HSZ CH07

Synthesis of CdTe Quantum Dots
And Their Use in Environmental Monitoring

A Major Qualifying Project
submitted to the faculty of
Worcester Polytechnic Institute
in partial fulfillment of the requirements for the
Chemical Engineering Bachelor of Science Degree

Sponsoring Agency:
Shanghai Jiao Tong University
School of Environmental Science and Engineering
Shanghai, China Project Center

By:

Lauren Swalec
Date: April 26, 2011

Project Advisor: Susan Zhou, PhD
WPI Professor

Project Co-advisor: David DiBiasio, PhD
WPI Professor

Project Co-advisor: Huisheng Zhuang, PhD
SJTU Professor

Abstract

An aqueous synthesis method was developed for the successful production of water-soluble CdTe quantum dots capped with thioglycolic acid and L-cysteine. Through evaluation of absorption and fluorescence spectrums as well as fluorescent quantum yield, it was found that the best ratio of the two buffers was TGA:L-cys = 1:1. This ratio produces quantum dots with high fluorescent intensity and a large fluorescent wavelength range with the potential to continue growing. The quantum dots produced were found to have possible application in the field of environmental monitoring.

Acknowledgements

I would like to thank those who helped to make this project a reality.

To Professor Huisheng Zhuang, my advisor at Shanghai Jiao Tong University, who provided me with goals, and allowed me the use of his laboratory and supplies and graduate students.

To Professor Susan Hong Zhou, my advisor at Worcester Polytechnic Institute, who made the project site in Shanghai possible, and provided much guidance throughout the process of writing this report.

To Guangxin Yang, PhD student at Shanghai Jiao Tong University, who was by my side throughout all of the experiments, and was an unending well of knowledge about both quantum dots and life in China.

And to all of the other SJTU graduate students, both in Professor Zhuang's lab and beyond, who helped me learn to use the machinery, showed me the ropes in lab, and helped to make my time in China truly enjoyable.

Thank you.

Table of Contents

Table of Figures

Table of Tables

1.0 Introduction

Quantum dots are compounds with specific characteristics and varied uses. Their high fluorescence and narrow spectrum shape makes them an excellent tagging alternative to conventional fluorescent dyes. During the past three decades, extensive research has been performed on the properties and uses of quantum dots. There are several viable methods to make quantum dots, but not all produce dots that can be used for environmental and biological testing. Properties (and therefore uses) are determined in part by the materials that quantum dots are made from as well as how the dots are made. All quantum dots (QDs) have a core made up of II-VI elements (Reiss, et al. 2003). Common II column elements are cadmium and zinc. Common VI column elements are selenium, tellurium, and sulfur. Perhaps the most studied combination is CdSe, with CdTe close behind. ZnS is also prevalent in research.

The II-VI core has very high fluorescence, but also a tendency to flash like a firefly (Chan and Nie 1998). To make the fluorescence constant, QDs are often coated with an outer layer of either a different II-VI compound, or a buffer, also known as a stabilizer or capper (see **Figure 1**). Common stabilizers include thioglycolic acid (TGA, also called mercaptoacetic acid), and trioctylphospine (TOP) and trioctylphosphine oxide (TOPO) (Talapin, et al. 2001). This second layer keeps the dots from flashing (Chan and Nie 1998), and can adjust the properties of the dots, such as increasing fluorescence or making them water soluble.

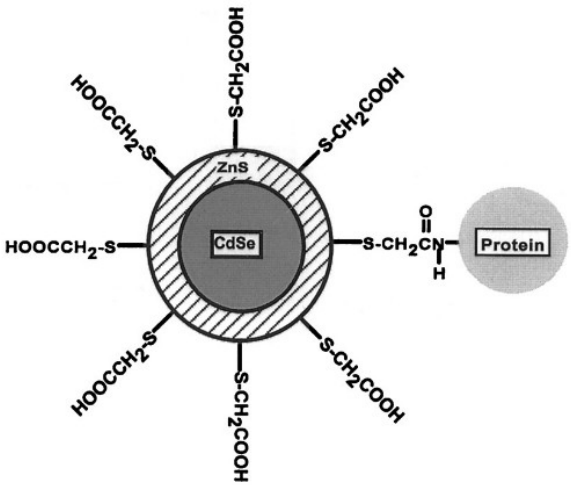

Figure 1 – A quantum dot with two II-VI layers and capped by TGA, with a conjugated protein. (Chan and Nie 1998)

Depending on how the dots are formed, they may or may not be suitable for biological tests. For example, dots grown in organic solvents cannot be used in biological tests (Chan and Nie 1998), while dots grown aqueously can be. This is because aqueous dots are water soluble, which is necessary for biological uses of quantum dots (Bruchez, et al. 1998).

Currently, there is no standardized method to synthesize and grow quantum dots. The methods are adjusted based on the materials the dots are made from and capped with, the ratios of the components, and what the dots will be used for. As such, it is difficult to compare dots grown

one way with dots grown another as there are so many variables that can affect the properties of the QDs.

Quantum dots are notable for their high fluorescent intensity. It is at least comparable to and sometimes better than the intensity observed in conventional fluorescent dyes, such as rhodamine 6G (Chan and Nie 1998). In addition, quantum dots have narrow, symmetrical fluorescence curves in the visible light spectrum, while organic dyes have A-symmetrical curves with a tail trailing into the red region (Bruchez, et al. 1998). The fluorescent spectrums of quantum dots have a narrower full width half maximum (FWHM, the width of the spectrum at half of the peak intensity) then fluorescent dyes, making dots more precise.

Fluorescent dyes also have a narrow excitation range when compared to quantum dots (Bruchez, et al. 1998) (Idowu, Lamprecht and Nyokong 2008). This, in combination with the red tail and wider FWHM, means that performing multiple simultaneous tests with fluorescent dyes is difficult. However, due to the properties of quantum dots, many different sizes can be used at once with the same excitation wavelength and can be clearly distinguished from each other, both to the naked eye and using spectrometers (Bruchez, et al. 1998).

Quantum dots also have a much longer shelf life then organic fluorescent dyes. Quantum dots can be stored for months with no deterioration of fluorescent properties (provided the dots do not precipitate) (Qu and Peng 2002). Quantum dots have also proved to be ~100 times as 'stable as rhodamine 6G against photobleaching' (Chan and Nie 1998).

Quantum dots fluoresce at room temperature in the visible light spectrum (Nose, et al. 2006). The wavelengths at which the dots fluoresce are directly dependent on the size of the dots (Qu and Peng 2002) (Idowu, Lamprecht and Nyokong 2008). Smaller dots fluoresce starting in the blue range of visible light. As the dots grow, they gradually move through the other colors and into the red range (see **Figure 2**). CdSe quantum dots form small enough to fluoresce in the blue range, while CdTe dots are only small enough to start at green (Tian, et al. 2009). It is quite easy to increase the size of quantum dots – simply let them grow for more time.

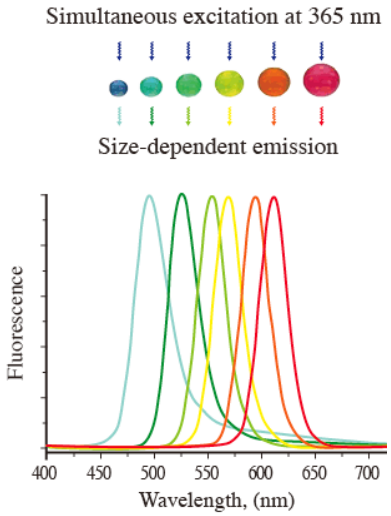

Figure 2 – As the size of the quantum dots increases, so does the peak fluorescent wavelength. (Ooba 2006)

The rate of growth of quantum dots is also very important. If the dots grow too, fast quantum rods will form instead of quantum dots (see **Figure 3**) (Peng, et al. 2000). Buffer ratios can also determine whether rods or dots form (Peng, et al. 2000). Quantum rods are very similar to quantum dots. For example, size can be controlled with time. However, Peng et al. found quantum rods to have significantly lower fluorescence then quantum dots, making dots more desirable. But quantum rods do have orientation, which means they can be aligned, and so have possible use in applications such as photovoltaic cells (Peng, et al. 2000).

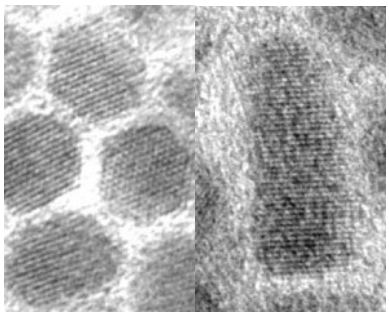

Figure 3 – Quantum dots (left) and a quantum rod (right). (Peng, et al. 2000)

Molecules such as antibodies can be conjugated to quantum dots (see **Figure 1**). These conjugated dots can then be used in tests such as immunoassays to target specific molecules (Chan and Nie 1998). There are many uses for conjugated quantum dots besides immunoassays. For example, to detect and track cancer cells (see **Figure 4**) (Hu, et al. 2010), and for targeted drug delivery (Rzigalinski and Strobl 2009). Fluorescent dyes have no such conjugation abilities. Research in this area has found that the properties of the dots are in no way negated by the conjugation, and that the dots function properly in seeking out a specific molecule (Chan and Nie 1998). The tests also showed that the conjugated dots were only attracted to the correct molecule, and did not show up in the cells when the target molecule was not there.

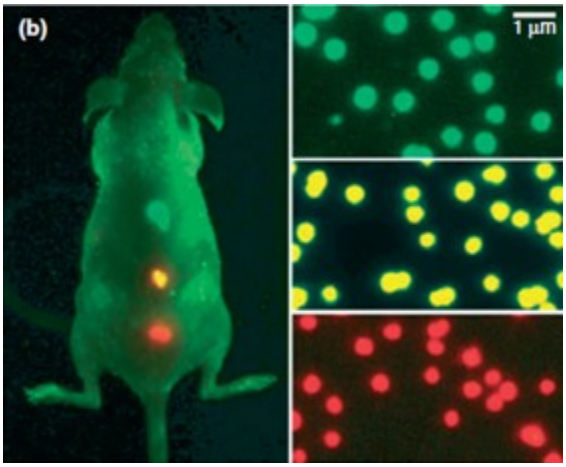

Figure 4 – Three sizes of quantum dots (close ups on the right side) at the same excitation wavelength used to test for cancer cells in a mouse. (Hu, et al. 2010)

However, the safety of quantum dots designed for use in biological and environmental testing capacities has not been thoroughly studied. Cadmium, often a component of quantum dots, is a known toxin. In humans it is devastating to, among others, the bones, kidneys, and liver

(Rzigalinski and Strobl 2009). Rzigalinski and Strobl make it clear that the effects of particles at the nano-scale are different then in bulk concentrations, and yet the effects of cadmium at the nano-level have *not* been fully studied. Quantum dots are very useful tags but they could be more harmful then helpful if the effects are not understood. Rzigalinski and Strobl even suggest that cadmium-containing quantum dots used to label cancer cells have killed the cells. While this is not necessarily bad, it could be if the target cells are not cancer cells. And it has been shown that quantum dots can remain within a body for four months or more (Rzigalinski and Strobl 2009).

Studies have shown that capping cadmium-containing cores with another layer, such as ZnS, does help to reduce the toxicity of the cadmium in the core (Rzigalinski and Strobl 2009). And if quantum dots are going to be used in immunoassays, the dose size must be determined. Exactly *who* would do that, and what their understanding of quantum dots would be is unclear (Rzigalinski and Strobl 2009).

Quantum dots also have the potential to be used to test for toxins and contaminates in the environment. One type of such environmental contaminates is persistent organic pollutants (POPs). POPs do not break down in the environment, and are found all around the world, including the USA and the People's Republic of China. They are usually found in pesticides and as a side effect of chemical processes (Persistent Organic Pollutant 2011).

Quantum dots for environmental monitoring purposes have not been extensively tested, but biological uses are currently being tested. The same kind of dots used for biological tests would be needed for environmental tests. This means water soluble quantum dots are required, which means aqueous growth methods will probably work best. Aqueous growth of quantum dots is known to be cheaper, environmentally friendly, and to produce quantum dots that can be used for biological (and thus environmental) purposes (Chen, et al. 2007).

The goals of these experiments are to develop an aqueous synthesis method, based on that of Tian et al., to produce water-soluble CdTe quantum dots capped with thioglycolic acid (TGA) and L-cysteine (L-cys) that can be used for environmental purposes, and to determine the best ratio of TGA:L-cys.

2.0 Background

2.1 II-VI Combinations

Core II-VI combinations include CdSe, and capping combinations include ZnS and ZnSe (Nose, et al. 2006). Another commonly studied core combination is CdTe (Idowu, Lamprecht and Nyokong 2008) (Chen, et al. 2007).

