

FLUORESCENCE ENHANCEMENT OF WHITE-LIGHT
CADMIUM SELENIDE NANOCRYSTALS

By

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CHAPTER I

INTRODUCTION

1.1 The Solid-State Lighting Problem

The study of semiconductor nanocrystals is important in the research of future efficient solid-state lighting technologies that could replace incandescent and fluorescent lights.^{2,3} Incandescent light bulbs, which utilize a tungsten filament heated by an electric current, have been the most common light source until recently. They give off a natural-looking, warm white light with a lifetime of 750-2000 hours.⁴ The major drawback to this type of light is that it emits infrared (IR) radiation along with the emission of visible light.⁴ IR radiation produces a great deal of heat, causing a loss of energy that could have been used instead to give off light. The efficacy of an incandescent light—how much light is produced per unit power—is about 10-18 lumens per Watt.⁴ These bulbs are only about 5% energy efficient.⁵

Fluorescent lights, in comparison, produce 35-60 lumens/Watt (compact lamp) or 50-100 lumens/Watt (linear tube).⁴ Inside fluorescent bulbs, electricity excites mercury atoms to emit ultraviolet radiation, which strikes the phosphor coating on the interior of the glass tube, resulting in the emission of visible light.⁴ Along with being more efficient than incandescent lights, fluorescent bulbs have a longer lifetime: 8000-10,000 hours (compact) or 20,000-30,000 hours (linear).⁴ However, they are still only about 20% energy efficient.⁵ One disadvantage of both fluorescent and incandescent lights is that the bulbs emit light in every direction. This can be beneficial when lighting a very large

area, but about 40-50% of the light is lost to the interior of the light fixture before reaching the area that was intended to be lit.⁴ Energy is therefore wasted on the light that is not being used, especially for intended directional lighting.

It has been estimated that, because of the energy that is spent on inefficient lighting, the United States is wasting nearly \$50 billion per year on energy consumption.⁵ The US Department of Energy is concerned with this issue and has proposed a plan to replace current lighting technology with solid-state lighting (SSL), mostly in the form of light-emitting diodes (LEDs).⁵ LEDs are quickly rising in popularity as the newest light source because they outlast the lifetime of both incandescent and fluorescent lights, with estimated useful lifetimes of 35,000-50,000 hours.⁴ They have comparable efficiency to compact fluorescent lights at 25-64 lumens/Watt, which is higher than that of incandescent bulbs.⁴ LEDs do not emit IR radiation, so no energy is lost directly from the LED itself through heat as it is in incandescent lights.⁶ The bulbs also have directional lighting, and this solves the problem of wasting light that shines back into the fixture, even without the use of reflectors or diffusers.⁴ Although they have high efficiency and a long lifetime, it is difficult to get pure white light from an LED, which is desirable for imitating natural light. An LED is constructed around a semiconductor, the band gap of which dictates one color from a single energy transition, so individual LEDs must be mixed to get white light. The common methods for making LEDs that appear white to the eye are a) an RGB system, in which red, green, and blue monochromatic LEDs are combined in different ratios, positions, and relative intensities, and b) phosphor conversion, which coats a blue LED with a yellow phosphor.^{4,7} The drawbacks to these methods are cost and complications in controlling more than one LED at a time in a

single device, a cool blue appearance of the white light, color variability and a “halo” effect, and absorption from adjacent LEDs, leading to reduced efficiency.^{4, 7, 8} If a single, unaltered semiconductor material that efficiently emits pure white light could be used in a solid-state lighting device, it would eliminate the color variability and complications of the current commercial LEDs.^{7, 8}

1.2 Semiconductor Nanocrystals

Quantum dots are semiconductor nanocrystals that obey the principle of quantum confinement.^{1, 9} There is strong quantum confinement in the nanocrystal if the diameter is shorter than the Bohr exciton diameter, and weak confinement is exhibited if the diameter of the nanocrystal is longer than the Bohr exciton diameter.¹⁰ The emission of light by these quantum dots can be explained using Figure 1.1. The electrons on the surface atoms of each nanocrystal exist primarily in the valence band, where they are in their ground energy state. Each electron is accompanied by a “hole,” or the absence of an electron with a positive charge to balance the negatively charged electron.⁹ The pair may be denoted by e^- and h^+ , and the ground state of the hole is in the conduction band. When a photon with energy equal to or greater than the energy of the nanocrystal band gap is absorbed by the nanocrystal, an electron is excited from the valence band (ground state) to the conduction band (excited state), while the hole is oppositely excited from the conduction band to the valence band. The exciton then has energy equal to that of the band gap. As the electron relaxes back down toward the valence band, the electron and hole recombine to emit a photon with energy approximately equal to the band gap energy

of the nanocrystal, taking into account a Stokes shift from the nanocrystal band edge to the emitted photon.⁴

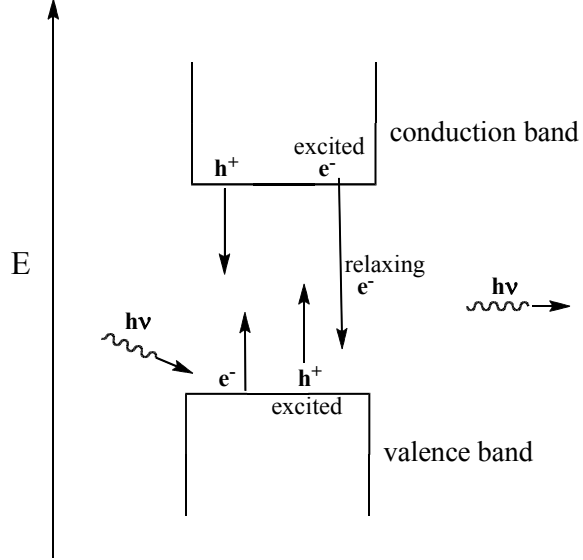


Figure 1.1: Excitation and relaxation of an electron-hole pair, resulting in emission of a photon. Excitation of electrons in the nanocrystal occurs in the presence of ultraviolet light, and the release of a photon upon recombination of the electron-hole pair produces the characteristic glow of quantum dots.

The electron-hole pair in a nanocrystal behaves approximately according to the quantum mechanical particle-in-a-box model, and it has an energy that is related to the size of the nanocrystal, according to Equation 1.1.^{1, 9, 11} Because energy is inversely proportional to wavelength, an electron-hole pair that recombines over a smaller band gap will emit a photon of a longer wavelength.

$$E = \frac{\hbar^2 \pi^2}{2R^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8e^2}{\epsilon_2 R} + \frac{e^2}{R} \sum_{n=1}^{\infty} \alpha_n \left(\frac{S}{R} \right)^{2n} \quad (1.1)$$

$$\alpha_n = \frac{(\epsilon - 1)(n + 1)}{[\epsilon_2(\epsilon n + n + 1)]} \quad \text{where } \epsilon = \frac{\epsilon_2}{\epsilon_1} \quad (1.2)$$

In Equation 1.1, R is the radius of the nanocrystal; m_e and m_h are the effective masses of the electron and hole, respectively; ϵ_1 and ϵ_2 are the dielectric constants of the solvent and semiconductor material, respectively; α_n is a constant for the material, calculated using ϵ_1 and ϵ_2 as shown in Equation 1.2; and S is the wavefunction of the electron.⁹ The first term in the equation accounts for the quantum energy of localization for both the electron and hole; it corresponds to the particle-in-a-box model.⁹ The second term represents the Coulomb attraction of the electron and hole, and the third term corresponds to the solvation energy loss.⁹

The wavelength of light that each nanocrystal emits depends on the size of the nanocrystal. The electron-hole pair of a relatively small nanocrystal takes more energy to excite, which then emits a photon of higher energy as it recombines because the band gap is larger. For example, a certain small nanocrystal with a large band gap emits blue light, and a larger nanocrystal with small band gap emits red. Cadmium selenide (CdSe) is a common material for quantum dots that absorbs and emits over the entire visible spectrum, thus making the changes in length of nanocrystal diameters easy to observe and tune.¹ Figure 1.2 shows nanocrystals that range from 1.7 to 5.2 nm in diameter under room light and under UV illumination. The size of the nanocrystals can be adjusted with the amount of time they are allowed to grow during synthesis. Figure 1.3 illustrates how nanocrystal size compared to the Bohr exciton diameter varies with band gap energy and wavelength of emitted photons. Spectroscopically, this means that as the nanocrystal diameter decreases, absorption and emission from the band edge shift to higher energies, or shorter wavelengths; this occurs because the nanocrystals follow the principle of quantum confinement.^{1, 9, 12, 13}



Figure 1.2: CdSe nanocrystals with diameters 1.7-5.2nm, arranged by size with the smallest on the left. The NCs above are under normal room light. The same NCs below are under UV light.¹¹

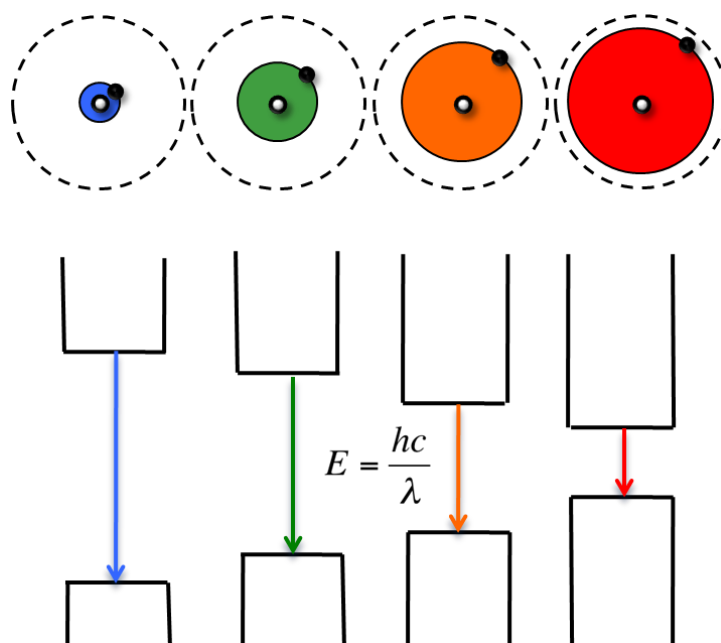


Figure 1.3: Relative nanocrystal sizes (top) compared to the Bohr exciton diameter (dotted line) vary with band gap energy and wavelength or color of emitted photons (bottom). The largest nanocrystals are closest to the Bohr exciton diameter, have the smallest energy band gap, and emit the longest wavelength of light.

