorescence peak. Figure A23 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. Although the QDs stopped fluorescing after the addition of N\textsubscript{2}H\textsubscript{4}, the optimal concentration of N\textsubscript{2}H\textsubscript{4} for this batch type was assumed to be 0.05 mL (orange line).

![Absorbance spectra](image1)

![Fluorescence spectra](image2)

![Photo of QDs](image3)

Figure A.23. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdS (OA & ODE) QDs dissolved in chloroform before treatment (blue), after treatment with 0.05 mL (orange), 0.10 mL (red), and 0.15 mL N\textsubscript{2}H\textsubscript{4}. (c) Photo of QDs that are from left to right, untreated, treated with 0.05 mL, 0.10 mL, and 0.15 mL N\textsubscript{2}H\textsubscript{4} excited with 365 nm UV light.
A.5.4 Benzoyl Peroxide ($C_{14}H_{10}O_4$)

Cadmium sulfide QD cores synthesized with oleic acid and ODE were treated with 0.001 g (0.004 mmol), 0.003 g (0.012 mmol), and 0.006 g (0.025 mmol) $C_{14}H_{10}O_4$ to determine which concentration yielded the highest fluorescence peak. Figure A.24 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of $C_{14}H_{10}O_4$ for this batch type was found to be 0.003 g (0.012 mmol) as represented by the red line.

Figure A.24. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdS (OA & ODE) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g $C_{14}H_{10}O_4$. (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g $C_{14}H_{10}O_4$ excited with 365 nm UV light.
A.5.5 tert-Butyl Hydroperoxide (C₄H₁₀O₂)

Cadmium sulfide QD cores synthesized with oleic acid and ODE were treated with 0.05 mL (0.519 mmol), 0.10 mL (1.04 mmol), and 0.15 mL (1.56 mmol) C₄H₁₀O₂ to determine which concentration yielded the highest fluorescence peak. Figure A25 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of C₄H₁₀O₂ for this batch type was found to be 0.10 mL (1.04 mmol) as represented by the red line.

![Absorbance and Fluorescence Spectra](image)

Figure A.25. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdS (OA & ODE) QDs dissolved in chloroform before treatment (blue), after treatment with 0.05 mL (orange), 0.10 mL (red), and 0.15 mL C₄H₁₀O₂. (c) Photo of QDs that are from left to right, untreated, treated with 0.05 mL, 0.10 mL, and 0.15 mL C₄H₁₀O₂ excited with 365 nm UV light.
A.6 CdS Quantum Dot Cores Synthesized with Oleic Acid and TOA

A.6.1 Sodium Borohydride (NaBH₄)

Cadmium sulfide QD cores synthesized with oleic acid and TOA were treated with 0.001 g (0.026 mmol), 0.003 g (0.079 mmol), and 0.006 g (0.159 mmol) NaBH₄ to determine which concentration yielded the highest fluorescence peak. Figure A26 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of NaBH₄ for this batch type was found to be 0.006 g (0.159 mmol) as represented by the green line.
Figure A.26. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g NaBH₄. (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g NaBH₄ excited with 365 nm UV light.

A.6.2 Calcium Hydride (CaH₂)

Cadmium sulfide QD cores synthesized with oleic acid and TOA were treated with 0.001 g (0.024 mmol), 0.003 g (0.071 mmol), and 0.006 g (0.143 mmol) CaH₂ to determine which concentration yielded the highest fluorescence peak. Figure A27 below
shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of CaH$_2$ for this batch type was found to be 0.003 g (0.071 mmol) as represented by the red line.

Figure A.27. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g CaH$_2$. (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g CaH$_2$ excited with 365 nm UV light.
A.6.3 Hydrazine ($N_2H_4$)

Cadmium sulfide QD cores synthesized with oleic acid and TOA were treated with 0.05 mL (1.58 mmol), 0.10 mL (3.16 mmol), and 0.15 mL (4.74 mmol) $N_2H_4$ to determine which concentration yielded the highest fluorescence peak. Figure A28 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of $N_2H_4$ for this batch type was found to be 0.05 mL (1.58 mmol) as represented by the orange line.