The quantum dot core is generally capped, sometimes by another II-VI combination, sometimes by another kind of molecule, sometimes by both. The second layer is added because the luminescence of the core flashes, like a firefly, which can cause difficulties in analyzing the quantum dots (Chan and Nie 1998) (Chen, et al. 2002) Reiss et al. proposes that a double-cap of II-VI compounds does the most to increase the fluorescent efficiency of the quantum dots.

Adding another layer has proved to be highly beneficial, both in terms of fluorescence and the stability of the dot itself (Talapin, et al. 2001) (Bruchez, et al. 1998) (Reiss, et al. 2003).

2.2 Capping Agents

Capping quantum dots with either a buffer or another II-VI layers can have significant advantages, including reducing toxicity of the core (Rzigalinski and Strobl 2009), making dots water soluble (Bruchez, et al. 1998), and increasing their quantum yield (Reiss, et al. 2003).

Nose et al. tested different capping amines to try to evaluate the effect of the different types on the fluorescence of CdSe quantum dots. They found that as the chain length increased, the fluorescent peak blue-shifted. Correspondingly, the particle size decreased as the chain length increased (Nose, et al. 2006). It was concluded by Nose et al. that longer amine chain length 'suppresses the crystal growth,' though chain-length has no observable effect on fluorescent intensity.

It was also found that peak fluorescent wavelength (and therefore size) were 'a function of the class of amines' (Nose, et al. 2006). Specifically, that bulky molecules have a slower diffusion rate, meaning QDs capped with bulky molecules form slower and consequently have a smaller size (Nose, et al. 2006). And so, it was concluded by Nose et al. that 'particle size was dependent on both the molecular mass and the stereochemical shape of the amines, which affect the diffusion rate.'

Nose et al. found that fluorescent intensity was dependent on *k*Pa, and that the weaker the dissociative properties were, the higher the intensity. And so, the fluorescent color and intensity of the quantum dots can be adjusted by changing the capping amine used (Nose, et al. 2006).

2.3 Size and Growth of Quantum Dots

The size and shape of quantum dots is directly dependent upon growth time, and depends at least in part upon the amines added (Nose, et al. 2006) (Qu and Peng 2002). Heat must be applied to the solution in order for quantum dots to grown, and it was found that size and size distribution

are also dependent upon growth temperature (Murray, Norris and Bawendi 1993) (Danek, et al. 1994).

If the 'overall growth rate' is fast quantum rods will form, while quantum dots will form if it is slow (Peng, et al. 2000). Peng et al. also observed that in pure TOPO growth was so fast that quantum rods always formed. But if an impurity, such as hexyl-phosphonic acid (HPA), was added, growth slowed enough that quantum rods would form. And just like quantum dots, the growth rate and so size of quantum rods can be controlled by time and other variables (Peng, et al. 2000). Quantum rods proved to be very similar to quantum dots, if significantly dimmer fluorescently, with the addition of orientation and alignment properties that dots do not have (Peng, et al. 2000) (Chen, et al. 2002).

As the size of a quantum dot increases, so does the fluorescent peak wavelength, meaning the dots shift from blue to red as their size increase (Idowu, Lamprecht and Nyokong 2008).

Quantum dots that fluoresce in the orange and red regions are difficult to make. Qu and Peng found that stearic acid is a good capper for growing orange- and red-fluorescing dots. These dots could also be grown at high temperatures, with is necessary for the growth of quantum dots (Qu and Peng 2002). For dots that fluoresce in the red range, it was found that primary amines are essential as capping agents, as the fluorescent quantum yield in these regions is naturally low (Qu and Peng 2002).

2.4 Conjugation of Quantum Dots

Quantum dots can be conjugated to other molecules. This greatly expands the uses and applications of quantum dots. Molecules that have been successfully conjugated include antibodies (Chan and Nie 1998), DN (Chen, et al. 2007) (Chan and Nie 1998), and other proteins and peptides (Chan and Nie 1998). Tests have shown that conjugation did not cause the QDs to aggregate, nor did the 'optical properties' of the dots change (Chan and Nie 1998).

There are several ways to conjugate quantum dots. One is to cap the dots with avidin and utilize the 'avidin-biotin system' to connect the dots to an antibody (Goldman, et al. 2002). Goldman et al. were able to successfully conjugate the quantum dots, and show that the dots were functional in immunoassays.

Another conjugation method is through 'coordination of the carboxylic group of the thiol with the amine group on BSA' (Idowu, Lamprecht and Nyokong 2008). This method was used to conjugate CdTe dots capped with TGA, L-cys, or 3-mercaptopropionic acid to bovine serum albumin. This also proved to be a successful conjugation method, and though the conjugated QDs were observed to have slightly decreased absorption intensity, the emission intensity was increased (Idowu, Lamprecht and Nyokong 2008). It was also found that conjugating BSA to quantum dots decreased the fluorescence of the BSA, but not that of the QDs (Idowu, Lamprecht and Nyokong 2008).

2.5 Absorption Properties

Different II-VI combinations have different characteristic absorption spectrum shapes (Murray, Norris and Bawendi 1993). CdSe quantum dots have a spectrum that has three bumps as the

absorption asymptotes. CdS quantum dots have a spectrum that has two bumps. And CdTe quantum dots have an absorption spectrum that has one bump. In addition 'sharp' absorption spectrums 'suggest highly monodisperse samples' (Murray, Norris and Bawendi 1993).

2.6 Fluorescence Properties

Fluorescent color of a quantum dot is tied directly to its size, and size is a direct function of growth. 'Color purity,' or monodispersity, is therefore also dependent of size and growth (Qu and Peng 2002), and can be measured by the narrowness (full width half maximum) of the fluorescent spectrum. FWHM is independent of the peak fluorescent wavelength (Qu and Peng 2002). QD nanocrystals have a higher FWHM then that of single particles, meaning that not all the dots in a sample are the same size and color (Qu and Peng 2002).

Fluorescent intensity can be measured by the potoluminescent quantum yield of the quantum dots, which varies between synthesis methods (Qu and Peng 2002). Brightness of a dot can be improved by adding another II-VI layer, such as ZnS (Talapin, et al. 2001). The same could be achieved by exchanging the capping ligands for primary amines (Talapin, et al. 2001).

The quantum yield of dots varies greatly with the synthesis method. Dots have been reported with QY at 15% for green and 6% for red (Bruchez, et al. 1998), 50% (Talapin, et al. 2001), all the way up to 80% (Qu and Peng 2002). Peng et al. say that even a spectacularly low fluorescence of ~5% is sufficient for use in biological tests.

2.7 Fluorescent Dyes

Fluorescent dyes have narrow excitation ranges, and the fluorescent spectrum is both wide and A-symmetrical with a tail trialing into the red region (Bruchez, et al. 1998). This makes analysis using multiple fluorescent dyes at once difficult (Bruchez, et al. 1998); the tail overlaps with other peaks, artificially increasing or decreasing the fluorescent intensity. Bruchez et al. say that the ideal characteristics for use in multi- tests are a narrow and symmetrical fluorescence spectrum, both of which quantum dots have.

Quantum dots have shown to be much more stable against photobleaching then fluorescent dyes (Chan and Nie 1998), in addition to being much brighter. It was estimated by Chan and Nie that 'the fluorescence intensity of a single CdSe QD is equivalent to that of ~20 rhodamine molecules.' This photostability means that quantum dots have been considered as an alternative to fluorescent dyes, notably in biological uses, since the 1980s (Reiss, et al. 2003).

2.8 Toxicity of Quantum Dots

Quantum dots often contain cadmium, a chemical that is known to be toxic to several major organ systems in humans (Rzigalinski and Strobl 2009). Rzigalinski and Strobl point out that reaction function and effects tend to differ greatly between bulk amounts and the nano-level, and that, even so, the effects of cadmium at the nano-scale have not be studied. However, it is known that coating a cadmium-containing core with something like ZnS will reduce the toxicity of the core (Rzigalinski and Strobl 2009).

Dosing parameters of quantum dots used in immunoassays are not set, though it is known that quantum dots remain in the body for some time (Rzigalinski and Strobl 2009). But since there

are not standards in the production of quantum dots, a standard dose would be difficult to define. Quantum dots need to be standardized and fully characterized before such standards can be set (Rzigalinski and Strobl 2009).

Tests have shown that conjugated quantum dots go to cells containing their target molecule, and not to cells that do not (Chan and Nie 1998). Tests have also shown that quantum dots used in biological tests can still be present in the body four months later (Rzigalinski and Strobl 2009). If dots are going to remain in the body this long, toxic effects of such exposure must be known.

Research also needs to be performed on the disposal of quantum dots after they have been used. The cadmium would classify them as hazardous waste, and they need to be treated as such.

2.9 Synthesis Methods

There is no standard synthesis method for quantum dots. Methods vary according the II-VI components, buffers, and the synthesis solution used.

Qu and Peng mention an organometalic method developed in the 1990s that utilizes 'safe and inexpensive cadmium precursors and ligands' that produces quantum dots that are relatively monodisperse. Talapin et al. further refined organometalic methods to produce highly fluorescent quantum dots, producing CdSe dots with quantum efficiency of '~50%.' They found that the ratio of the organic solvents affected growth of the QDs (Talapin, et al. 2001). Organometalic methods often occur under a nitrogen atmosphere (Danek, et al. 1994).

The ratio between the components has been studied in several different cases. Qu and Peng found that if the Cd:Se ratio was increased to 1:10, the fluorescent quantum yield increased to 80%. They also found that the FWHM increased as the II component became larger than the VI component in the ratio (Qu and Peng 2002). This would imply that when the VI element is added in higher proportions then the II element, the quantum dots produced would be brighter and more monodisperse.

2.10 Aqueous Synthesis

Aqueous synthesis is the synthesis of quantum dots in a water solution, as opposed to the organic solvents used in many organometalic synthesis methods. Aqueous synthesis produces water soluble quantum dots, and has several advantages over simply capping or using surface exchange on quantum dots grown with other synthesis methods. Aqueous growth of quantum dots occurs at a lower temperature, which means that these dots have a naturally lower quantum yield then dots produced with organometalic methods (Chen, et al. 2007).

Aqueous methods are known to be cheap, easy, and environmentally friendly (Chen, et al. 2007). It is simply good sense to use quantum dots produced in an environmentally friendly-manner to test for environmental contaminates.

Chen et al. (2007) found that the optimum ratios for producing CdTe dots with aqueous methods are as follows. Cd^{2+}:Te should be 2:1 when Cd^{2+}:buffer is 1:2, otherwise precipitation would occur. This leaves a minimum ratio of Cd^{2+}:Te:buffer of 2:1:4 (Chen, et al. 2007) for optimal growth of CdTe quantum dots with high fluorescent intensity.

2.11 Biological Uses

Fluorescence is a common indicator in biological tests (Bruchez, et al. 1998). Quantum dots are useful fluorescent indicators. The use of quantum dots for biological tests seems only natural. However, the dots must fill certain requirements before their use can be considered. First of all, the quantum dots must be water-soluble, which dots growth with organometalic synthesis methods are not (Bruchez, et al. 1998).

The conjugation abilities of quantum dots, as well as the ability to use and distinguish more than one size/color of quantum dots at once, means that quantum dots can be used for biological applications for which fluorescent dyes simply cannot be used (Bruchez, et al. 1998).

Biological applications include clinical diagnosis and pathogen and toxin detection (Idowu, Lamprecht and Nyokong 2008), as well as immunoassays and drug delivery (Rzigalinski and Strobl 2009).

2.12 Environmental Uses

Environmental applications of quantum dots are just starting to be considered. Quantum dots used in environmental testing would need to fulfill the same requirements as those used in biological testing – namely, they must be water soluble. And the same considerations would need to be taken into account – quantum dots would not be useful environmental monitors if they have toxic effects on the environment.

Quantum dots could be used for environmental testing in two ways, concentration and conjugation. Conjugation of dots has been previously discussed, and quantum dots can be developed as a conjugated marker to test for specific chemicals. 'Concentration' testing would require no conjugation of the dots. Just simply expose the dots to chemicals, and measure the effect on the fluorescence. This will tell if something capable of affecting the dots is present, and possibly its quantity as well.

One of the main groups of chemicals to test for is persistent organic pollutants (POPs). These are chemicals that remain in the environment and do not break down. Many POPs were useful pesticides, some were used as solvents in chemical processes (Persistent Organic Pollutant 2011). They have low water solubility and high molecular mass (Persistent Organic Pollutant 2011). POPs accumulate in animals at the tops of food chains. Perhaps the most well known POP is DDT (Persistent Organic Pollutant 2011). Polychlorinated biphenyls are no less of a problem. PCBs, highly toxic and problematic as they are, are capable of penetrating latex and skin (Polychlorinated Biphenyl 2011). In addition to being highly toxic, PCBs are extremely difficult to break down (Persistent Organic Pollutant 2011). It is important to know when PCBs are present in order to start cleaning them up.