1.3 Ultrasmall Nanocrystals

In recent years, nanocrystals have been synthesized to be extremely small. The term “ultrasmall” has been applied to nanocrystals that have a diameter shorter than 2 nm.^{1, 14, 15} At this tiny size, they can exhibit different physical and optical properties from the bulk materials of the same compositions and even just from larger nanocrystals.¹ Ultrasmall nanocrystals have very few total atoms, and most of the atoms are at the surface of the particle, giving them a higher surface-to-volume ratio compared to larger particles.^{1, 14} Certain nanoparticles have been studied in particular for their distinct properties on the ultrasmall scale, including gold and iron nanoparticles. As the size of nano-gold particles decreases from monolayer-protected gold clusters to ultrasmall, the bonding interactions in the clusters become dominant over electrostatic processes in the gold.¹⁶ When iron nanoparticles are synthesized to be ultrasmall, they have a significantly increased effective anisotropy constant compared to the bulk material.¹⁷ Since different materials of nanocrystals and nanoparticles have been found to behave differently on the ultrasmall scale, ultrasmall CdSe also must be tested for its unique optical properties.

1.4 White-Light CdSe Nanocrystals

It was discovered in 2005 by Bowers *et al.* that when CdSe quantum dots are synthesized to be especially small, about 1.5 nm in diameter or smaller, they emit broad-spectrum white light.² The white light-emitting ultrasmall nanocrystals display this optical property because of trap states or defects on the surface of the nanocrystal.^{1, 14} When synthesized, the fluorescence emission from these nanocrystals can be nearly pure

white with chromaticity coordinates of about 0.322, 0.365.⁶ The Commission Internationale de L'Eclairage (CIE) defines pure white with its 1931 coordinates of 0.333, 0.333.¹⁸ The coordinates of the emission of a light source can be plotted on a chart to see the color in the visible spectrum to which the numbers correspond (Figure 1.4). The area in the center is deemed "white to the eye," with the coordinates of pure white at the center. The discovery of white-light nanocrystals has given rise to the possibility that they may be used as an efficient white-light source.^{2, 19, 20} These nanocrystals offer a solution to the drawbacks of LEDs because they are synthesized of only one material and emit close to pure white light,^{1, 21} as opposed to a combination of monochromatic materials which together emit white light.²² These nanocrystals have been encapsulated in various polymers and incorporated into prototypical frequency down-converting devices (LEDs) and in electroluminescent devices.^{20, 23, 24} In the work of Schreuder *et al.*, when biphenylperfluorocyclobutyl (BP-PFCB) polymer was used as an encapsulant for the nanocrystals, the resulting device had potential to be a practical white light-emitting device.²⁴ However, this application is currently limited by the nanocrystal efficiency of just 8-9%, which is too low for commercial use.^{1, 24, 25} The efficiency must be greatly improved if these nanocrystals are to be used widely as a commercially viable single-source, broad spectrum solid-state lighting device.²⁴

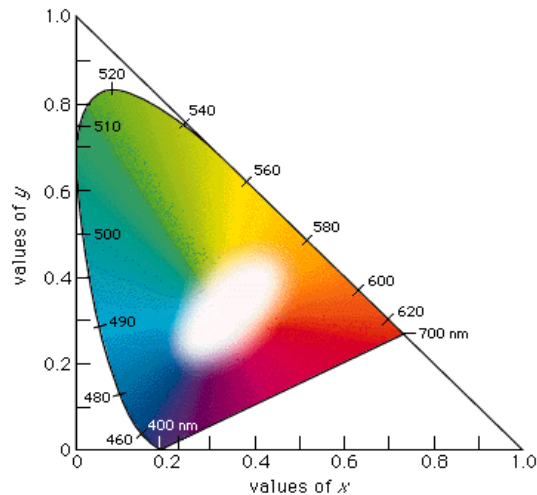


Figure 1.4: Chromaticity chart for visualization of CIE 1931 coordinates.

1.5 Fluorescence Enhancement

Various efforts have been made in the past to brighten CdSe quantum dots, which would aid in their use for solid-state lighting. The most common method currently of brightening nanocrystals is to synthesize core-shells, such as CdSe/ZnS.^{26, 27} Core-shells are made by synthesizing nanocrystals of one composition and then shelling or encasing them with a semiconductor of a wider band gap in order to keep the exciton confined to the nanocrystal core, thus making its emission brighter and long-lasting.²⁶ The problem with shelling white-light nanocrystals is that the shell passivates surface trap states on the nanocrystal, which in the case of these ultrasmall nanocrystals is the origin of their white-light emission.² As a result, the nanocrystals may be brightened if the trap states are covered, but it is at the expense of the broad emission spectrum in these small nanocrystals—it collapses to nearly monochromatic emission.³ In order to increase

emission in white-light nanocrystals, a different approach must be taken that involves altering the surface of the nanocrystal without eliminating the trap states.

Another effective way to enhance the emission of nanocrystals is to change the organic ligands surrounding the nanocrystals or to treat them with different chemical substances.^{12, 28} In particular, Kalyuzhny and Murray used monochromatic CdSe nanocrystals with diameters of 2-2.3 nm, which they treated with many ligands and other substances, including metal salts of acids.²⁸ Their experiments resulted in increased quantum yield, especially after treatment with metal acetates, but there was no theoretical conclusion to explain their findings. Ultrasmall white-light nanocrystals were tested with comparable treatments in the research presented here to determine if they react similarly to the nanocrystals in the previous study.

CHAPTER II

EXPERIMENTAL

2.1 White-Light CdSe Synthesis

Ultrasmall CdSe nanocrystals were synthesized and purified as previously reported by Bowers *et al.*³ with some modifications.

For the synthesis of ultrasmall white light-emitting CdSe nanocrystals, 4 g hexadecylamine (HDA), 6 g trioctylphosphine oxide (TOPO), 0.5 g dodecylphosphonic acid (DDPA), and 0.128 g (1 mmol) cadmium oxide (CdO) were combined in a 100 mL three-neck round-bottom flask on a stir-plate with a heating mantle. A temperature probe was inserted into one of the side necks, and the other side was closed with a rubber septum. The center of the flask was attached to a self-washing bump trap, with argon gas flowing through the flask to purge and maintain an inert atmosphere. The reaction was heated to 150 °C while purging, the purge needle was removed, and heating continued to 330 °C. When the solution changed from opaque brown to clear and colorless, 4.5 mL of 0.2 M selenium tributylphosphine solution (Se:TBP) was injected through a 12-gauge needle through the septum into the reaction. At the first sign of a yellow color in the solution, occurring about five to eight seconds after adding the Se:TBP, 20 mL butanol was injected through an 18-gauge needle to cool the solution. The flask was then immediately cooled to below 90 °C with compressed air to prevent further nanocrystal growth.

The nanocrystals were precipitated with methanol in four 50 mL centrifuge tubes and collected by centrifugation at 6000 rpm for three minutes. The nanocrystal pellets were dried in the centrifuge tubes and then redispersed in 6 mL hexanol per tube and centrifuged at 6000 rpm for 20-60 min. The supernatant containing the nanocrystals was decanted into clean tubes, precipitated with methanol, and collected by centrifugation at 6000 rpm for 20 min. The final solid nanocrystals were dried, dissolved in toluene, and stored in the dark.

Absorption and emission spectra for white-light CdSe nanocrystals are shown in Figure 2.1. The size of nanocrystals from a single batch can be calculated from the band edge absorption wavelength using calculations from Yu, *et al* (Appendix A).²⁹ The white-light emission spectrum exhibits three peaks in the spectrum at approximately 440, 488, and 550 nm, extending over the visible spectrum. The first peak in the spectrum has been shown to be related to the surface-passivating phosphonic acid ligand.^{12, 14} This peak is pinned at 440nm in CdSe nanocrystals with diameters of 1.7 nm or smaller, instead of blue-shifting with decreasing diameter.¹⁴ This blue peak is a direct result of the phosphonic acid ligands on the nanocrystal, and it is absent when a different ligand is used in place of the phosphonic acid or is shifted depending on the alkyl chain length of the phosphonic acid.^{12, 14} The origin of the second peak at 488 nm is unknown, though it is thought to be related to the surface state at the Se atoms on the nanocrystal.¹⁴ The third broad peak at about 550 nm is a result of conventional deep trap emission, confirmed with ultrafast fluorescence upconversion spectroscopy.^{2, 3, 14} The peak close to 750 nm is the second order diffraction peak, which is an effect of the diffraction grating in the fluorometer.