Figure A.28. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), after treatment with 0.05 mL (orange), 0.10 mL (red), and 0.15 mL $N_2H_4$. (c) Photo of QDs that are from left to right, untreated, treated with 0.05 mL, 0.10 mL, and 0.15 mL $N_2H_4$ excited with 365 nm UV light.
A.6.4 Benzoyl Peroxide ($C_{14}H_{10}O_4$)

Cadmium sulfide QD cores synthesized with oleic acid and TOA were treated with 0.001 g (0.004 mmol), 0.003 g (0.012 mmol), and 0.006 g (0.025 mmol) $C_{14}H_{10}O_4$ to determine which concentration yielded the highest fluorescence peak. Figure A29 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of $C_{14}H_{10}O_4$ for this batch type was found to be 0.001 g (0.004 mmol) as represented by the orange line.

![Absorbance and Fluorescence Spectra](image_url)

Figure A.29. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), after treatment with 0.001 g (orange), 0.003 g (red), and 0.006 g $C_{14}H_{10}O_4$. (c) Photo of QDs that are from left to right, untreated, treated with 0.001 g, 0.003 g, and 0.006 g $C_{14}H_{10}O_4$ excited with 365 nm UV light.
A.5.5 tert-Butyl Hydroperoxide (C₄H₁₀O₂)

Cadmium sulfide QD cores synthesized with oleic acid and TOA were treated with 0.05 mL (0.519 mmol), 0.10 mL (1.04 mmol), and 0.15 mL (1.56 mmol) C₄H₁₀O₂ to determine which concentration yielded the highest fluorescence peak. Figure A30 below shows the absorbance spectrum, the fluorescence spectrum, and a picture of the samples. The optimal concentration of C₄H₁₀O₂ for this batch type was found to be 0.10 mL (1.04 mmol) as represented by the red line.

![Absorbance and fluorescence spectra with QDs treated with different concentrations of tert-Butyl Hydroperoxide](image)

Figure A.30. Absorbance spectra (a) and fluorescence spectra (b) of a solution of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), after treatment with 0.05 mL (orange), 0.10 mL (red), and 0.15 mL C₄H₁₀O₂. (c) Photo of QDs that are from left to right, untreated, treated with 0.05 mL, 0.10 mL, and 0.15 mL C₄H₁₀O₂ excited with 365 nm UV light.
Appendix B. Determining the Effect of Reducing/Oxidizing Agents on CdS (OA & TOA) QDs

Included in this appendix are plots and pictures that illustrate the effect of treating CdS (OA & TOA) QDs with various reducing and oxidizing agents. The agents investigated include: (1) sodium borohydride (NaBH₄), (2) calcium hydride (CaH₂), (3) hydrazine (N₂H₄), (4) benzoyl peroxide (C₁₄H₁₀O₄), and (5) tert-butyl hydroperoxide (C₄H₁₀O₂). The absorbance of the QD solution prior to treatment was ~ 0.08 a.u.
B.1 Treatment with Sodium Borohydride (NaBH₄) in Chloroform

Figure B.1. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.159 mmol NaBH₄. Photos of untreated QDs (left) and QDs treated with NaBH₄ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
B.2 Treatment with Sodium Borohydride (NaBH₄) in Toluene

Figure B.2. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.159 mmol NaBH₄. Photos of untreated QDs (left) and QDs treated with NaBH₄ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
B.3 Treatment with Calcium Hydride (CaH₂) in Chloroform

Figure B.3. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.071 mmol CaH₂. Photos of untreated QDs (left) and QDs treated with CaH₂ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
B.4 Treatment with Calcium Hydride (CaH$_2$) in Toluene

![Figure B.4](image)

Figure B.4. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.071 mmol CaH$_2$. Photos of untreated QDs (left) and QDs treated with CaH$_2$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
B.5 Treatment with Hydrazine (N$_2$H$_4$) in Chloroform

Figure B.5. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 1.58 mmol N$_2$H$_4$. Photos of untreated QDs (left) and QDs treated with N$_2$H$_4$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
B.6 Treatment with Hydrazine ($\text{N}_2\text{H}_4$) in Toluene

Figure B.6. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 1.58 mmol $\text{N}_2\text{H}_4$. Photos of untreated QDs (left) and QDs treated with $\text{N}_2\text{H}_4$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
B.7 Treatment with Benzoyl Peroxide (C\textsubscript{14}H\textsubscript{10}O\textsubscript{4}) in Chloroform

Figure B.7. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.004 mmol C\textsubscript{14}H\textsubscript{10}O\textsubscript{4}. Photos of untreated QDs (left) and QDs treated with C\textsubscript{14}H\textsubscript{10}O\textsubscript{4} (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
B.8 Treatment with Benzoyl Peroxide (C$_{14}$H$_{10}$O$_4$) in Toluene