3.0 Methods

3.1 Supplies

Production and testing of CdTe quantum dots requires many chemicals and equipment. The cadmium comes from cadmium chloride in a powder form, while the tellurium is from tellurium powder. Thioglycolic acid and L-cysteine were both used in various proportions as buffers and capping agents.

Various rudimentary chemical apparatus, as well as particular equipment, were used in these experiments. This includes a glass 3-neck flask in which the quantum dots were grown, as well as an absorption spectrometer and a spectrofluorophotometer to measure the absorption and fluorescence properties, respectively, of the dots.

3.1.1 Chemicals

- Cadmium chloride ($CdCl_2 \cdot 2.5H_2O$)
- Tellurium powder (Te powder)
- Sodium borohydride ($NaBH_4$)
- Thioglycolic acid (TGA)
- Cysteine (L-cys)
- Sodium hydroxide (NaOH)
- Clean water (pure H_2O)
- Ethanol
- Hydrochloric acid (HCl)
- Rhodamine 6G
- Nitrogen gas (N_2 gas)
- Polychlorinated biphenyls (PCB 37)
- Bovine serum albumin (BSA)
- N,N-Dimethylformamide

Safety Note

Table 1 shows the harmful properties of the chemicals used in this experiment.

Table 1- Properties of the chemicals used in the experiments.

	Inhaled	Swallowed	Absorbed	Other
$CdCl_2$	toxic/fatal	toxic/fatal	toxic/fatal	carcinogen, irritant
Te powder		toxic		
$NaBH_4$	harmful	harmful	harmful	corrosive, flammable
TGA	fatal	fatal	fatal	corrosive
L-cys		harmful		irritant, *strong* smell of garlic
Rhodamine 6G	hazardous			hazardous if ingested and for skin and eye contact
PCB	harmful	harmful	harmful	carcinogen, irritant, reproductive hazard, attacks plastics and rubber (e.g. latex)
N,N-dimethyl…	harmful	harmful	harmful	irritant to skin, eyes, respiratory tract; affects kidneys, cardiovascular system, nervous system; toxic to liver
BSA				mostly harmless, eating large doses can cause indigestion

Cadmium chloride is also marked ‘dangerous for the environment.’

Taking these safety concerns into account, a lab coat, goggles, and gloves are recommended to prevent skin contact. Latex gloves are adequate for most of the experiments. Plastic gloves should be worn when working with PCBs, as it penetrates latex. The lab should also be well ventilated to prevent inhalation of chemicals.

3.1.2 Equipment

Many pieces of standard lab equipment were used. The following is an equipment list which contains specific and specialized equipment used for tests and experiments.

- Glass tubes
- Plastic tubes
- Glass beakers, various sizes (5 mL to 10 mL)
- Mass balance
- Magnetic stirrer and magnet
- Pipette
- Glass stirring rod
- Plastic wrap
- PHS-3C pH meter (see **Figure 5**)
- 3-neck flask
- Magnetic stirrer and condenser
- Xin Mao UV-7504 absorption spectrometer (see **Figure 6**)
- Shimadzu RF-5301 Spectrofluorophotometer (see **Figure 7**)
- Cuvettes (absorption and fluorescence)
- Centrifuge
- 100 mL volumetric flask

All glasswear was cleaned in nitric acid (HNO_3) and then washed once with soap and tap-water, and then 3 to 4 times with pure water.

Some equipment can be seen in the following pictures:

Figure 5 - The pH meter used to adjust the pH in later experiments.

Figure 6 - The absorption spectrometer.

Figure 7 - The spectrofluorophotometer.

3.2 Procedure

The experimental procedure was based on the paper published by Tian, et al., and adapted for CdTe quantum dots by Professor Huisheng Zhuang and graduate student Guangxin Yang, both of Shanghai Jiao Tong University. Synthesis of the quantum dots was repeated many times in order to get a good range of proportions of the two buffers (TGA and L-cys) in an effort to determine which ratio is best.

The quantum dots were compared to rhodamine 6G, a fluorescent dye that was diluted and evaluated. Fluorescent dyes are the current standard for many of the applications for which quantum dots can be used. Fluorescent quantum yield was calculated, allowing the quantum dots produced to be compared to rodamine 6G.

The dots were tested in the presence of polychlorinated biphenyls, a persistent organic pollutant, and bovine serum albumin, a protein widely used in biological tests, to see if the dots responded to the presence of environmental contaminates.

3.2.1 Synthesis of Quantum Dots

This synthesis method of CdTe quantum dots takes place in several steps over a two-day period.

3.2.1.1 Synthesis of NaHTe

Te powder and $NaBH_4$ were combined in a dry glass vial. The tellurium should be the limiting factor, so the Te and $NaBH_4$ were always combined in the ratio Te:$NaBH_4$ = 1:4. Usually 1 molar, but sometimes 2 molar, Te powder was used. The vial was shaken and tapped to mix the powders. Te powder is a metallic black, and $NaBH_4$ is white. Together, they made a grainy grey mixture (see **Figure 8**).

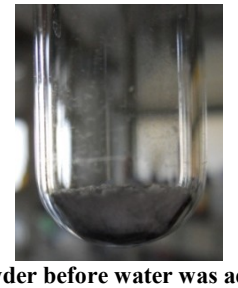

Figure 8 – Mixture of Te powder and $NaBH_4$ powder before water was added.

Pure water (3 mL) was then added to the vial to give the powders a medium in which to react. The vial was again shaken to mix the powders into the water. The mixture became a dark grey or black, and quickly lightened to a very translucent grey as the vial was shaken (see **Figure 9**). Generally a black layer of powder formed at the top of the water and there was some powder at the bottom, with bits floating in the liquid. At this point, bubbles could be observed within the vial. This meant that hydrogen gas was forming, and that the following reaction was taking place:

$$NaBH_4 + Te + H_2O \rightarrow NaHTe + H_2 + sediment$$

Figure 9 – The Te powder and $NaBH_4$ mixture after pure water was added and the solution was shaken to mix.

The vial was then sealed with plastic wrap. Holes were poked into the plastic wrap with a micropipette so that the hydrogen gas could escape. The vial was placed in the refrigerator for about 24 hours. The reaction occurs best in a place that is cold and dark (Tian, et al. 2009). During this time the $NaBH_4$ and Te powder were allowed to react as fully as possible to form NaHTe.

After 24 hours the NaHTe solution was a bright, clear purple (see **Figure 10**). There was still black powder in the bottom of the vial, as well as on the sides of the vial above the liquid surface. Sometimes a film of the black sediment formed across the vial.

Figure 10 – The NaHTe solution (purple) after ~24 hours in the refrigerator. Black sediment can be seen above and in the bottom of the solution.

3.2.1.2 Cadmium Ion Solution

After the NaHTe solution was made and had reacted for about 24 hours, the second half of the process could begin. And so a cadmium-ion solution was made. The ratio Cd^{2+}:Te:(TGA and L-cys) = 3:1:6 was used for most of the experiments, so the amount of cadmium ion and buffer used was determined by the amount of Te powder used.

Cadmium chloride ($CdCl_2 \bullet 2.5H_2O$) was dissolved in a small amount of pure water. The cadmium compound was a white powder, but when dissolved in water, the solution was clear (see **Figure 11**).

Figure 11 – Dissolved L-cys (left beaker) and dissolved cadmium chloride (right beaker). Both were dissolved in pure water, and both are clear and colorless.

Next the buffer, L-cys and/or TGA, was added. When both were used, L-cys was added before TGA. L-cys came in a powdered form, and had to be dissolved in a small amount (5 to 25 mL) of pure water before it could be added to the Cd ion solution. L-cys was a white powder, and when dissolved became clear (see **Figure 11**). When the L-cys was added to the Cd-ion solution, a white precipitate immediately formed (see **Figure 12**).

Figure 12 – A white precipitate has formed in the Cd ion solution after the addition of a buffer.

TGA was a clear liquid, but had to be diluted before being added to the solution. A white precipitate also formed upon adding TGA to the cadmium ion solution. TGA smells *extremely* strongly of garlic, so it was important to make sure the lab was well ventilated when it was being handled.

Different ratios of L-cys and/or TGA were tested. One of the goals of the experiment was to find the ratio of these two buffers that yielded quantum dots with the longest and brightest fluorescent

range. Test were performed using only TGA and only L-cys, as well as the ratios TGA:L-cys of 3:1, 2:1, 1:1, 1:2, and 1:3. The 1:1 batch was repeated several times, as that ratio appeared to yield the best results. The dots made using just L-cys or high ratios of L-cys were also repeated, in an attempt to get a better understanding of the growth rate in the beginning.

2.2.1.3 Growth of Quantum Dots

When both the NaHTe solution and the Cd-ion solution were formed, they could be mixed, and the quantum dots would begin to grow. But first the pH of the Cd-ion solution had to be adjusted.

After the addition of the buffer, the pH was usually around 2 or 3. The solution was a milky white. Sodium hydroxide (NaOH) was diluted in pure water and then added to the mixture. NaOH was added until the solution cleared. This usually occurred at a pH around 6 or 7. After that, NaOH was added slowly with many pH checks until the pH was between 10 and 11 (or 11 and 12 for some of the later trials). In a couple of the trials, the pH became too basic, and hydrochloric acid (HCl) was added to bring the pH back to the target range.

It was found early on in the experiments that if the NaOH was added too quickly, the white precipitate did not dissolve back into solution. Or it did, but then precipitated out again so quickly that it could not be noticed, and in these cases the pH often ended up somewhere around 14, from which it could not be rescued as that would necessitate too much HCl. Generally in these cases the Cd-ion solution had to be remade.

After the pH was adjusted, the solution was transferred to a 3-neck flask. Nitrogen gas (N_2 gas) was bubbled through the solution for ~15 minutes, to remove oxygen (O_2) from the mixture.

The flask was then placed in a magnetic stirrer, and attached to a condenser, and the stirrer was turned on. The mixture was going to be heated, so the condenser was necessary to retain as much product as possible. The NaHTe solution prepared the previous day was then added. Only the purple solution was added, not the black or grey sediments. When the NaHTe was added, the clear cadmium-ion solution immediately turned a brownish orange (see **Figure 13**). The solution generally lightened to a golden-orange within the first 10 or 15 minutes of growth.

Figure 13 – The quantum dot solution after the NaHTe has been added to the Cd ion solution. The first was purple and the second colorless, together they formed an orange solution. Photo was taken directly after addition of NaHTe, at the beginning of the growth of the quantum dots.

After the NaHTe was added, growth of the quantum dots began. The water for the condenser had to be turned on, and then the heater in the stirrer could then be turned on. The dots take time

to grow. With the various buffer combinations, complete growth took between 2 and 12 hours. An initial sample was taken soon after growth was initiated. These samples would not yet have any quantum dots, and could be used as a control when evaluating the other samples from the same batch. Samples (~3 mL) were taken at every hour. A sample was also taken at the first half hour, as more rapid growth occurs during the first hour of growth.

3.2.2 Rhodamine 6G

Rhodamine 6G came in a powder form and had to be made aqueous so that it could be compared to the quantum dot samples. The powder was dark red. When rhodamine was diluted in ethanol, it was a luminous orange. The solution stained pink.

A 1.0×10^{-6} mol/L solution was made (see **Figure 14**). Approximately 0.1 mmol (=0.047902 g) R6G was measured, and placed in a 100 mL volumetric flask. Ethanol was added to make up the 100 mL volume.

Figure 14 – The 100 mL sample of rhodamine 6G. 0.1 mmol of r6G dissolved in ethanol. The solution appeared as a luminous orange, but stained paper and latex pink.

Rhodamine 6G, like all fluorescent dyes, photobleaches quickly, though R6G is more stable than most. The fluorescence and absorption tests for the rhodamine solution were performed as quickly as possible in an effort to get the most accurate results. The solution was stored in a refrigerator between tests.

3.2.3 Environemental Tests

Tests were performed to see if the quantum dots could be used to test for the presence of environmental contaminates. Polychlorinated biphenyls (PCBs) and bovine serum albumin (BSA) were used.

PCBs are *very* hazardous to environmental and human health, so great care had to be taken when handling them. The PCBs used in this experiment were a sample already stored in the lab, and labeled 'PCB 37.' *Extremely* small amounts and concentrations of the PCBs were used.

BSA is a protein typically used in immunoassays, and one that it was known the quantum dots would react too. BSA is a generally harmless chemical; it is usually used as a nutrient or stabilizer.

Both tests were performed the same way. Six samples were made that contained a combination of the quantum dots grown on December 11, 2010 and either PCBs or BSA dissolved in n,n-dimethylformamide or pure H_2O, respectively. These particular dots were used as they had what had by this point been determined to be the best TGA:L-cys ratio (1:1), and were made three days before the tests were performed, so the dots were still fresh.