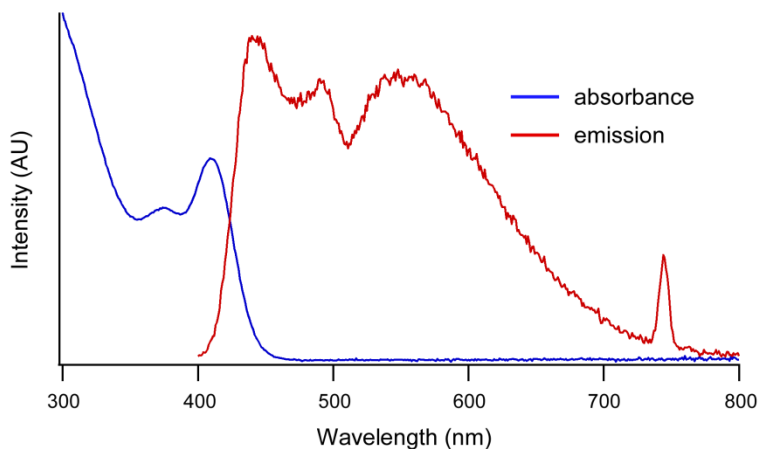


Figure 2.1. Absorbance spectrum (blue line) of white-light nanocrystals with band edge absorption at 409 nm. Emission spectrum (red line) of white-light nanocrystals with quantum yield of 8.2% and CIE coordinates of 0.302, 0.337.

2.2 Carboxylic Acid Treatment

The white-light nanocrystals were treated with various carboxylic acids in the following manner. A 0.3-1 mM solution of nanocrystals in toluene (usually about 3-8 mL) was added to a 50 mL three-neck round-bottom flask. The flask was fitted with a heating mantle and temperature probe and placed onto a stir-plate, while leaving two necks of the flask open to air. This reaction was set up in a hood without any direct light on the flask (room lights on, hood light off). The acid was added to the nanocrystals in a 30,000 molar excess via syringe injection to the flask at the same time that the heating was started. The solution was heated from 24 °C to 60 °C in five to six minutes. Upon reaching 60 °C, the flask was immediately removed from heat and cooled with compressed air to 28 °C while stirring. If the yellow nanocrystal solution was cloudy, as in the case of formic acid treatment, it was transferred to a glass vial and centrifuged at

2500 rpm for 15 min to separate the excess formic acid from the treated nanocrystals in toluene. The top nanocrystal layer was then transferred to 2-mL microtubes and centrifuged at 15,500 rpm for 15 min (or until layers are completely separated) to further remove any excess acid. This transfer had to be done extremely gently, with as little disturbance to the sample as possible, or the cloudiness would return to the sample, increasing the turbidity to interfere with emission testing, and possibly knocking nanocrystals or ligands out of solution. The quantum yield of both the original nanocrystals and the acid-treated nanocrystals were taken within a few hours of the treatment in reference to either Coumarin 152A or Coumarin 153 as the standard (Appendix C). The spectra of nanocrystals after treatment are in the results.

This method was used to successfully treat nanocrystals with the following carboxylic acids: formic, acetic, hexanoic, octanoic, and oleic. Other acids were attempted at random simply to test if they had an effect on brightness; no quantitative conclusion or trend has been made, as some acids brightened the nanocrystals and some quenched the emission (reported later in Table 3.3). Both liquid and solid acids can be used, and the solid additives were simply added through the top of the flask.

2.3 Thiol Treatment

As later discussed, the aforementioned formic acid treatment shifts the balanced white emission of the nanocrystals to a bluer white light. Thus, while formic acid is successful in brightening the nanocrystals, the CIE coordinates are shifted toward blue, which is not optimal for a pure white lighting device. To correct for this shift, a warmer white-light nanocrystal synthesis was attempted, which involved changing the

TOPO:HDA ratio to lessen the intensity of the first blue peak in the emission spectrum. This technique resulted in warmer white-light nanocrystals but while the different synthesis adjusted the original nanocrystal emission, it had no consistent effect on the formic acid problem. It was determined that something needed to change the surface of the nanocrystals after synthesis that would interfere with how the formic acid was interacting with the final product. A thiol molecule was chosen for this treatment because thiol ligands are known to bind to nanocrystals favourably and more strongly than even the synthesis ligands, and they can also quench part or all of the nanocrystal emission.³⁰ Dodecanethiol was used because of its similar length to the existing phosphonic acid ligand. The concentration of the thiol used for treatment was determined by preliminary studies of different concentrations added to aliquots of one batch of nanocrystals. Several of these trials are shown in Figure 2.2.

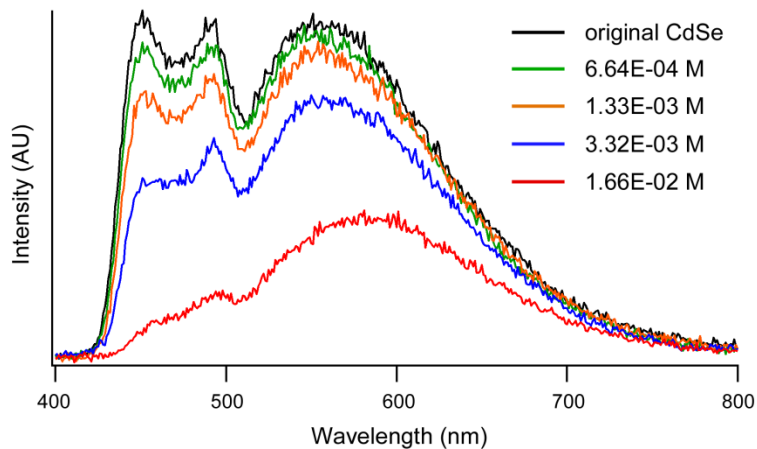


Figure 2.2. Emission spectra of original nanocrystals treated with differing concentrations of DDT. Each treatment consisted of 0.5 mL 5.4E-04 M nanocrystals with 0.5 mL of the particular noted concentrations of DDT.

The dodecanethiol (DDT) treatment to make nanocrystals warmer is currently simple and unrefined. The CdSe nanocrystals were prepared as though ready for a formic acid treatment: diluted in toluene, in a 50mL three-neck round-bottom flask with a stirbar. A solution of DDT in toluene was first prepared in a 1.66×10^{-2} M concentration. This DDT worked best when prepared the same day so as to have the full effect on the nanocrystals, possibly due to the chemical's instability and degradation in under prolonged light exposure. The DDT solution was added via syringe in a 100-300 molar excess to the nanocrystals. The solution was stirred at room temperature for 1-5 min, while the emission was monitored with a UV lamp set close to the flask. The emission color visibly changed from pale yellow-white (nanocrystal solution) to a warmer yellow-orange after the addition of DDT. The UV lamp was removed, and a small aliquot of the solution was taken for analysis before a formic acid treatment was performed. The effect of the combination of DDT and formic acid treatments is shown in the results and discussion.

2.4 Characterization Techniques

The original and treated CdSe nanocrystals are monitored by photoluminescence to determine nanocrystal size, absorption, color and quality of emission, and quantum yield. Absorption measurements were performed on a Varian Cary 50 Bio ultraviolet-visible (UV-Vis) spectrophotometer. The size of nanocrystals was calculated from the band edge absorption wavelength and equations found in Appendix A. Emission spectra were obtained with an ISS PC1 Photon Counting Spectrofluorimeter, with Vinci version 1.6.SP5 software. Intensities of the white-light emission peaks were analyzed with Excel,

and quantum yield measurements were made with these intensities and the equation in Appendix C. The CIE coordinates were calculated from emission intensities via the process in Appendix B.

CHAPTER III

RESULTS AND DISCUSSIONS

3.1 Brightening with Carboxylic Acids

The first tests done in this study to improve the quantum yield of white-light nanocrystals were with zinc acetate (ZnAc_2). This was first attempted by undergraduate Ben Stratton in the Rosenthal group in 2007 to test select metal acetates on white-light nanocrystals, following the treatments done by Kalyuzhny and Murray on larger nanocrystals.²⁸ The current project with the previously described treatment technique reproduced an increase in quantum yield with ZnAc_2 . This trial resulted in an average quantum yield to $13.6 \pm 1.3\%$. The reason for the brightening was possibly a result of trace acetic acid in the ZnAc_2 reagent, considering the metal acetate is synthesized using its precursor acid. For this reason, acetic acid was used as the next treatment, and it resulted in an average quantum yield of $19.3 \pm 2.5\%$. The comparison between ZnAc_2 and acetic acid treatments on a single batch of nanocrystals is shown in Figure 3.1. The quantum yield and CIE coordinates are compared for these reactions in Table 3.1. Following immediate testing after treatment, the nanocrystals were stored for 18 hours, and their quantum yield was measured again to find how much the emission intensity changed over time. The emission of both samples decreased in intensity; however, both of them remained brighter than the original white-light nanocrystals (Table 3.1), supporting the potential of these treatments to be used for the long-term brightening. Kalyuzhny and Murray argued that the increase in emission was not a result of ligand

exchange or the filling of empty sites on the nanocrystal surface with extra ligands because the acetic acid did not have as great of an effect as the metal acetates did on the larger nanocrystals.²⁸ It is apparent from these results, however, that ultrasmall white light-emitting nanocrystals behave differently, since the acid had a greater effect on the quantum yield.