Figure B.8. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.004 mmol C$_{14}$H$_{10}$O$_4$. Photos of untreated QDs (left) and QDs treated with C$_{14}$H$_{10}$O$_4$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
B.9 Treatment with tert-Butyl Hydroperoxide ($\text{C}_4\text{H}_{10}\text{O}_2$) in Chloroform

Figure B.9. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 1.04 mmol $\text{C}_4\text{H}_{10}\text{O}_2$. Photos of untreated QDs (left) and QDs treated with $\text{C}_4\text{H}_{10}\text{O}_2$ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
B.10 Treatment with tert-Butyl Hydroperoxide (C₄H₁₀O₂) in Toluene

Figure B.10. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 1.04 mmol C₄H₁₀O₂. Photos of untreated QDs (left) and QDs treated with C₄H₁₀O₂ (right) excited with 365 nm UV light (c) 1 d, (d) 5 d, and (e) 10 d after treatment.
B.11 Summary of CdSe/OA & ODE Treatments

Figure B.11. Photos of CdS (OA & TOA) QDs that are from left to right: untreated, treated with 0.159 mmol NaBH₄, 0.004 mmol C₁₆H₁₀O₄, 0.071 mmol CaH₂, 1.58 mmol N₂H₄, and 1.04 mmol C₄H₁₀O₂ excited with 365 nm UV light. The QDs in the left column were suspended and treated in chloroform while those in the right column were in toluene. Photos were taken 1 d (top row), 5 d (middle row), and 10 d (bottom row) after treatment.
Appendix C. Determining the Effect of Concentration on the Surface Treatment of QDs with tert-Butyl Hydroperoxide ($C_4H_{10}O_2$)

Included in this appendix are plots and pictures that illustrate the effect of treating each batch of QDs with varying concentrations of tert-butyl hydroperoxide ($C_4H_{10}O_2$).
C.1 CdSe/Oleylamine Quantum Dot Cores

C.1.1 Chloroform

![Absorbance and Fluorescence Spectra](image)

Figure C1. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C₄H₁₀O₂.
Figure C2. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C₄H₁₀O₂.
Figure C3. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C$_4$H$_{10}$O$_2$.

Figure C4. Photos of CdSe (oleylamine) QDs dissolved in chloroform that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, 0.0726 mmol C$_4$H$_{10}$O$_2$ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.
C.1.2 Toluene

Figure C5. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C_4H_10O_2.
Figure C6. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C₄H₁₀O₂.
Figure C7. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C₄H₁₀O₂.

Figure C8. Photos of CdSe (oleylamine) QDs dissolved in toluene that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, 0.0.726 mmol C₄H₁₀O₂ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.
C.2 CdSe/OA & ODE Quantum Dot Cores

C.2.1 Chloroform

Figure C9. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C$_4$H$_{10}$O$_2$. 
Figure C10. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C_{4}H_{10}O_{2}. 
Figure C11. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C₄H₁₀O₂.

Figure C12. Photos of CdSe (OA & ODE) QDs dissolved in chloroform that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, 0.0726 mmol C₄H₁₀O₂ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.
C.2.2 Toluene

Figure C13. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C$_4$H$_{10}$O$_2$. 
Figure C14. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C₄H₁₀O₂.
Figure C15. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C₄H₁₀O₂.

Figure C16. Photos of CdSe (OA & ODE) QDs dissolved in toluene that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, 0.0726 mmol C₄H₁₀O₂ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.
C.3 CdSe/OA & TOA Quantum Dot Cores

C.3.1 Chloroform

Figure C17. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C$_4$H$_{10}$O$_2$. 
Figure C18. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C$_4$H$_{10}$O$_2$. 
Figure C19. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C$_4$H$_{10}$O$_2$.

Figure C20. Photos of CdSe (OA & TOA) QDs dissolved in chloroform that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, 0.0726 mmol C$_4$H$_{10}$O$_2$ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.
Figure C21. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C₄H₁₀O₂.
Figure C22. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C₄H₁₀O₂.
Figure C23. Absorbance spectra (a) and fluorescence spectra (b) of CdSe (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C₄H₁₀O₂.