The six samples were made as follows. All samples contained 2 mL of QD solution, and 2 mL of the contaminate mixture. The first was blank, and so contained 2 mL of either n,n-dimethylformamide or water. After that, the samples had 1 mL of the solvent, and 1 mL made up of 0.2, 0.4, 0.6, 0.8, or 1.0 mL of the diluted contaminate with the remainder of that mL made up by the solvent. The fluorescence of these samples was then tested.

4.0 Results

Batch results are identified by the date on which the quantum dots were grown.

The quantum dots were analyzed using fluorescence and absorption spectrums. Fluorescence spectrums were taken from 450 to 700 nm with an excitation wavelength of 380 nm, and the highest slit widths available, unless otherwise stated.

An effort was made to take absorption and fluorescence spectrums as quickly as possible after the samples were taken, though this was not always possible. The first absorption spectrums were taken on November 12, 2010, two weeks after the first batch was grown. And fluorescence spectrums were at first saved incorrectly in the spectrometer computer program, and had to be repeated starting on November 23, 2010, a month after the first batch was grown. The effects of this at times sizable time period between growth and testing can be seen in some of the spectrums.

For absorption and fluorescence spectrums, samples were compared to a blank sample of pure water, as the dots were in aqueous solution. Samples were not diluted, as the volume (~3 mL) was too small.

Graphs of absorption and fluorescence spectrums were made using a computer program called 'OriginPro 8.' In each absorbance spectrum, a single bump between 300 and 700 nm is desired. For the fluorescence spectrums, narrow, symmetrical curves with high intensity are desired. A good range of peak intensities, hopefully from green to red (see **Table 2**) was also anticipated.

The full width half maximum (FWHM) was calculated as follows. Find the peak fluorescent intensity. Calculate the value of half of this intensity. Find the wavelengths on either side of the peak at which this intensity occurs, and find the difference between them.

Fluorescence colors were calculated from the fluorescence spectrums using the wavelength ranges shown in **Table 2**.

Table 2 – Wavelength regions of colors in the visible light spectrum (cite wikipedia).

Color	Wavelengths (nm)
Violet	380-450
Blue	450-475
Cyan	475-495
Green	495-570
Yellow	570-590
Orange	590-620
Red	620-750

4.1 October 29, 2010

The first batch of quantum dots was made using only TGA as a buffer. Analysis was performed mainly to see if the method was yielding quantum dots. These dots were made using 1 M Te powder, and the ratio Cd^{2+}:Te:TGA = 5:1:6. Solution initial volume was 200 mL.

An initial sample was taken five minutes after the solutions were combined and the heat turned on, and a sample was taken after 1 hour of growth. Both samples had an orange color. It was observed that the initial sample did not fluoresce, while the 1 hour sample fluoresced green under an UV light.

Figure 15 shows the absorption spectrums of the Oct. 29th batch. These spectrums show that the 1hour sample did have increased absorbance when compared to the initial sample, though the desired shape, a single bump, cannot be clearly seen in the spectrum.

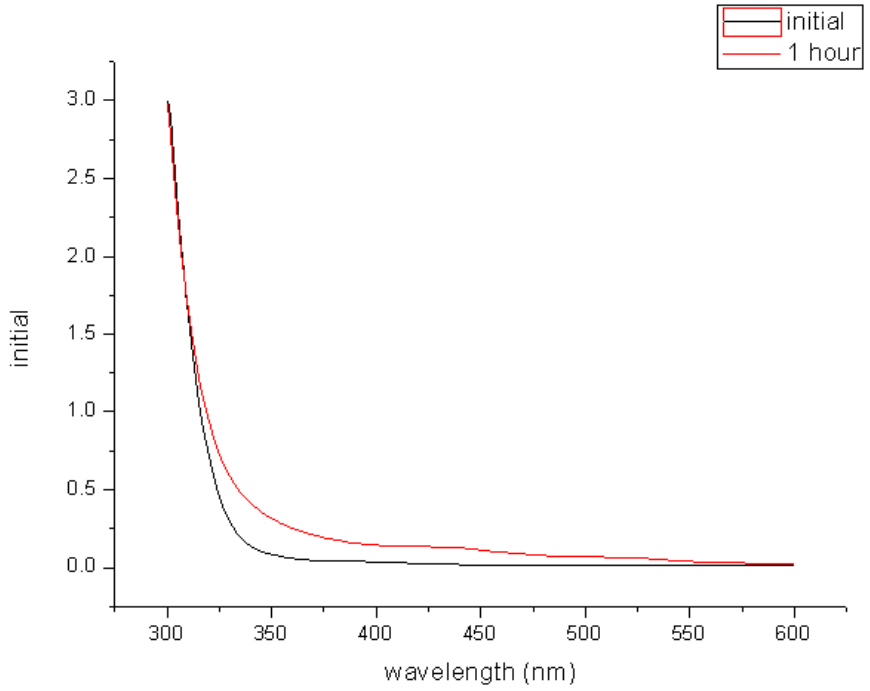

Figure 15 – Graph showing absorption spectrums for initial and 1-hour sample from the batch made on October 29, 2010. (Spectrums were taken on November 12, 2010.)

The fluorescence spectrums in **Figure 16** show that the1-hour sample does fluoresce, which means that CdTe quantum dots did grow. The spectrums also show that the initial sample contained no quantum dots as there is no fluorescence. The 1 hour sample spectrum exhibits a symmetrical bell shape, except for the levels of the tails. This is probably because the spectrum was taken several weeks after the sample was grown and taken, and it is possible that some degradation of the samples occurred in that time, though there was no observed precipitation in these particular samples.

The initial sample does not have a fluorescent peak, so it does not have a full width half maximum. The 1-hour sample does, and it is shown in **Table 3**. The FWHM for the 1-hour

sample was found to be 58 nm, rather large for a quantum dot, but still narrow enough to be acceptable.

This batch was successful in proving that this method can be used to grow aqueous CdTe quantum dots for use in biological-type tests, and that the dots are functional.

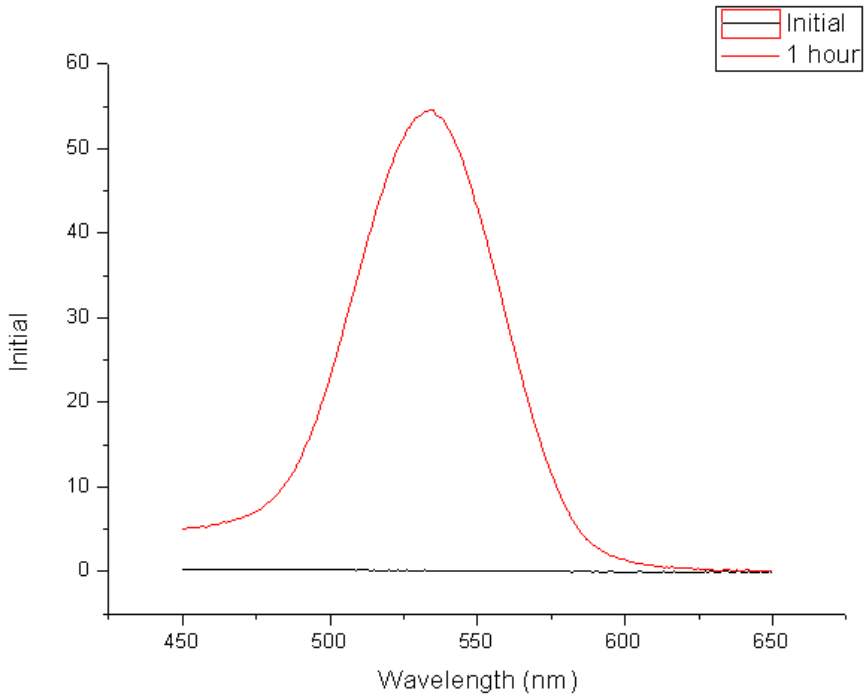

Figure 16 – Fluorescence spectrums from the batch made on October 29th. (Taken on November 23rd.)

Table 3 – Calculation of FWHM for October 29, 2010

Sample	Peak intensity	Peak Wavelength (nm)	Color	FWHM (nm)
Initial	-	-	-	-
1 hr	54	530	Green	58

4.2 November 2, 2010

The dots grown on Nov. 2nd were also made using just TGA as a buffer, though more samples were taken over time in order to get a more complete spectrum of the growth and fluorescence of these quantum dots. This batch was made using 2 M Te powder, and the amounts of the other chemicals were adjusted accordingly. Total solution volume started at ~200 mL. From this batch on the ratio Cd^{2+}:Te:(TGA, L-cys) = 3:1:6 was used. So this batch was made using 2 M Te, 6 M Cd-ion, and 12 M TGA in a 200 mL solution.

The color of the samples ranged from orange to yellow to a pinkish-orange. These dots were observed the same day to fluoresce from green to yellow under a UV light. While any range in color is good, this is not quite the green-to-red range that was hoped for.

The absorption spectrums (see **Figure 17**) show the desired trend, a single hump. The absorption for all samples is above that of the initial sample. Here for the first time it can be seen that absorption increases in intensity with increased growth time. The peak intensity wavelength also seems to increase until sometime between the 4 and 5 hour samples, at which point the peak wavelength blue-shifts.

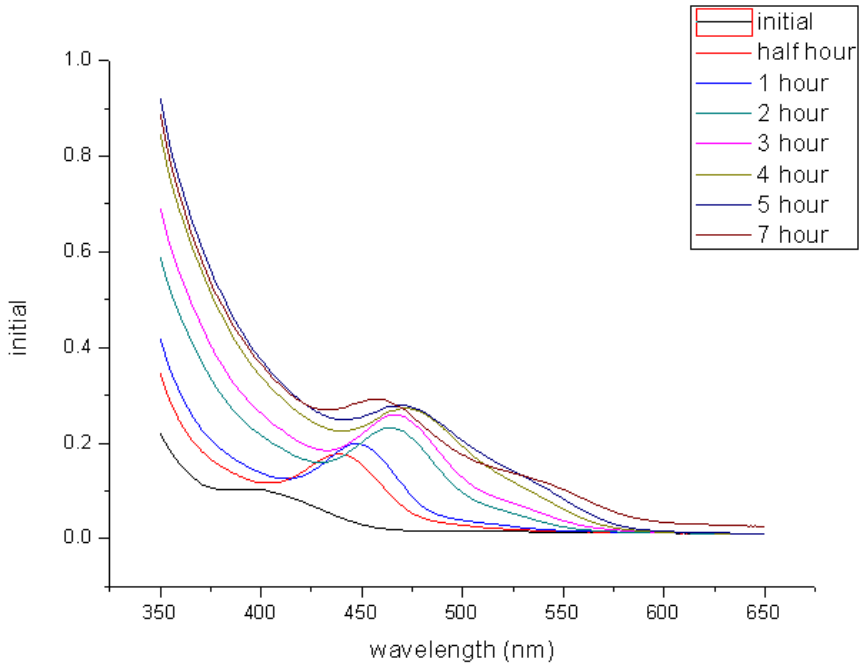

Figure 17 – Absorption spectrums for November 2nd batch. (Taken on November 12th.)

The fluorescence spectrums (see **Figure 18**) show the trend one would expect having seen the absorbance spectrums. The fluorescence increases in intensity until sometime between the 5 and 7 hour samples, and then decreases. And in this graph it can be seen that as the dots grow in size over time, the peak fluorescence wavelength is increasing from the green area towards the red, even when the intensity starts to decrease. This means that (for each buffer combination) there should be a time at which the highest intensity is achieved. It also means that in order to get a good range in fluorescence from green to red intensity must be sacrificed.

FWHM (see **Table 4**) for all these samples are around 60 nm. This is consistent with the October 29th batch. The shift in the peak wavelengths is about 3 nm up until the 3- hour sample, and then about 10 nm between samples after that. This means that the rapid growth at the beginning is quantum dots *forming*, but these particular dots don't start growing rapidly in size until after about 3 hours.

Table 4 – FWHM for the November 2nd batch.