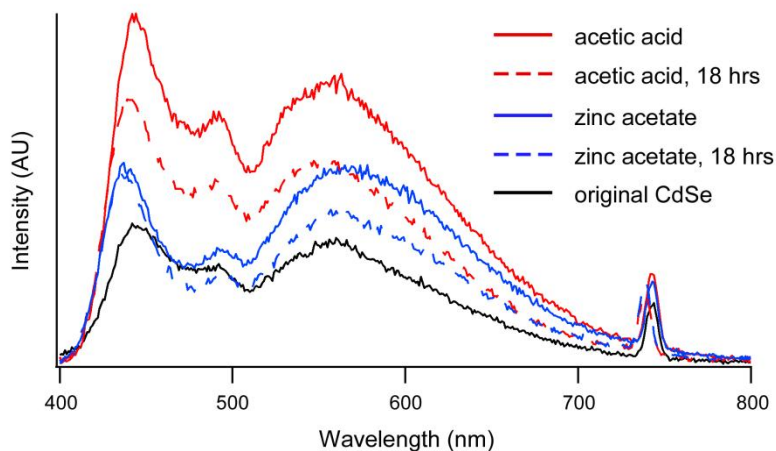


Figure 3.1. Emission spectra and quantum yields of CdSe nanocrystals treated with ZnAc₂ and acetic acid. The acid treatment resulted in significantly brighter nanocrystals.

Table 3.1. Quantum yield and CIE coordinates of the specific ZnAc₂ and acetic acid treatments shown in Figure 3.1.

Sample	Quantum Yield	CIE coordinates
Original CdSe	7.8%	0.311, 0.334
Acetic acid	18.7%	0.309, 0.334
Zinc acetate	12.4%	0.348, 0.335
Acetic acid, 18 hrs later	13.5%	0.299, 0.326
Zinc acetate, 18 hrs later	9.7%	0.330, 0.335

Treatments with formic, hexanoic, octanoic, and oleic acids were then carried out because acetic acid was successful as a straight-chain carboxylic acid. The average post-treatment quantum yields from original nanocrystals (~8%) were as follows: formic $31\pm 6.4\%$ (n=31), acetic $19\pm 2.5\%$ (n=19), hexanoic $15\pm 1.4\%$ (n=2), octanoic $18\pm 1.3\%$ (n=2), and oleic 10% (n=1). Formic acid demonstrated the greatest quantum yield increase compared to the other alkylcarboxylic acids (Figure 3.2, Table 3.2). This may be due to the shorter carbon chain length. A longer chain length may hinder the ability of the acid to reach the nanocrystal surface, past the bulky TOPO and the long-chain phosphonic acid and HDA ligands on the nanocrystal. The acid chain length also affects the pKa of the acid, increasing in acidity and electronegativity with shorter alkyl chain lengths. Consequently, formic acid is the most acidic and electronegative of these acids. This implies a possible correlation between a more acidic ligand and a higher increase in quantum yield.

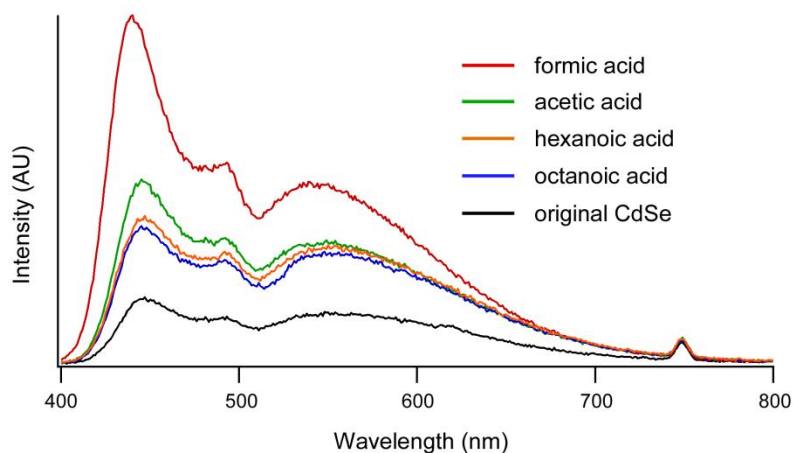


Figure 3.2. Emission spectra and quantum yields of one batch of CdSe nanocrystals, treated with carboxylic acids of varying chain lengths: formic, acetic, hexanoic, and octanoic. A shorter carbon chain of the alkylcarboxylic acid results in a greater increase in quantum yield.

Table 3.2. Quantum yield and CIE coordinates of the specific alkylcarboxylic acid treatments shown in Figure 3.2.

Sample	Quantum Yield	CIE coordinates
Original CdSe	7.3%	0.313, 0.332
Formic acid	28.4%	0.267, 0.282
Acetic acid	18.2%	0.291, 0.314
Hexanoic acid	15.8%	0.309, 0.333
Octanoic acid	16.8%	0.307, 0.333

Additional carboxylic acids were tested briefly and qualitatively to roughly determine their effects on white-light nanocrystals. The results are summarized in Table 3.3. For the most part, dicarboxylic acids (with the exception of citric acid) and very long chain acids did not brighten the nanocrystals. The results of more acid treatments will have to be examined, including the successful ones here.

Table 3.3. Quantum yields of nanocrystal emission after treatment with various other acids (mostly carboxylic).

Acid	Quantum Yield	Problem
Benzoic	18%	--
Citric	26%	--
Chloroacetic	28%	--
Dichloroacetic	15%	--
Lauric	16%	No increase from originals
Oxalic	2%	Dimmer
Maleic	--	Quenched emission
Stearic	--	Solid
Phosphoric	--	Quenched emission

3.2 The Formic Acid Effect

Since this research focused on significantly increasing the quantum yield of white-light nanocrystals, formic acid was chosen as the treatment to perfect and to study in depth. The formic acid treatment demonstrated the highest reported quantum yield increase, with an example emission spectrum shown in Figure 3.3 and a photo in Figure 3.4. The average quantum yield was $31 \pm 6.4\%$ with a maximum recorded yield of 45%. Comparing the absorption spectra before and after formic acid treatment, it is clear that the size and monodisperse characteristic of the nanocrystals have not significantly changed (Figure 3.5). The band edge absorption consistently tends to shift to a lower wavelength by one or two nanometers, but the features in the spectrum remain the same.

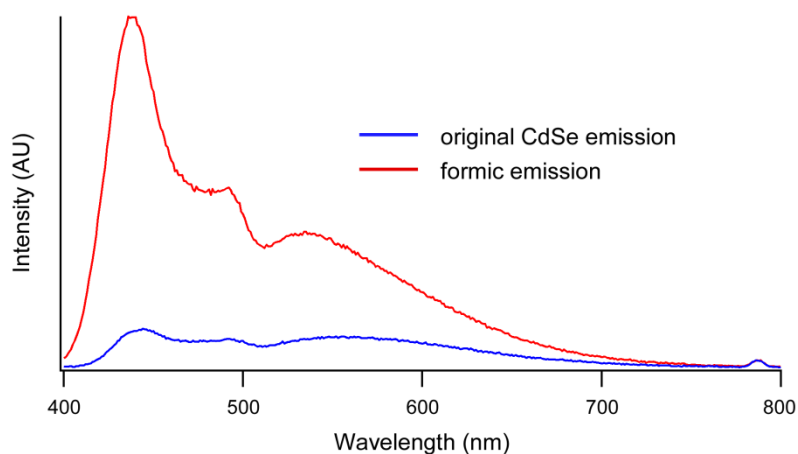


Figure 3.3. The comparison of the emission spectra of original and formic acid-treated CdSe nanocrystals show a significant increase in the quantum yield from 9% to 43%, while the CIE coordinates changed to a bluer emission (0.311, 0.333 to 0.238, 0.243).

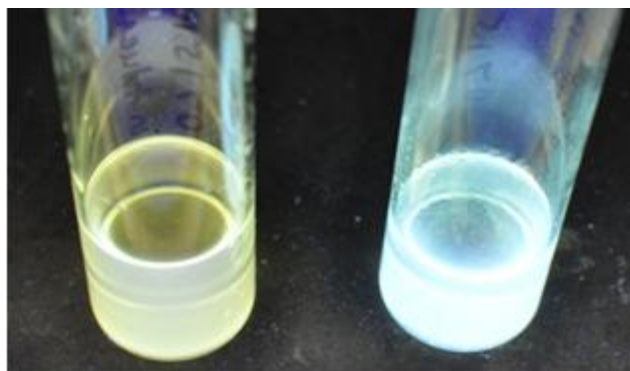


Figure 3.4. Vials containing concentrated white-light CdSe nanocrystal solutions before (left) and after (right) formic acid treatment.