Figure C24. Photos of CdSe (OA & TOA) QDs dissolved in toluene that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, and 0.0726 mmol C₄H₁₀O₂ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.
C.4 CdS/Oleylamine Quantum Dot Cores

C.4.1 Chloroform

Figure C25. Absorbance spectra (a) and fluorescence spectra (b) of CdS (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C₄H₁₀O₂.
Figure C26. Absorbance spectra (a) and fluorescence spectra (b) of CdS (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C$_4$H$_{10}$O$_2$. 
Figure C27. Absorbance spectra (a) and fluorescence spectra (b) of CdS (oleylamine) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C₄H₁₀O₂.

Figure C28. Photos of CdS (oleylamine) QDs dissolved in chloroform that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, and 0.0726 mmol C₄H₁₀O₂ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.
C.4.2 Toluene

Figure C29. Absorbance spectra (a) and fluorescence spectra (b) of CdS (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol $C_4H_{10}O_2$. 
Figure C30. Absorbance spectra (a) and fluorescence spectra (b) of CdS (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C$_4$H$_{10}$O$_2$. 
Figure C31. Absorbance spectra (a) and fluorescence spectra (b) of CdS (oleylamine) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C$_4$H$_{10}$O$_2$.

Figure C32. Photos of CdS (oleylamine) QDs dissolved in toluene that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, and 0.0.726 mmol C$_4$H$_{10}$O$_2$ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.
C.5 CdS/OA & ODE Quantum Dot Cores

C.5.1 Chloroform

Figure C33. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C₄H₁₀O₂.
Figure C34. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C₄H₁₀O₂.
Figure C35. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & ODE) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C₄H₁₀O₂.

Figure C36. Photos of CdS (OA & ODE) QDs dissolved in chloroform that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, and 0.0726 mmol C₄H₁₀O₂ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.
C.5.2 Toluene

Figure C37. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C$_4$H$_{10}$O$_2$. 
Figure C38. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C$_4$H$_{10}$O$_2$. 
Figure C39. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & ODE) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C₄H₁₀O₂.

Figure C40. Photos of CdS (OA & ODE) QDs dissolved in toluene that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, and 0.0726 mmol C₄H₁₀O₂ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.
C.6 CdS/OA & TOA Quantum Dot Cores

C.6.1 Chloroform

Figure C41. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C₄H₁₀O₂.
Figure C42. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol $C_4H_{10}O_2$. 
Figure C43. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in chloroform before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C₄H₁₀O₂.

Figure C44. Photos of CdS (OA & TOA) QDs dissolved in chloroform that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, and 0.0.726 mmol C₄H₁₀O₂ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.
C.6.2 Toluene

Figure C45. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0311 mmol C₄H₁₀O₂.
Figure C46. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0519 mmol C₄H₁₀O₂.
Figure C47. Absorbance spectra (a) and fluorescence spectra (b) of CdS (OA & TOA) QDs dissolved in toluene before treatment (blue), immediately after treatment (yellow), 1 d (red), 5 d (green), and 10 d (purple) after treatment with 0.0726 mmol C$_4$H$_{10}$O$_2$.

Figure C48. Photos of CdS (OA & TOA) QDs dissolved in toluene that are from left to right: untreated, treated with 0.0311 mmol, 0.0519 mmol, and 0.0.726 mmol C$_4$H$_{10}$O$_2$ excited with 365 nm UV light (a) 1 d, (b) 5 d, and (c) 10 d after treatment.
Appendix D . Thermogravimetric Analysis (TGA)

Figure D.1. TGA of CdSe (oleylamine) QDs heated from 30 °C to 600 °C at a constant rate of 10 °C/min under nitrogen. wt % remaining = 11.2%

Figure D.2. TGA of CdSe (OA & ODE) QDs heated from 30 °C to 600 °C at a constant rate of 10 °C/min under nitrogen. wt % remaining = 0.481%
Figure D.3. TGA of CdSe (OA & TOA) QDs heated from 30 °C to 600 °C at a constant rate of 10 °C/min under nitrogen.

wt % remaining = 10.7%

Figure D.4. TGA of CdS (oleylamine) QDs heated from 30 °C to 600 °C at a constant rate of 10 °C/min under nitrogen.

wt % remaining = -0.057 5
Figure D.5. TGA of CdS (OA & ODE) QDs heated from 30 °C to 600 °C at a constant rate of 10 °C/min under nitrogen.

Figure D.6. TGA of CdS (OA & TOA) QDs heated from 30 °C to 600 °C at a constant rate of 10 °C/min under nitrogen.