Sample	Peak Intensity	Peak Wavelength (nm)	Color	FWHM (nm)
Initial	-	-	-	-
Half hr	13.5	508	Green	58
1 hr	37.5	510	Green	64
2 hr	173.5	12	Green	55
3 hr	243.6	515	Green	65

4 hr	498.9	528	Green	64
5 hr	576.8	538	Green	67
7 hr	395.8	547	Green	72

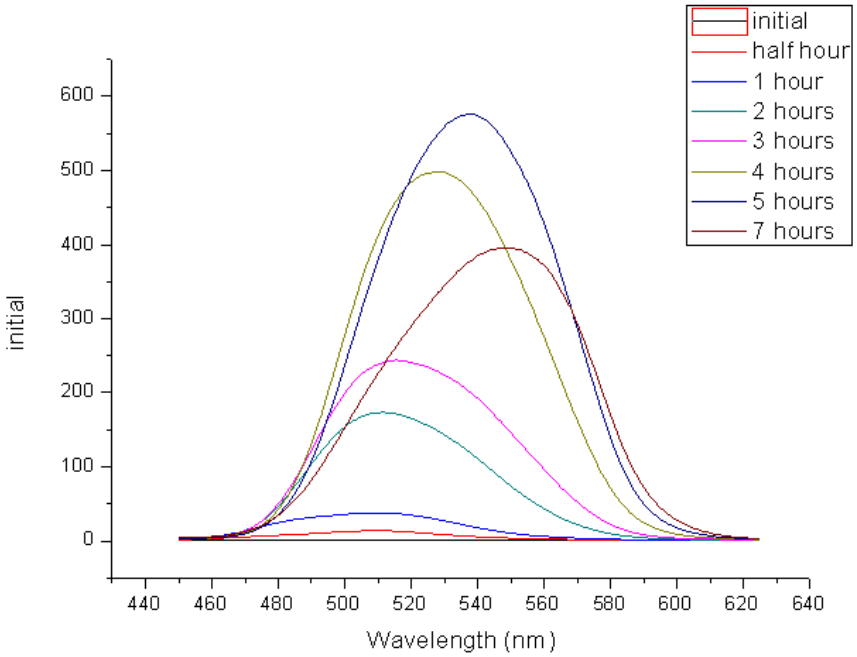

Figure 18 – Fluorescence spectrums for November 2nd. (Taken on November 23rd.)

4.3 November 5, 2010

These dots were made using just L-cys as a buffer/capping agent. They were also made using 2 M Te and a 200 mL volume. It must be noted that these dots were not made over the normal 2-day period. The NaHTe solution was mixed on November 3, 2010, and the Cd ion solution on November 4th. But due to time constraints, the solutions were not combined and heated until November 5th. It is possible that the extra day allowed more NaHTe to form then in other trials, facilitating the growth of more quantum dots, which would mean an artificial increase in fluorescence, relative to other trials. Also, in this case the L-cys was not dissolved before it was added to the Cd ion solution. It did dissolve in that solution, but because it did not dissolve before, this could mean that the L-cys did not react as fully as it might otherwise have done.

These dots grew *much* faster than the previous batch made using only TGA. When the 2 hour sample was taken a cloudy white sediment was observed in it, and the reaction was stopped.

The L-cys dots also had a much better color range, observed fluorescing from green to orange (or possibly red) under an UV light the same day. The visible colors of the samples themselves ranged from orange to a bright red (the 2 hour sample).

The absorption spectrums (see **Figure 19**) clearly show the correct shape, and absorption intensity is also much higher than that of the Nov. 2nd batch. These have peak intensities of up to

1.3, while the previous batch only reached 0.5. These samples are very distinct, and the growth within the first half hour appears to be extremely rapid.

The fluorescence spectrums (see **Figure 20**) show a much broader range in peak wavelength then the just-TGA samples from Nov. 2nd. The peak wavelength for the 2-hour sample is ~600 nm, while the 7 hour sample from Nov. 2nd only made it to ~560 nm. This implies that L-cys enables the QDs to grow faster than the TGA does.

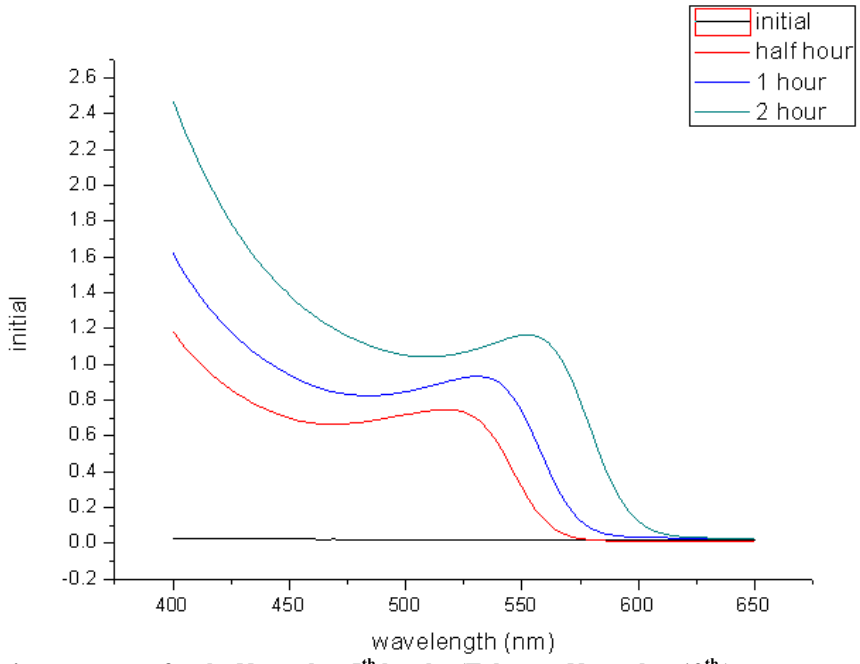

Figure 19 – Absorption spectrums for the November 5th batch. (Taken on November 12th.)

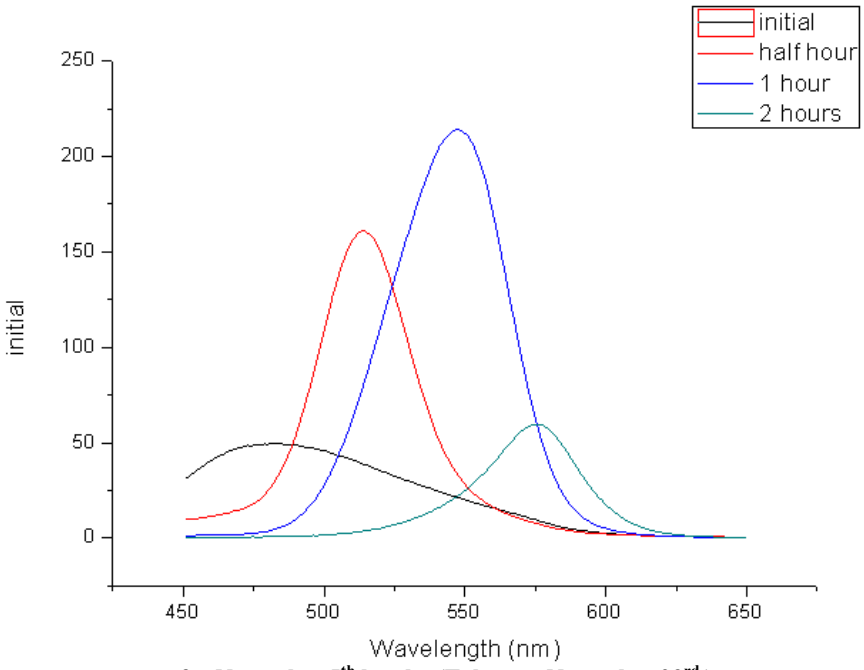

Figure 20 – Fluorescence spectrums for November 5th batch. (Taken on November 23rd.)

It should be noted that these fluorescence spectrums were taken 2 and a half weeks after the samples were obtained, by which point sample colors had faded, and black sediment had appeared in the initial, half-hour, and 1 hour samples. This means the samples had degraded and/or precipitated by this point. Sediment had been observed in the samples as early as Nov. 16th. The sediment and time gap possibly account for the fluorescence of the initial sample, seeing as how it has no absorption on Nov. 12th, meaning there were no dots in the sample. By Nov. 29th, the samples were observed to have almost no color, and all had a black sediment at the bottom.

Also, a significant portion of the 2 hour sample volume had been lost due to an attempt to dilute it to see if there was any observable effect on fluorescence (there was not). Because of this volume loss, the fluorescence spectrum for the 2-hour sample was difficult to take, and the intensity was decreased because of that. However, based on the unsaved fluorescent spectrum taken November 16, 2010 it is believed that the fluorescent intensity does decrease between the 1 and 2-hour mark.

These dots have smaller FWHM (see **Table 5**) then the previous batch (ignoring the initial sample). These have FWHM of 40 or 50 nm while the previous bunch was around 60 nm. The wavelength shift between the samples is about 30 nm. This is excellent, as it means the dots are growing in size very rapidly.

Table 5 – FWHM for the November 5th batch.

Sample	Peak Intensity	Peak Wavelength (nm)	Color	FWHM (nm)
Initial	49.2	479	Cyan	90
Half hr	161.2	514	Green	39
1 hr	214.0	547	Green	49
2 hr	59.8	576	Yellow	39

The initial sample has a peak even though there should be no quantum dots at that time. That sample also fluoresces cyan, a color that CdTe dots should not be able to achieve. This is possibly due to precipitate in the sample when the fluorescence spectrums were taken. It is also possible that these dots are growing so fast that in the few minutes it took to clean the pipette in order to take the initial sample, some dots (or perhaps proto-dots) grew. But again, this is a color CdTe dots simply cannot be. The initial sample was also observed to have very weak fluorescence under a UV light, and it is possible that it's not dots at all, and something else in the solution is fluorescing, such as reactants.

The overlying results of these data are that quantum dots grown with L-cys give a larger fluorescence color range, higher intensity, and faster growth than those dots grown with only TGA.

4.4 November 10, 2010

These dots were the first grown with a combination of the buffers. Equal proportions of the buffers were used, so TGA:L-cys = 1:1. However, the Cd^{2+}:Te:buffer ratio was kept at 3:1:6.

This batch was also made using 2 M Te, so 6 M of each buffer were added. For this batch also the L-cys was added directly to the Cd ion solution without being first dissolved.

Precipitate was observed in the samples from the 5-hour sample on. However this precipitate was not observed until after the samples had settled, as it did not appear to be the same precipitate as that of the Nov. 5th batch, and was much harder to see both in solution and in the samples.

The fluorescence color was observed on November 16th to be green for all samples except for the initial sample. It's not the desired color range. Samples were taken over 9 hours, and that means the rate of growth is extremely slow.

The absorption spectrums (see **Figure 21**) show the characteristic bump. What they also show is that the absorption peak wavelength and intensity are virtually unchanged from 1.5 hours to 9 hours. This is very discouraging, it means that the peak fluorescent wavelengths are also likely to be close, and thus there is almost no point to growing these dots for more than about 2 hours.

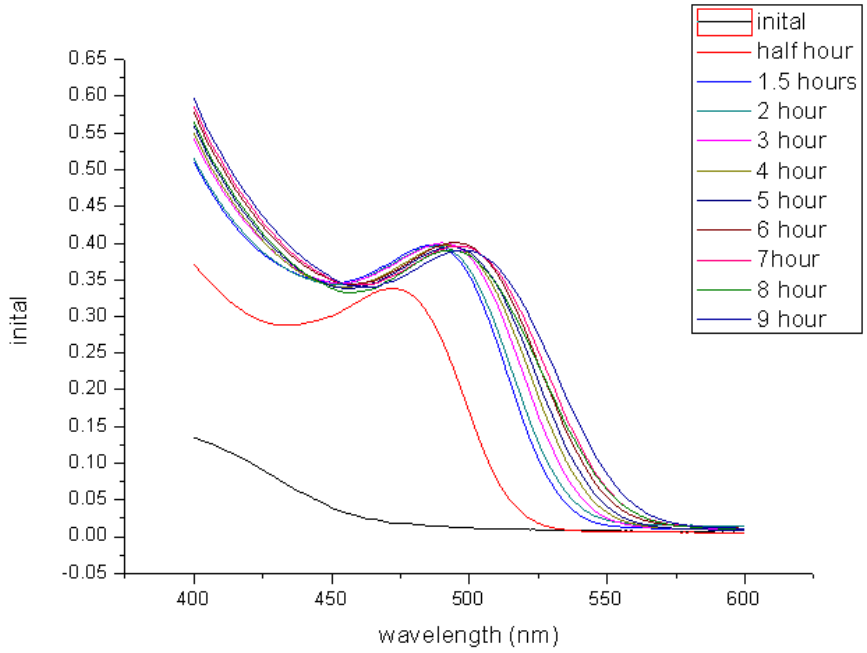

Figure 21 – Absorption spectrums for November 10th batch. (Taken November 12th)

The fluorescence spectrums (see **Figure 22**) show the results expected based on the absorption spectrums. There is very little change in the peak wavelength after 1.5 hours. It manages to move from 516 nm at 1.5 hours to 528 nm at 9 hours. This shows very little growth in that long time period. However, the intensity does increase. This means that if high intensity is important, it is worth it to grow these dots for about 6 hours, as that is when the peak intensity occurs.

Oddly, the 8-hour sample has blue-shifted and decreased in intensity from the 7-hour sample (see **Table 6**). This was seen in a few other batches, and it is expected that this is an anomaly, as the 9-hour sample fits with the wavelength trend of the other samples.