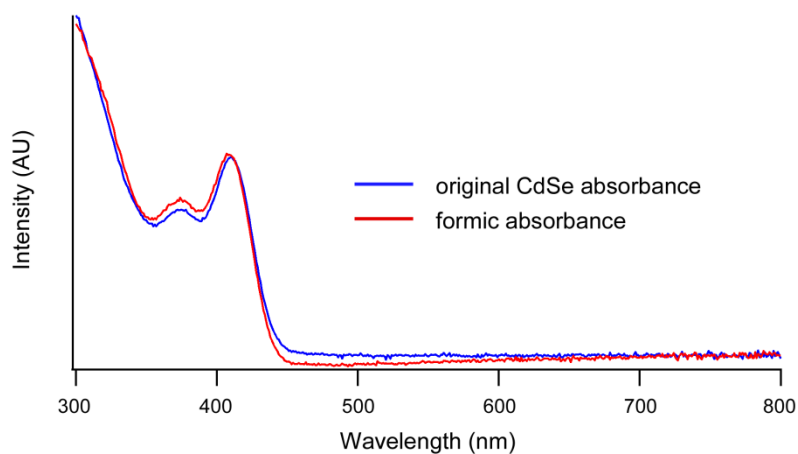


Figure 3.5. The absorption spectra of the nanocrystals before and after formic acid treatment show that the nanocrystals stay monodisperse with an almost identical size, shifting from 410 nm to 407 nm band edge absorption.

As with the acetic acid and ZnAc_2 treatments, a single formic acid treatment sample was tested over time (Figure 3.6). Immediately after treatment, without centrifuging the sample, the quantum yield increased from 7% to 30%. Over the course of 41 hours, it only degraded to 23%, keeping the same emission features. This result is promising because it demonstrates that the increase in the quantum yield is not an

extremely temporary effect and that the nanocrystals do not decrease to their original brightness over at least a two-day period. This increases the chance to stabilize the higher quantum yields for lighting applications by encapsulation.²⁴ However, after centrifugation of a different batch of treated nanocrystals, there was not as much of a drop in emission, but a greater shift towards a bluer emission (Figure 3.7). This suggests that too much excess formic acid in the nanocrystal solution causes more degradation in emission and thus a decrease in quantum yield. On the other hand, an increase in the blue peak seems to suggest that there is excess formic acid interacting with the surface compared to the first spectrum directly after treatment. More tests remain to be done on the decrease in quantum yield over time after treatment. The reasons for the degradation and bluing of these samples need to be further examined in future experiments that concentrate on emission changes over time.

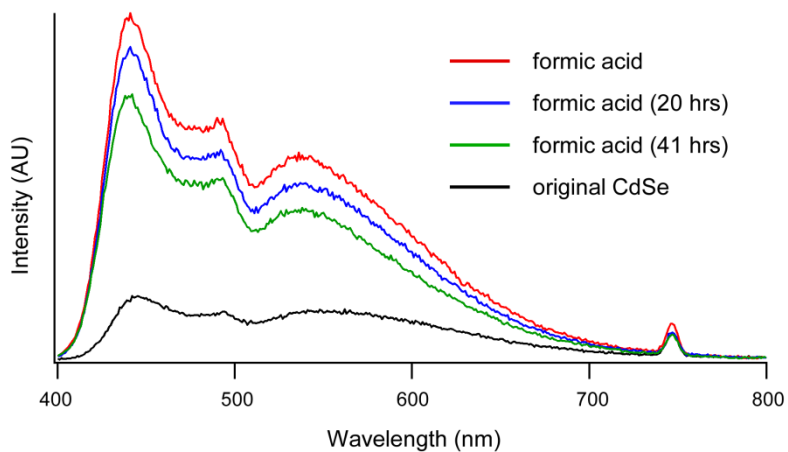


Figure 3.6. Emission spectra of formic acid-treated nanocrystals, showing the decrease in emission over time.

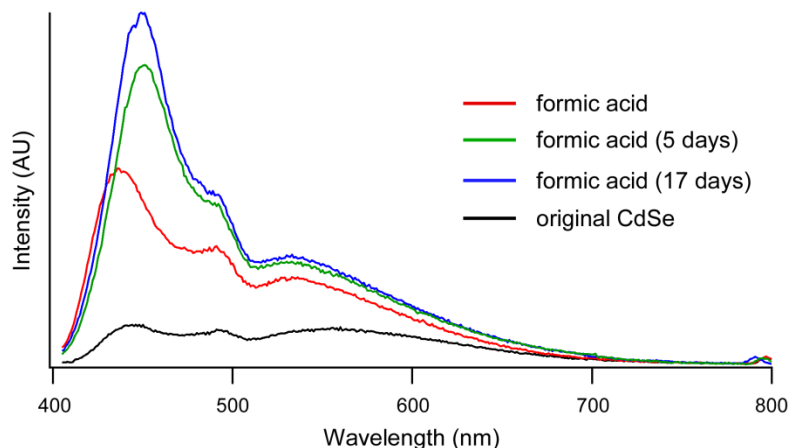


Figure 3.7. Emission spectra of formic acid-treated nanocrystals, showing an increase in quantum yield and bluer CIE coordinates over time.

Table 3.4. Band edge absorption, quantum yield, and CIE coordinates of the formic acid treatment over time shown in Figure 3.7.

	Absorption	Quantum Yield	CIE coordinates
Original CdSe	409 nm	8%	0.311, 0.340
Formic acid	407 nm	25%	0.237, 0.250
Formic, after 5 days	415 nm	36%	0.221, 0.215
Formic, after 17 days	418 nm	38%	0.222, 0.218

As for the initial increase in quantum yield, several explanations are possible. One explanation is a ligand exchange process. In this study, after synthesis and cleaning, the nanocrystal surface is mostly covered with phosphonic acid ligands,^{14, 31} with trioctylphosphine oxide (TOPO) and hexadecylamine (HDA) likely present to a lesser degree. Upon treatment with formic acid, a ligand exchange model would dictate that the acid molecules replace most or all of the original ligands, changing the ligand coverage of the nanocrystal. Ligand exchanges are commonly used to change the solubility or functionality of nanoparticles.³² The process relies on adding either a more strongly

binding molecule or a large molar excess of a weakly binding molecule to displace some or all of the native surface ligands. In the case of replacing a phosphonic acid, TOPO, or HDA ligand with a carboxylic acid, the carboxylic acid interaction is actually less favorable.³³ Thus, an exchange would have to occur solely as a result of the large molar excess of the added acid.³⁴ Also, during the cleaning process after synthesis, some ligands from the nanocrystal will also be lost, creating vacant surface sites for the formic acid to easily attach. An entire ligand exchange would then not be necessary for the formic acid to have an effect on the surface chemistry. A complete ligand exchange is doubtful because exchanges on nanocrystal surfaces have been shown to be partial process.³⁵ In addition, phosphonic acid and formic acid are different in their solubility, which would suggest that nanocrystals with only formic acid ligands would likely precipitate out of the original toluene solution. The formic acid-treated nanocrystals do not seem to precipitate any faster than the untreated nanocrystals.

A more plausible explanation for the increased quantum yield could be that there are non-radiative surface trap sites that already exist on the surface of the nanocrystal, which can be passivated with the carboxylic acid ligands (Figure 3.8). A pure exchange with the original ligands would not have to occur if the smaller formic acid molecules simply passivated some of the existing trap states in between the phosphonic acid ligands. In the work of Schreuder *et al.* concerning the effect of phosphonic acid surface ligands on ultrasmall CdSe nanocrystals, changing the ligand affected the wavelength and intensity of the first blue emission peak, as well as the overall quantum yield of the nanocrystals, which ranged from 0.2% to 9% depending on the phosphonic acid variant.¹² Tuning the wavelength of that first emission feature was concluded to be

caused by the electronegativity (inversely proportional to chain length) of the surface ligand, while the quantum yield increase was probably a result of the sterics and physical structure of the ligand.¹² (As chain length increased, quantum yield increased, suggesting that a long chain might guard the surface of the nanocrystal against quenching agents by bending around, covering surface traps.) In this study with formic acid, the first emission peak blue-shifts an average of 7 nm from the original nanocrystals. This result corresponds with the finding of Schreuder *et al.* because a ligand of a shorter chain length (higher electronegativity) blue-shifted the emission peak, ranging up to 20 nm difference between varying chain lengths.¹² Thus an explanation involving partial ligand exchange or the addition of formic acid ligands to the surface is supported.