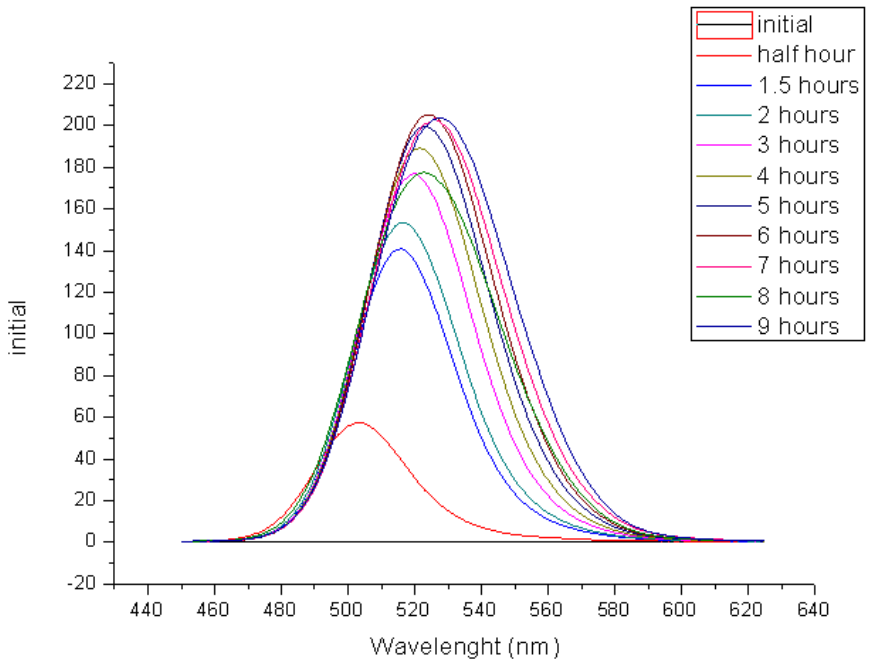

Figure 22 – Fluorescence spectrums for November 10th batch. (Taken on November 26th.) Note: the intensity of some of the samples was higher than the spectrometer could measure, resulting in a plateau instead of a peak, so the spectrums were redone at a lower light intensity.

These dots have a FWHM (see **Table 6**) range comparable to those of Nov. 5th, ranging from less than 40 nm to about 50 nm. The fluorescence spectrums were redone because the intensities were too high for the spectrophotometer to measure at the same settings as the other trials. However, for the samples for which the spectrums taken on November 23rd did have peaks, some of the peak wavelengths blue-shifted on Nov. 26th, but only by about 1 or 2 nm so the results can be assumed to be about the same. As expected, the shift between peak wavelengths after the first hour and a half is very small, meaning that while the dots are increasing in quantity, the sizes are about the same after this time.

Table 6 – FWHM for November 10th batch. Calculations were made using the data from the spectrums at the lower light intensity.

Sample	Peak Intensity	Peak Wavelength (nm)	Color	FWHM (nm)
Initial	-	-	-	-
Half hr	57.3	503	Green	33
1.5 hr	140.8	516	Green	36
2 hr	153.5	516	Green	38
3 hr	177.2	520	Green	40
4 hr	189.0	521	Green	41
5 hr	199.7	524	Green	43
6 hr	205.3	525	Green	43
7 hr	203.4	526	Green	46
8 hr	177.7	523	Green	49
9 hr	203.6	528	Green	49.5

4.5 November 11, 2010

These dots were grown with a TGA:L-cys ratio of 1:3, to see if more L-cys really does grow better dots. These dots were made with 2 M Te powder, and the accompanying ratio of Cd^{2+}:Te:(TGA, L-cys) = 3:1:6, meaning they were made with 3 M TGA and 9 M L-cys. Also, these dots were grown using a NaHTe solution that was made on Nov. 9th, as opposed to the day before, so there may be effects from the solution being left to complete for a longer time period, such as an increased amount of quantum dots formed. The NaHTe solution itself appeared to be a much darker purple than usual.

This test was also an instance when the Cd ion solution did not clear as NaOH was added, and a pH of about 13 was seen. The goal of this batch was originally to have a run with Cd^{2+}:Te:buffer = 3:1:3 and TGA:L-cys = 1:1, but when the pH became so low, more L-cys was added to increase the acidity, and changed the ratios to those listed in the previous paragraph. The pH was still below 12, and so HCl was added to make the solution more acidic, and water was added to increase the volume to ~200 mL, yielding a final pH of 10.87.

When the NaHTe was added to the Cd ion solution, it made it purplish-blood-orange and much darker than usual. But by a half hour of growth, the color had lightened to be comparable to the other samples. This run, like the just-L-cys test of Nov. 5th, was also observed to have a precipitate very quickly. Possibly after an hour, and definitely after two, a precipitate was observed and the experiment was stopped.

Samples had a visible color from brownish-orange to yellow and back to a reddish-orange. Samples were observed on November 16th to fluoresce from teal to yellow under an UV light. Again, the teal color is unexpected, and CdTe quantum dots should not be able to form at a size small enough to achieve this color.

The absorption spectrums (see **Figure 23**) again show the correct shape, and it can even be seen in the half hour sample, showing just how quickly the dots were growing. These dots do not have the much higher absorbance of the Nov. 5th dots, possibly because of the TGA.

Again, the fluorescence spectrums (see **Figure 24**) show data very similar to that of the Nov. 5th dots. The symmetrical bell shape can be seen in all the spectrums. The half hour sample has remarkably low intensity when compared to the others. This would imply that L-cys makes the dots grow very fast, while TGA slows growth at the beginning. There is a decrease in fluorescent intensity by about a third between the 1-hour and 2-hour samples, though the peak wavelength has red-shifted significantly. This supports previous conclusions that, after a point, in order to get the longer wave-length dots, intensity will be lowered.

FWHM values (see **Table 7**) are nice and tight, all are below 50 nm. The spectrums at lower intensity were observed to have blue-shifted by about 4 nm from the spectrums taken on November 23rd, as this was another batch that had to be retaken at a lower light intensity. These results are still felt to be accurate. Again, the initial sample did not have a fluorescent peak. The shift between peak wavelengths, at 30 nm, is very large.

The fluorescent range for these samples under a UV light was the most interesting of all. The 1-hour sample was green, and the 2-hour was yellow, a lovely range for dots grown so quickly. But, the half hour sample appeared teal under the UV light. Given that growth of the dots seems to be very slow at this point, it is possible that these are not CdTe dots fluorescing teal, but some sort of precursors or partially formed dots.

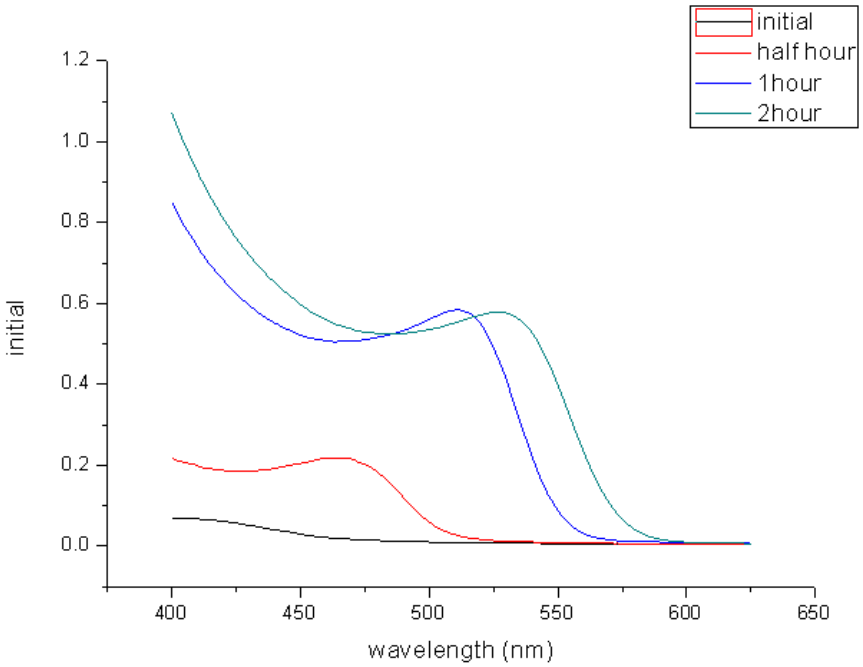

Figure 23 – Absorption spectrums for November 11th batch. (Taken on November 12th.)

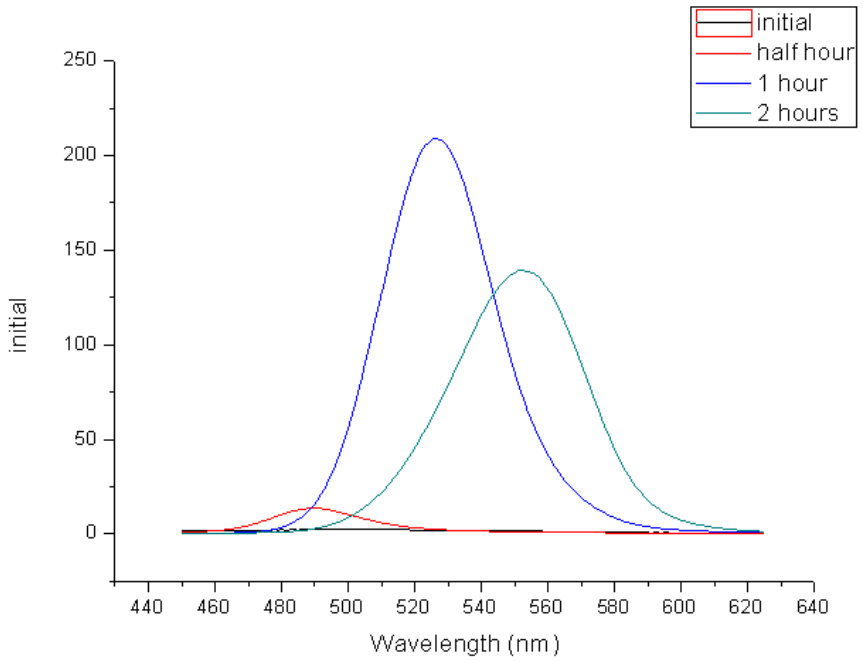

Figure 24 – Fluorescence spectrums for November 11th batch. (Taken on November 26th.) Note: these spectrums were also taken at a lower light intensity, as the 1-hour sample plateaued above the range the spectrometer could measure.

Table 7 – FWHM for November 11th batch. Calculations were made based on the fluorescence spectrums taken at the lower light intensity.

Sample	Peak Intensity	Peak Wavelength (nm)	Color	FWHM (nm)
Initial	-	-	-	-
Half hr	13.4	489	Cyan	34
1 hr	209.4	526	Green	40
2 hr	139.2	551	Green	46

4.6 November 12, 2010

This run was the first repeat of a previous run. The ratio TGA:L-cys = 1:1 was used again, but this time the dots were grown with a solution made with 1 M Te powder and an initial volume of ~100 mL. Comparing this batch and that of Nov. 10th would be an effective way to see if having more raw ingredients has any effect on the growth. Due to time constraints, the second sample was taken after 10 minutes instead of 30, and the data shows that this is too early for dots to have grown (see **Figure 26**), as this sample is closer in characteristics to the initial sample in both absorption and fluorescence.

The samples had visible colors starting at a very light, clear yellow, and working through orange to a pink-orange. Samples were observed on Nov. 16th to fluoresce from green to yellow under an UV light – a decent range.

The absorption spectrums (see **Figure 25**) show the desired 1-hump shape, and the peak intensity increases and red-shifts nicely. But the spectrums do not asymptote at 0, as all the previous batches have. It is unknown why this has happened, or what it means, however it is not believed that it has a significant effect on the results.

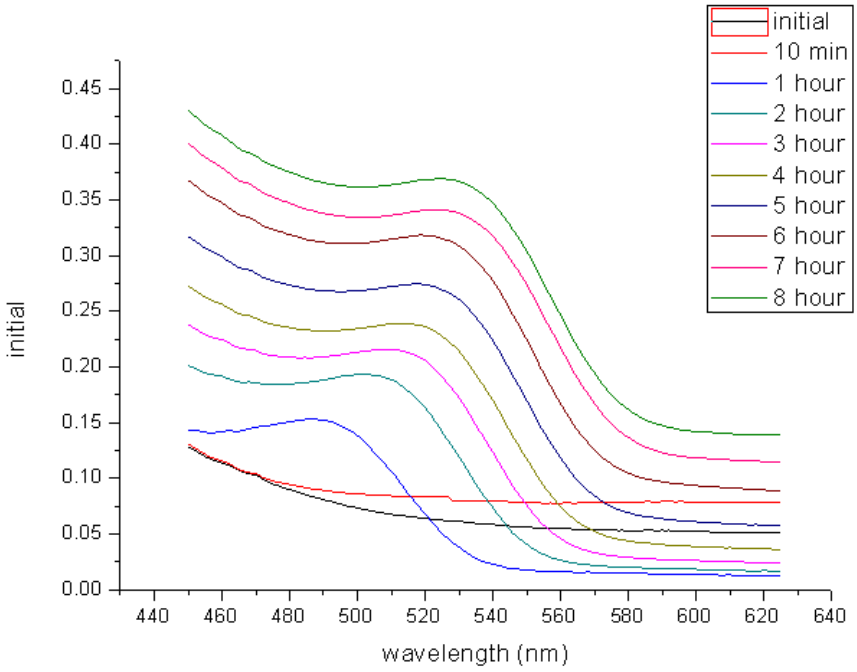

Figure 25 – Absorption spectrums for November 12th batch. (Taken on November 12th.)

Figure 26 shows dramatically how the fluorescence intensity increases the longer the samples grow, and after 8 hours, there is not observable drop in intensity. The peak wavelength is also shifting nicely from 512 nm to 549 nm (see **Table 8**), although the shifts get rather small between the 4- and 5-hour samples. The intensity trend suggests that these particular dots could be grown for many more hours before the fluorescence intensity becomes too low, but the wavelength shifts suggests that they might not get much further then 570 nm. This is a situation in which it must be decided if it is worth the time to wait longer for a higher intensity.

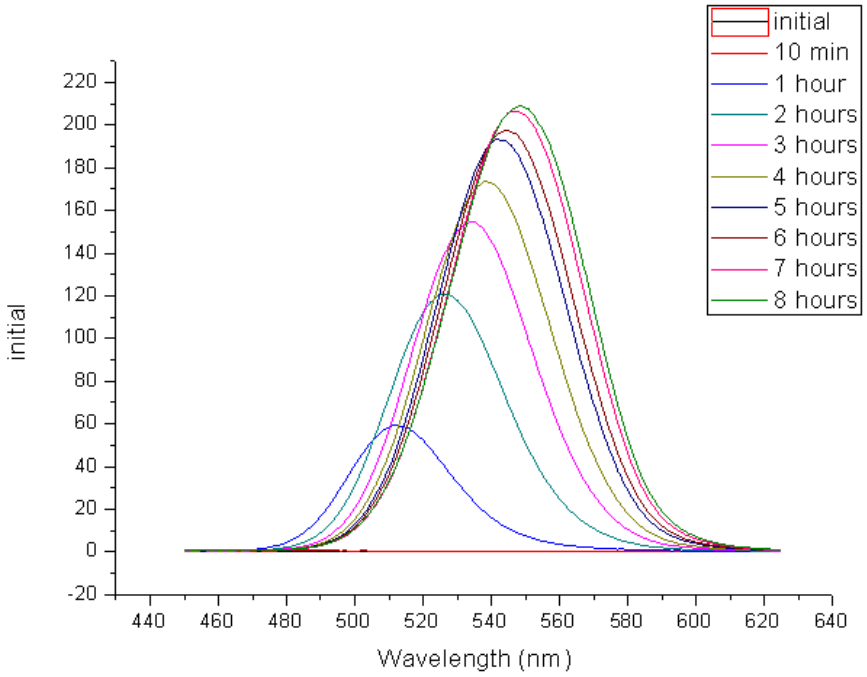

Figure 26 – Fluorescence spectrums for November 12th batch. (Taken on November 26th.) Note: these spectrums were taken at a lower light intensity due to plateauing above the range of the spectrometer.

The FWHM (see **Table 8**) for the samples are generally between about 40 and 45 nm. The shift between peak wavelengths is very high at first, about 10 nm, but then decreases to about 2 nm after 5 hours. This means the dots are growing rapidly in both quantity and size, and then the growth of both slows around 5 hours.

These dots have properties very close to the 2 M dots grown on Nov. 10th. The Nov. 10th dots do have much faster growth initially (as can be seen by the higher comparative fluorescent intensity in earlier samples), but in the Nov. 10th samples the peak wavelengths settle very quickly, and only varied from 520 to about 530 nm over 9 hours, while the Nov. 12th samples reached 550 nm in 8.

This could imply that more materials yields more dots faster, but that growth, for all intents and purposes, is finished quicker as well. This would mean that the rate of reaction is dependent in part on the concentration of the components, in addition to ratios and time.

Table 8 – FWHM for the November 12th batch. Calculations made based on fluorescence spectrums taken at lower light intensity. In this case, the 10-min sample also did not have a peak.

Sample	Peak Intensity	Peak Wavelength (nm)	Color	FWHM (nm)
Initial	-	-	-	-
10 min	-	-	-	-
1 hr	59.3	512	Green	35
2 hr	120.9	527	Green	40
3 hr	154.7	535	Green	41.5
4 hr	173.6	538	Green	43
5 hr	193.1	542	Green	44
6 hr	197.5	545	Green	45
7 hr	206.6	547	Green	46
8 hr	209.1	549	Green	46.9

4.7 November 16, 2010

These dots finished out the spectrum of dots with more L-cys, as they were grown with 1 M Te and TGA:L-cys = 1:2. Also, the 10.5 hour sample is a bit of an anomaly, as the heater had been turned off about half an hour before that sample was taken, so it cannot be easily compared with the other samples. And again, the half hour sample was taken too quickly, this time after 15 minutes of growth. The results show that for this ratio this is not enough time for any dots to have grown (see **Figures 27 and 28**).

The solution started very dark, a purple-brown-orange again, but had lightened to an orange after 15 minutes. It eventually darkened to a red color. The first samples visibly were a dark orange. After that they lightened to yellow, and then darkened to orange again.

The samples were found to fluoresce from green to yellow under a UV light on Nov. 16th. This is not quite the range hoped for, and should be reflected in peak fluorescence wavelengths bellow 600 nm.

The absorption spectrums (see **Figure 27**) all exhibit the hump shape, but the intensity is about the same for all of them. This trend was seen in the spectrums for the Nov. 10th dots, which had a TGA:L-cys ratio of 1:1. This would imply that the more TGA in the dots, the closer the absorption spectrum peak intensities will be.

The fluorescence spectrums (see **Figure 28**) show beautiful bell shapes, both in the samples themselves and combined. The graph demonstrates how very smoothly the intensity rises and then falls (around 4 hours of growth), with the peak wavelength increasing all the while. The spectrum trends also fit between those of the 1:3 batch (Nov. 11th) and the 1:1 batch (Nov. 12th). From the spectrums it can be seen that while growth is slow, there is still a significant shift in the peak wavelength over time. Also, the intensity starts to fall after some point, as was seen in the 1:3 samples and had not yet happened in the 1:1 samples.

These samples also have very good FWHM (see **Table 9**), from about 40 to 45 nm. The exception is the 5-hr sample, which has a FWHM of 54 nm. Shift between the peak wavelengths

at ~10 nm is relatively good for the first 4 hours. After that, the shifts are closer to 5 nm, which does not bode well for making it to the red zone.

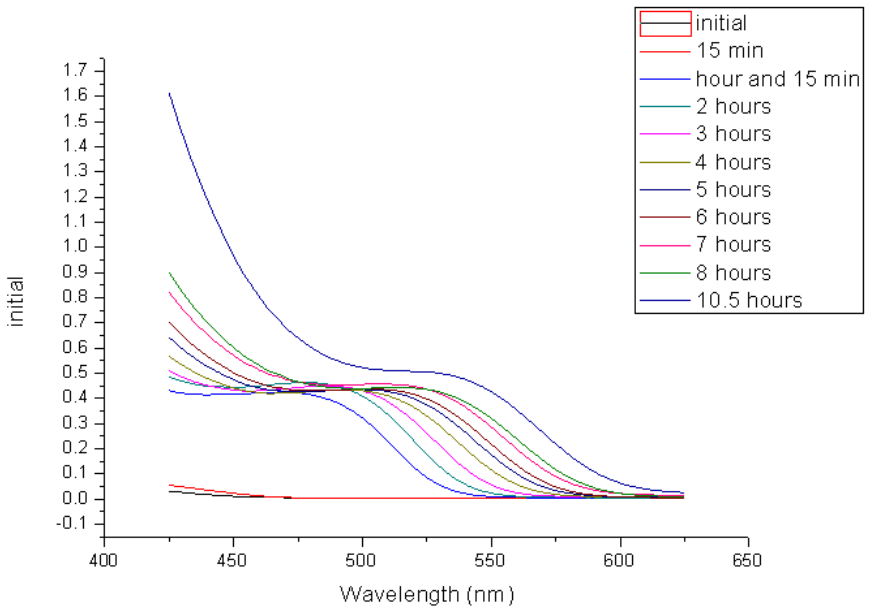

Figure 27 – Absorption spectrums for November 16th batch. (Taken on November 26th.)

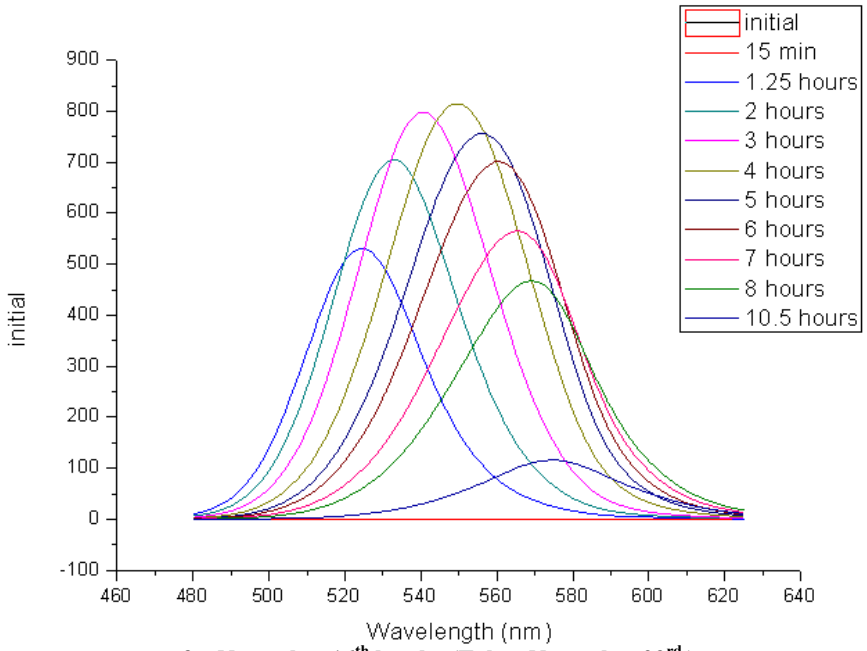

Figure 28 – Fluorescence spectrums for November 16th batch. (Taken November 23rd.)

Up to this point, this method (1 M Te, TGA:L-cys = 1:2) seems to be one of the best, along with the 1:1 batches. It gives high intensity and variation in growth. It's true that the dots grown with more L-cys got further towards the red area then these did, but these samples did not show any precipitates.

Table 9 – FWHM for November 16th batch. The 15-min sample also does not have a fluorescent peak.

Sample	Peak Intensity	Peak Wavelength (nm)	Color	FWHM (nm)
Initial	-	-	-	-
15 min	-	-	-	-
1.25 hr	530.5	524	Green	36.5
2 hr	704.5	533	Green	39
3 hr	797	541	Green	42
4 hr	814.8	550	Green	44
5 hr	757	557	Green	54
6 hr	702	560	Green	44
7 hr	565	566	Green	44
8 hr	468	569	Green	44
10.5 hr	116	574	Yellow	45

4.8 November 18, 2010

To complete the spectrum of buffer ratios, dots with more TGA then L-cys were grown. This batch has a ratio of TGA:L-cys = 2:1, and was made with 1 M Te and a volume of ~100 mL.

The visible sample colors ranged from light yellow to light orange. Suspect the lighter color is because of the increased TGA. It was a trend in the previous batches that the more L-cys they had, the darker and redder the sample and batch colors got.

The absorption spectrums (see **Figure 29**) exhibit characteristics close to the Nov. 2nd samples, which were grown with just TGA. The bump is definitely present in each spectrum, but the absorbance is very low. The bump is also not as accentuated as it is in some of the spectrums from samples containing more L-cys, such as those from November 11th (see **Figure 23**). The spectrums also show the correct trend in sequence, with the peak wavelength red-shifting.

The 12-hour sample seems to be almost in sequence after the 5-hour sample, despite the 7 hour gap between them. This means that though the growth appears fairly constant for the first five hours it decreased rapidly after that. Another possible explanation is that the 12-hour sample has blue-shifted, which was also seen in the absorption spectrums for the November 12th samples (see **Figure 25**).