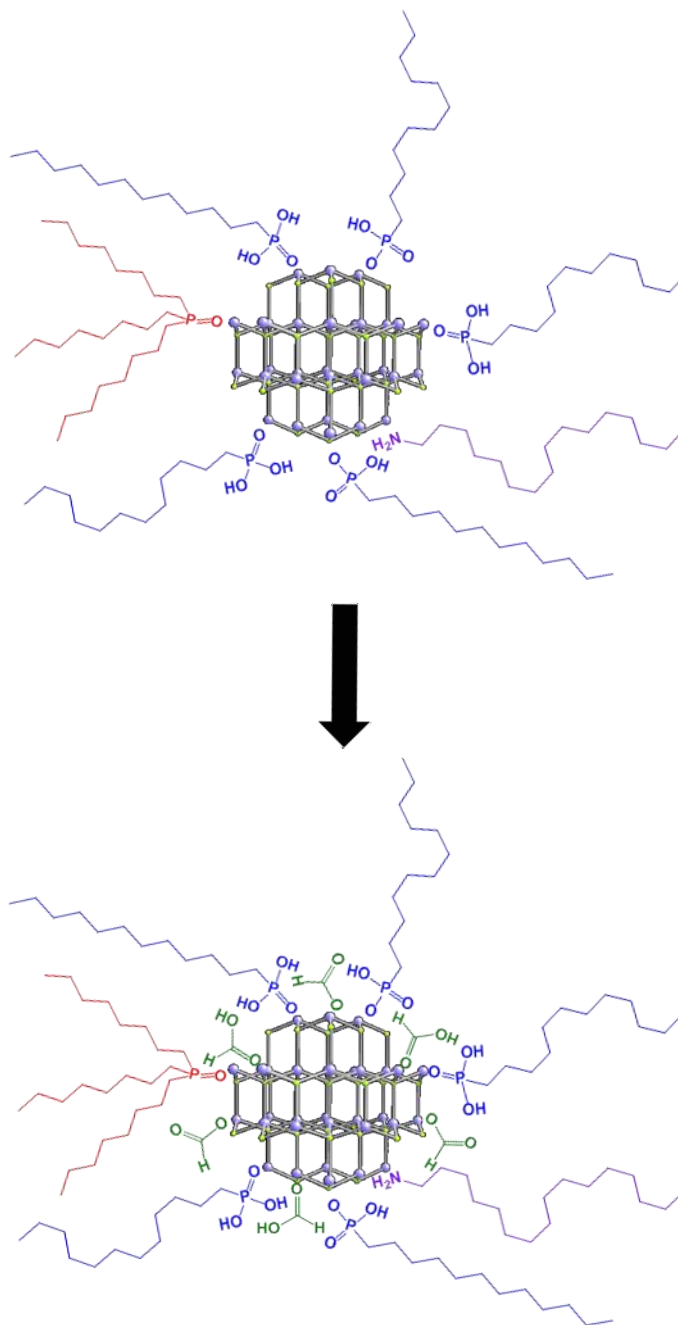


Figure 3.8. Addition of formic acid ligands to existing surface trap states, in between the original ligands on the nanocrystal. This is one plausible explanation of the formic acid effect.

There are two ways that formic acid molecules could bind or coordinate with the nanocrystal surface. After losing a proton to form the formate ion, the molecule could associate with the surface Cd atoms, as the original ligands on the nanocrystal do. The formic acid molecules could also remain complete and form hydrogen bonds between the acidic hydrogen and the dangling bonds on the Se surface atoms. Both options are shown in Figure 3.8.

One effect of using formic acid is that after the nanocrystals are treated, their emission spectrum deviates from pure white, compared to the emission of the original nanocrystals. The CIE coordinates become more blue or “cool,” relative to the white 0.333, 0.333 center.¹⁸ This is an interesting consequence of the treatment with all the acids and is most pronounced with the formic acid (Figure 3.2). The mechanism for this result is not yet evident. Upon examination of a brightened spectrum, it is apparent that all three emission peaks are retained and enhanced, with the first blue peak simply brightened to a greater degree than the other two. The disproportionate increase thus cannot be explained by merely differentiating the reasons for the existence of each peak (See Section 2.1). During the treatment, the middle emission peak may be enhanced due to the overlapping spectral features of the first and last peak. The blue and deep trap peaks, however, are clearly brightened on their own. Because of the different origins of emission, it would seem that formic acid would only affect one mechanism, especially the one influenced by the surface ligand, which would explain the disproportionate increase of the blue peak. Nonetheless, the data suggests that more than one mechanism is affected.

In order to compare the shades of the white-light emission graphically, the CIE coordinates were calculated (Appendix B) and plotted. Figure 3.9 shows the change in color between the original and formic acid-treated nanocrystals.

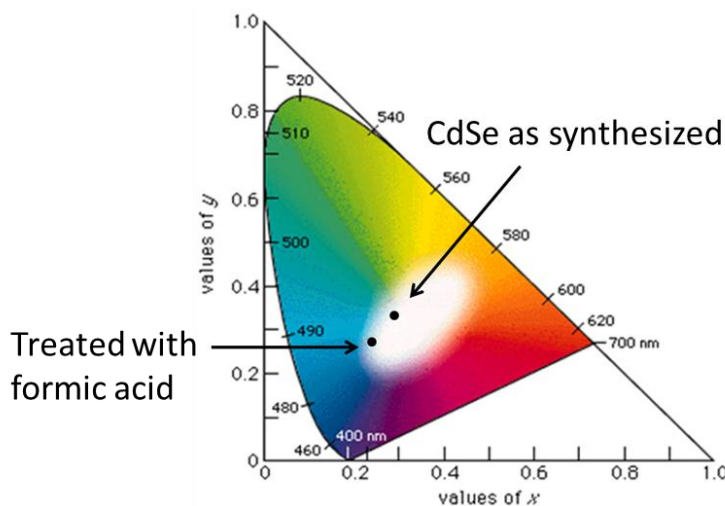


Figure 3.9. Visual comparison of color coordinates of original nanocrystals with formic acid-treated nanocrystals. The CIE coordinates changed from (0.311, 0.333) to (0.238, 0.243). (Data from Figure 3.3 spectra.)

In several batches of nanocrystals that were synthesized and then treated, the emission of the originals was unintentionally a warmer white than usual (Figure 3.10). This shift from cool to warm suggests that if the original emission was adjusted first, the “bluing” effect of the formic treatment might bring the enhanced emission back to a more balanced white near 0.33, 0.33. The CIE plot for this comparison is shown in Figure 3.11. The result here, while it looks promising for changing CIE coordinates, is currently uncontrollable and unplanned: while the original emission spectrum can be changed with a different ratio of HDA and TOPO ligands during synthesis, the emission of formic acid-

treated samples does not always follow the warmer trend. Thus there needs to be a method for warming the nanocrystal emission that is not accidental or unexpected.

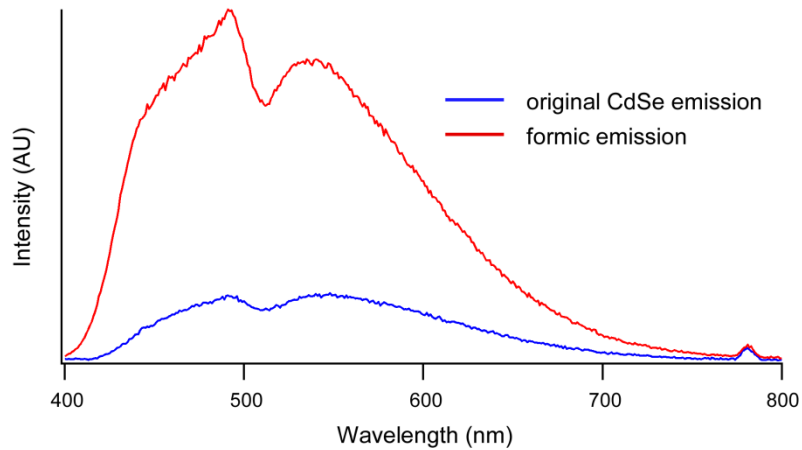


Figure 3.10. Unintentional synthesis of warmer original nanocrystals (10%) leads to warmer emission than usual after formic acid treatment (44%).

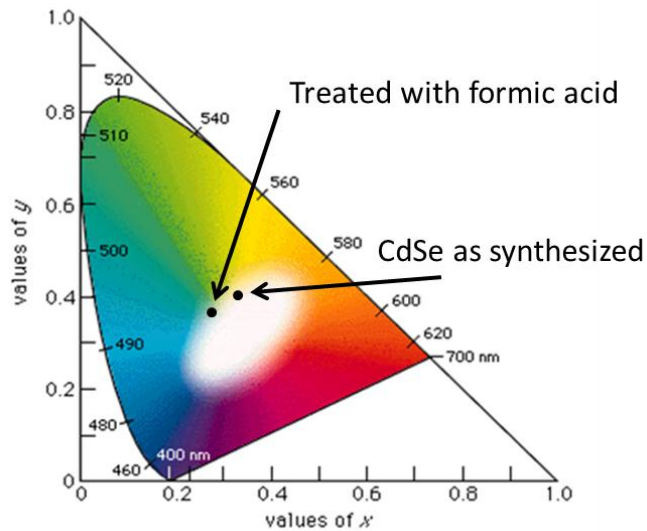


Figure 3.11. CIE coordinates of warmer nanocrystals: (0.328, 0.404) original to (0.285, 0.358) treated.

3.3 Warming Treatment Before Brightening

While the “bluing” effect is currently unexplained, it can be compensated for by modulating the color of the original nanocrystals after synthesis to exhibit a warmer white emission prior to the addition of formic acid. After the acid treatment to enhance the blue peak, the resultant nanocrystals should then ideally achieve a more balanced white emission. To this end, dodecanethiol (DDT) was added to the nanocrystals, significantly decreasing the first two emission peaks down to negligible emission, which changed the CIE coordinates from 0.30, 0.32 to 0.47, 0.44. A normal formic acid treatment was then able to restore those peaks, resulting in a spectrum that is close to balanced white-light again at 0.34, 0.36 (Figures 3.12, 3.13 and Table 3.5). These twice-treated nanocrystals have a quantum yield between that of original nanocrystals and samples treated with only formic acid, since the DDT somewhat quenches CdSe emission.³⁰ Modulating the amount of excess dodecanethiol that is added to the nanocrystals should make it possible to tune the CIE coordinates for a desired white light.

Once again, the mechanism for this reaction or ligand association is not yet known. The addition of dodecanethiol will most likely cause a full ligand exchange, since a thiol bond to a nanocrystal is stronger and more favorable than the binding of a phosphonic acid. The ease of this ligand exchange is obvious because of the immediate color change that is observed when DDT is added to the nanocrystal solution at room temperature. This is also supported by the fact that the first blue peak is the most drastically affected by the DDT addition, and that feature is due to the surface ligands, namely phosphonic acid.¹² The thiol is known to quench the fluorescence of larger nanocrystals, so it is possible that it acts as another trap on the nanocrystal surface,

competing with the trap state emission that leads to the blue peak emission.³⁰ Upon treatment with formic acid, the short-chain acid must still go into open surface trap states, since the blue peak is restored while the carboxylic acid bonding is much weaker than that of thiols. The DDT treatment may have to be adjusted for each batch in order to result in the best balanced emission, depending on the starting CIE coordinates of the original nanocrystals. The absorption spectrum retains the same features throughout these two successive treatments, although the band edge absorption redshifts with the addition of DDT and then returns to the usual relative wavelength after the formic acid is added (Figure 3.14).

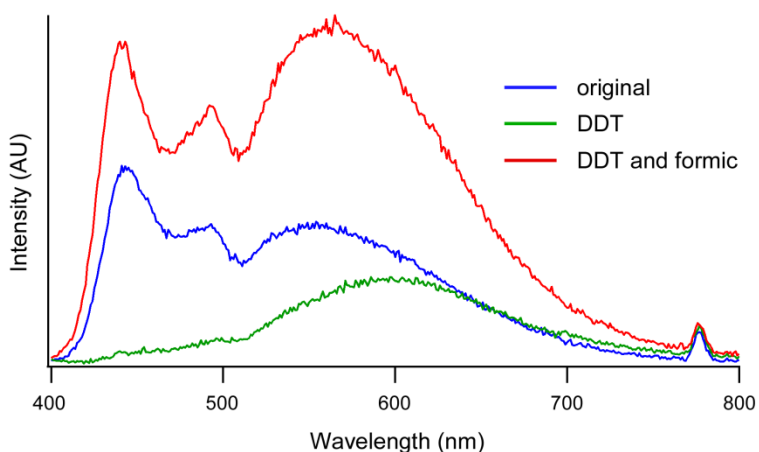


Figure 3.12. Emission spectra of nanocrystals after original synthesis (9%), DDT treatment (6%), and formic acid treatment (26%).

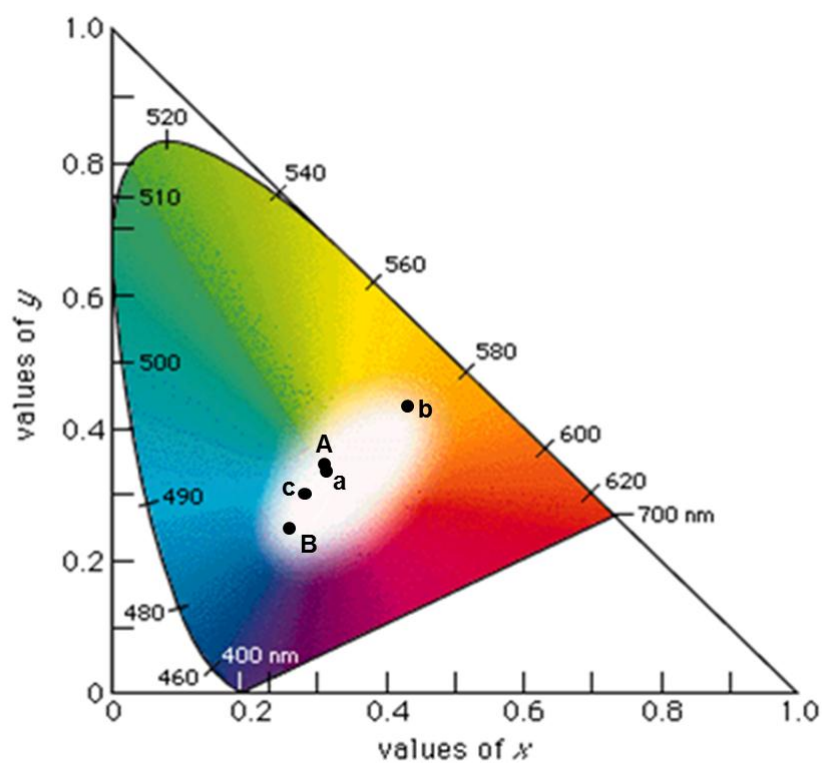


Figure 3.13. Visualization of CIE coordinates comparing a regular formic acid treatment (A, B) to a DDT and formic acid treatments (a, b, c).

Table 3.5. CIE coordinates corresponding to Figure 3.13.

	Sample	CIE coordinates
A	Original CdSe	0.311, 0.340
B	Formic acid	0.237, 0.250
a	Original CdSe	0.312, 0.336
b	Dodecanethiol	0.428, 0.433
c	Formic acid	0.278, 0.301

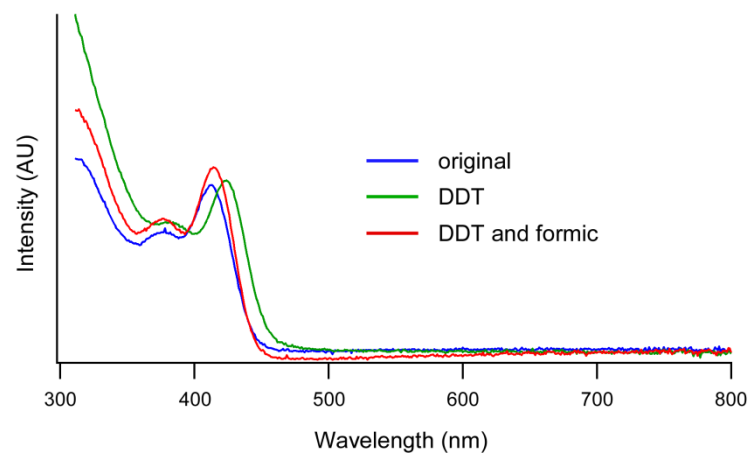


Figure 3.14. Absorption spectra of original nanocrystals (413 nm), after DDT treatment (424 nm), and after final formic acid treatment (414 nm).

CHAPTER IV

CONCLUSIONS AND FUTURE DIRECTIONS

4.1 Increased Quantum Yield

This work demonstrates that enhancement of the complex trap state emission exhibited by white light-emitting CdSe nanocrystals can be achieved. Post preparative treatments with formic acid improved the fluorescent quantum yield up to 45% as the maximum quantum yield, with an average of 31%. A likely explanation for the brightening is that of a greater passivation or filling in of some non-radiative surface traps, suggested by the bluer emission of the treated nanocrystals. This bluish emission may be compensated for by incorporating a preliminary treatment after synthesis that first warms the emission of the nanocrystals with a chemical such as dodecanethiol before cooling it with the acid. In testing various acids, it was apparent that acids with shorter alkyl chain lengths cause a greater increase in quantum yield, indicating a possible correlation with acidity and steric effects. Once the nanocrystals can be sufficiently brightened and their CIE coordinates can be controlled, the treated nanocrystals can be incorporated into a device, leading to their potential use in commercially viable solid-state lighting.

4.2 Future Analysis: Original vs. Formic

In order to continue this work to brighten white-light nanocrystals for possible commercial use, optimal conditions and the mechanism behind the acid effect need to be

studied in more detail. Changes in the procedure for acid treatment have the potential to greatly improve quantum yield and CIE coordinates of the brightened nanocrystals.

There are many variables that affect this nanocrystal brightening treatment. In the testing of formic acid alone, there are very inconsistent results that seem to shift quantum yield and CIE coordinates significantly for no apparent reason. Some small variation in experimental procedure (adjustment in temperature, time of reaction, molar ratio, etc.), water present in the air, exposure to oxygen, age of the original nanocrystals, or quality of the reagents could very well have an as yet unknown effect on the properties of treated nanocrystals. For example, upon initial testing of some variables, significant exposure to light during the treatment process has an effect on the quantum yield. Also, the ratio of 30,000 mol acid to 1 mol nanocrystals was settled on because lower ratios did not produce as high quantum yields, but using much higher ratios also sometimes had adverse effects. Finding the optimal balance of all experimental variables will require extensive, careful testing.

Few variables are absolutely known to positively or negatively affect the outcome of this treatment with formic acid without question. The following things were varied with inconclusive results as to their effect on quantum yield: concentration of nanocrystals in toluene to be treated, heating between room temperature and 60 °C, molar excess of acid, time after treatment before centrifugation. The only known constant in this experiment is that if formic acid is added in at least a 15,000 molar excess to the nanocrystals in toluene, the quantum yield is increased, with a slight bias to increasing the blue emission peak, while the absorption spectrum remains relatively constant (as discussed earlier). It has also been determined that the quantum yield is batch-

dependent—a certain batch of white-light nanocrystals can be tested repeatedly with similar results, but another batch will not necessarily follow suit, possibly varying from 20% to 40%, even when the experiment is performed correctly.

One unexpected variable that has been suggested is the concentration and quality of selenium in tributylphosphine (Se:TBP) used in the synthesis of the original nanocrystals. The quantum yield after the formic acid treatment tends to be higher when the Se concentration is higher and the metal in solution is not oxidized, which happens when exposed to air. Sarah Claiborne in the Rosenthal group first found this correlation and is performing further experiments to find how concentration and oxidation affect quantum yield. This result would imply that the formic acid behavior has to do with the Se dangling bonds at the surface of the nanocrystal and not with the Cd, while the original ligands bind to the surface Cd atoms.¹² This would support the idea that the formic acid molecules do not lose their H⁺ and simply hydrogen bond with the partial negative charge on the Se. Then the formic acid effect is definitely not a ligand exchange with the phosphonic acid or TOPO. Also, if increasing the concentration of reagent Se can lead to more surface Se atoms than in a nanocrystal following regular synthesis, then there are more sites for the formic acid to affect, thus increasing the quantum yield even more.

The preliminary results from treating warm-white nanocrystals suggest the possibility of making the treated nanocrystals a purer white by controlling original nanocrystal emission. It was determined that the tunable emission during synthesis does not have an effect on the post-treatment emission, but the use of dodecanethiol alters the emission between synthesis and treatment, producing the promising result of a warmer

yet brighter emission after treatment. More research should be done so as to understand what the dodecanethiol does to the nanocrystal surface and if other chemicals, especially other thiols, would do the same. Then the nanocrystal CIE coordinates should be able to be purposefully tuned to obtain the desired CIE coordinates of pure white light after brightening. It will be very helpful to explore the possibility of pure white light, considering the potential for use in commercial white solid-state lighting.

Several analytical instruments may be of assistance in comparing original nanocrystals to formic acid-treated samples, in order to uncover the mechanism of brightening on the molecular level. Proton and phosphorus NMR spectroscopy would be helpful in finding any change in binding on the nanocrystal surface, as well as simply the increased or decreased presence of ligands and formic acid in the sample after treatment and after centrifugation. IR spectroscopy could also reveal the presence of ligands, especially carboxylic acids, in the nanocrystal sample. X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy (RBS), which both give information about the abundance of certain elements on the surface of a material, would be helpful to examine which ligands remained attached to the nanocrystals before and after treatment.^{36, 37} XPS also shows how atoms on and near the surface are bound to each other, which would be a great benefit for these ultrasmall nanocrystals, since all of the atoms are near the surface. Aberration-corrected atomic number contrast scanning transmission electron microscopy (Z-STEM) is extremely useful in looking at the nanocrystals and seeing the atomic arrangement.³⁶

4.3 Future Tests: Changing Variables

More acid treatments need to be tested on white-light nanocrystals to further study the relationship between different acids and an increase in quantum yield, working to understand the reason behind changes in quantum yield. Relevant acids to use might be more straight-chain carboxylic acids in addition to formic, acetic, hexanoic, octanoic, and oleic to test the chain-length trend that was previously found. Also, acids with an electron-donating or electron-withdrawing group, such as various halogens or aromatic rings, should be tested to determine whether the electronic properties of acids of similar lengths affect the quantum yield.

APPENDIX A

Nanocrystal Size Calculation

The size of a single CdSe nanocrystal is calculated from the band edge absorption wavelength (λ), using the following calculations developed by Yu *et al.*²⁹ After calculating the diameter (D) of the nanocrystal as a function of the wavelength, the concentration of a particular sample can be calculated from the extinction coefficient (ϵ) and the Beer-Lambert Law.

$$D = (1.6122 \cdot 10^{-9})\lambda^4 - (2.6575 \cdot 10^{-6})\lambda^3 + (1.6242 \cdot 10^{-3})\lambda^2 - (0.4277)\lambda + 41.57 \quad (\text{A.1})$$

$$A = \epsilon bc \quad \text{where} \quad \epsilon = 5857(D)^{2.65} \quad (\text{A.2})$$

APPENDIX B

CIE COORDINATES AND CALCULATIONS

When synthesized, the fluorescence emission from these nanocrystals can be nearly pure white with chromaticity coordinates of 0.322, 0.365.² Pure white is defined by the Commission Internationale de L'Eclairage (CIE) in 1931 as having chromaticity coordinates of 0.333, 0.333.¹⁸ The coordinates x and y are calculated with the following procedure and equations.⁵

An emission spectrum of a sample is collected over the visible spectrum (400 to 800 nm). As shown below, the intensity (I) at each wavelength is multiplied by coordinates x , y , and z from constants in the CIE 1931 XYZ color-matching functions database, and calculations proceed according to the following equations.³⁸

$$X_1 = x * I \quad Y_1 = y * I \quad Z_1 = z * I$$

$$X = \frac{X_1}{X_1 + Y_1 + Z_1} \quad Y = \frac{Y_1}{X_1 + Y_1 + Z_1} \quad Z = \frac{Z_1}{X_1 + Y_1 + Z_1}$$

$$u = \frac{4X}{X + 15Y + 3Z} \quad v = \frac{6Y}{X + 15Y + 3Z}$$

$$x = \frac{3u}{2u - 8v + 4} \quad y = \frac{2v}{2u - 8v + 4}$$

The final coordinates x and y are the 1931 color coordinates of emitted light that can be plotted on a chart to see the color in the visible spectrum to which the numbers correspond. The area in the center is “white to the eye,” with the coordinates of pure white.

APPENDIX C

QUANTUM YIELD CALCULATIONS

In the application of quantum dots to solid-state lighting, it is important to know how efficient the nanocrystals are in emitting light, since efficiency is one of the factors in determining whether the nanocrystals should be used in place of other light sources. One way to measure efficiency here is to take the fluorescence quantum yield (QY) of the nanocrystals, which is a percentage measurement of how much light is emitted by a nanocrystal sample compared to the amount of light it absorbs.

Quantum yield calculations were performed on original white-light nanocrystals and on treated nanocrystals. In order to track emission changes accurately, the measurements were made within a few hours of treatment, and the original and treated nanocrystals were measured together with both samples in toluene. The white-light nanocrystals were usually made one or two days before treatment.

Coumarin 152A (in hexanes) and Coumarin 153 (in ethanol) were both used on different samples as the reference dye. The optical density or absorbance of the samples and dyes were adjusted using a UV-Vis spectrometer. Solutions of the original sample, treated sample, and reference dye were diluted to similar optical densities (0.08-0.1) at a wavelength slightly shorter than that of the nanocrystal band edge (380-400 nm). The emission spectra of the samples were taken from 400 nm to 800 nm on a fluorometer, using the chosen wavelength near the band edge as the excitation wavelength on the instrument. The quantum yield was then calculated using Equation C.1.¹²

$$QY_{NC} = \left(\frac{E_{NC}/A_{NC}}{E_{STD}/A_{STD}} \right) \times \left(\frac{\eta_{NC}}{\eta_{STD}} \right)^2 \times QY_{STD} \quad (C.1)$$

where E_{NC} and E_{STD} are the integrated emission intensities of the nanocrystals and standard dye, respectively, A_{NC} and A_{STD} are the optical densities of the nanocrystals and standard at the excitation wavelength, η_{NC} is the refractive index of toluene, η_{STD} is the refractive index of the standard's solvent, and QY_{STD} is the quantum yield of the standard from literature. The solvent refractive indices were 1.4969 for toluene, 1.375 for hexanes, and 1.3624 for ethanol. The QY_{STD} was 1.00 for Coumarin 152A and 0.38 for Coumarin 153.³⁹

APPENDIX D

LUMINOUS EFFICIENCY CALCULATIONS

With nanocrystals that have a 40% quantum yield, LEDs could be coated with a higher luminous efficiency than previously calculated with 8% efficient nanocrystal emission.⁵ This efficiency in lumens per Watt is calculated using Equations D.1 and D.2:⁴⁰

$$Efficiency = \eta_{LED}\eta_{NC}\eta_{extrac} \times 331 \quad (D.1)$$

$$\text{with } \eta_{NC} = \eta_{abs} \times QY \times S \quad (D.2)$$

where η_{LED} and η_{NC} are the efficiencies of the LED source and nanocrystal encapsulant, and η_{extrac} is the extraction efficiency. The conversion constant of 331 lumens/Watt is based on a 100% efficient ultrasmall white-light CdSe spectrum and should only change if the emission spectral characteristics change, at which point they would no longer be the same white light nanocrystals. The nanocrystal efficiency is dependent on η_{abs} (the absorption efficiency), QY (the quantum yield of the nanocrystals), S (the Stokes loss efficiency). The only variable in the luminous efficiency calculation that is alterable within the nanocrystal chemistry is the quantum yield of the nanocrystals. A predicted value for 40% efficient quantum dots, using a standard commercial LED, is 4.67 lm/W, which is five times more efficient than with the 8% nanocrystals.⁵ This value demonstrates progress toward the desired efficiency of a commercially viable solid-state lighting device.

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