The fluorescence spectrums (see **Figure 30**) show very nice narrow, bell-shaped curves. And they also show constant growth over the first 5 hours, as expected from the absorption spectrums. The shifts between peak wavelengths are not fantastic, ranging from 499 nm at half an hour to 536 nm at five hours.

As was suspected from the absorption spectrums, there is not a great peak wavelength shift between the 5- and 12-hour samples (see **Table 10**). Nor is there a great decrease in fluorescence. This suggests that fluorescent intensity would continue to increase after 5 hours of growth before decreasing. It also means that the growth rate decreases sometime after the first 5 hours, and that dots fluorescing in the red range probably cannot be achieved with this particular combination.

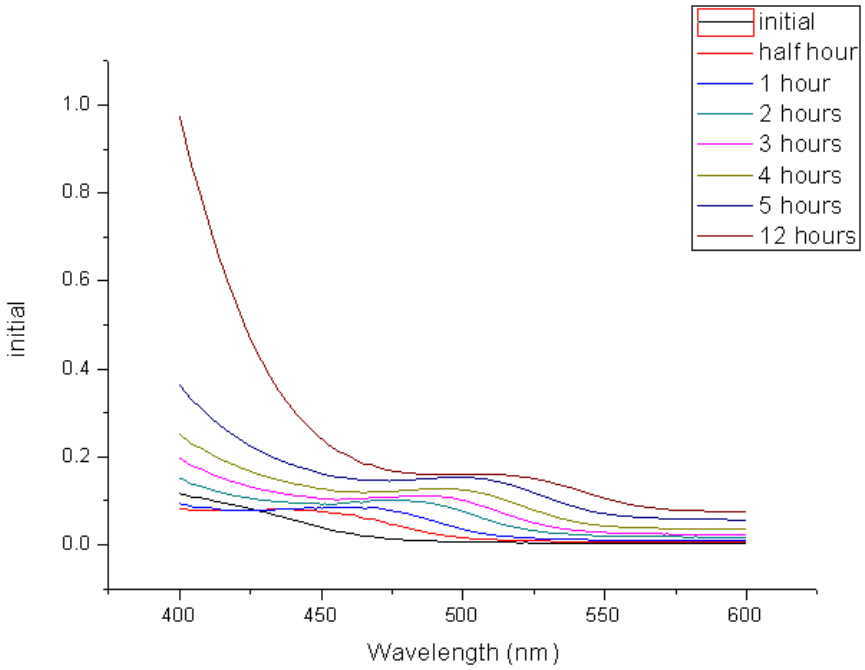

Figure 29 – Absorption spectrums for November 18th batch. (Taken on November 26th.)

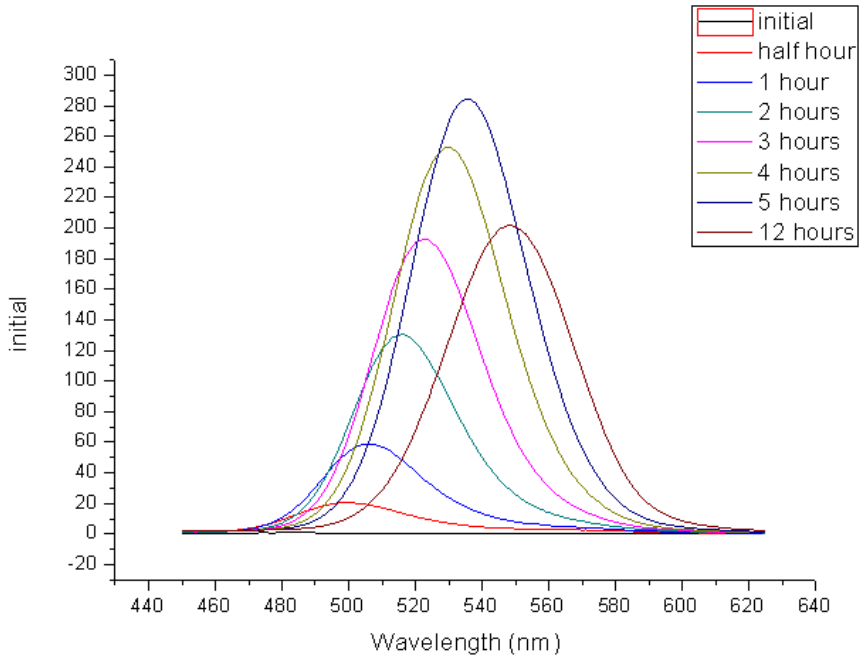

Figure 30 – Fluorescence spectrums for November 18th batch. (Taken November 24th.)

These dots show the smallest FWHM (see **Table 10**) so far, with most at or below 40 nm. The wavelength shift is about 7 nm. But, it's only 13 nm between the last two samples, which covers 7 hours. This means that the growth rate of the size has slowed down significantly over this time period.

As had been found previously in batches with larger proportions of TGA, the color range is not all that great. These dots would all fluoresce green in UV light, virtually indistinguishable from

each other to the human eye. However, a spectrometer would be able to tell the difference between the dots, as is shown above.

Table 10 – FWHM for November 18th batch.

Sample	Peak Intensity	Peak Wavelength (nm)	Color	FWHM (nm)
Initial	-	-	-	-
Half hr	20	499	Green	40
1 hr	58	506	Green	36
2 hr	130	515	Green	37
3 hr	192	523	Green	38.5
4 hr	253	530	Green	39.5
5 hr	284	536	Green	41
12 hr	201	549	Green	45

4.9 November 23, 2010

This batch of dots completes the whole buffer spectrum. The TGA:L-cys ratio used was 3:1. 1 M Te powder was used and the initial solution volume was ~100 mL. As expected, these dots grew slowly over a long period of time, and no precipitate was ever observed.

Visible sample colors ranged from orange at the beginning to yellow and then back to orange. This follows the previously established trend of dark initial color, then lightening within the first 15 to 20 minutes, and then darkening again over time.

The absorption spectrums (see **Figure 31**) are similar to those of November 18th, but more pronounced. The absorptive intensity of this batch is slightly higher, reaching 0.3 as opposed to 0.2. It is interesting to see that the spectrums of the first three samples are decreasing before the trend really becomes the proper trend. This may be because growth was so slow that these samples have unreacted TGA in them, and there are simply not enough quantum dots in the samples to show the quantum dot spectrum trend. The rest of the samples have the expected trend, with the peak wavelength shifting towards red and increasing in intensity.

The fluorescence spectrums (see **Figure 32**) show the expected trend, a symmetrical, bell-shaped curve. The first three samples also have very low intensity, as was expected from the absorption spectrums, meaning there is a very small amount of quantum dots in each sample. The spectrums for the last three samples were taken on a different day then the first nine, but they still appear to fit the growth trend when this discrepancy is taken into account.

The only anomaly is the 9-hour sample, which has decreased fluorescence when compared to the 8.5-hour sample (see **Table 11**). This normally would be fine, many batches have shown that fluorescence eventually decreases over time. However, the 10-hour sample has the highest fluorescent intensity of all of them, meaning that the intensity for the 9-hour sample should be higher than that of the 8.5-hour sample. The absorption spectrums seem to support this growth theory, so it is assumed that there was some error in the fluorescence spectrum for the 9-hour sample, and that the growth trends are upheld.

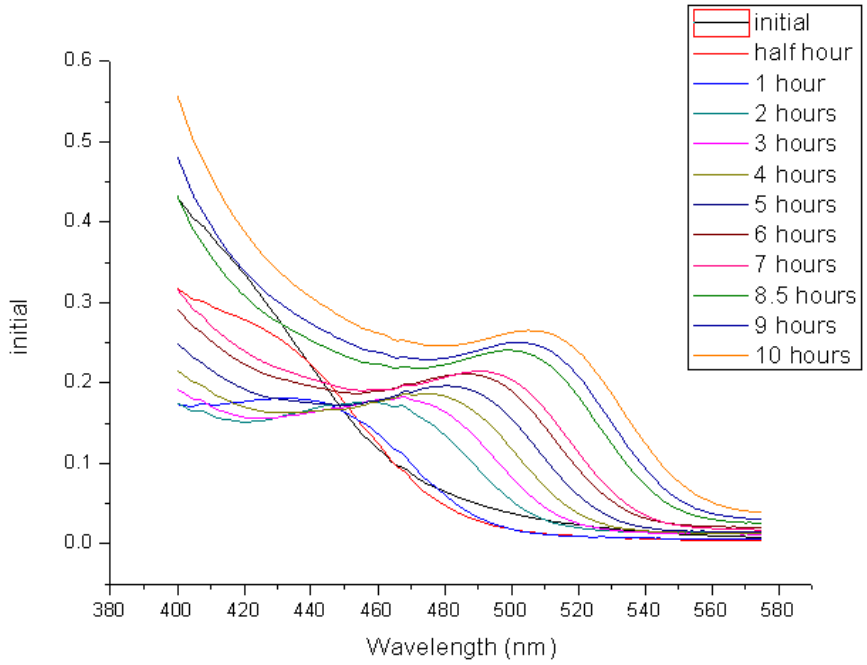

Figure 31 – Absorption spectrums for November 23rd batch. (Taken on November 26th.)

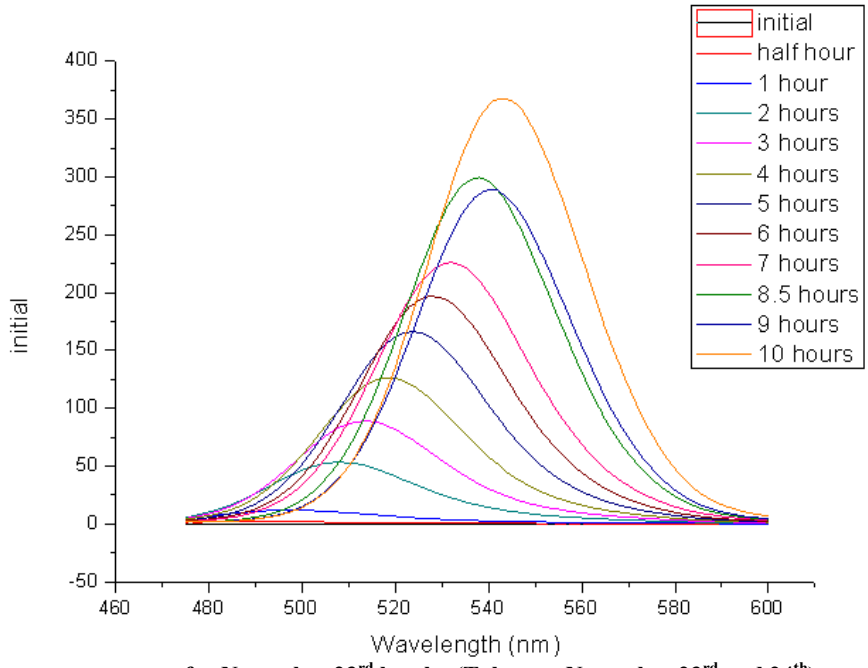

Figure 32 – Fluorescence spectrums for November 23rd batch. (Taken on November 23rd and 24th)

The FWHM (see **Table 11**) for these dots are very consistent and low, hovering around 39 nm for all of them. Again, the only thing out of the ordinary is the lower intensity of the 9-hour sample when compared to the 8.5- and 10-hour samples. The wavelength shifts are also rather small, shifting about 5 nm every hour. This is not a fast enough growth rate to give the color range that is desired.

Table 11 – FWHM for November 23rd batch.

Sample	Peak Intensity	Peak Wavelength (nm)	Color	FWHM (nm)
Initial	-	-	-	-
Half hr	-	-	-	-
1 hr	11.9	497	Green	43
2 hr	53.4	508	Green	39
3 hr	89	513	Green	37.5
4 hr	126	518	Green	38
5 hr	165	523	Green	39
6 hr	196	528	Green	39
7 hr	226	532	Green	39
8.5 hr	299.2	538	Green	39
9 hr	289.2	540	Green	39
10 hr	368	543	Green	40

4.10 November 25, 2010

Since the TGA:L-cys ratio spectrum was complete, a repeat of a previous trial was performed. Attempting to better understand the growth rate of the fastest growing batch, the TGA:L-cys = 1:3 batch was repeated, but this time at 1 M Te instead of 2 M.

Samples were taken more often, about every 5 minutes, in an attempt to observe the growth rates over the first hour. Unfortunately, this did not take solution volume into account. The solution was only ~100 mL, and samples are about 3 mL. This means 6 samples every half hour = 18 mL, or about 1/5th of the total volume. This means that while the earlier results are probably accurate, the later ones show effects of the volume of the solution being drastically reduced.

Due to the volume of samples taken, the key for both the absorption and fluorescence graphs was cut off. The last two samples were taken at 180 and 211 minutes, and are shown by the last green and blue lines, respectively, in both graphs.

The samples show the expected absorption trend (see **Figure 33**), though they are all very close, as is usually only observed in the batches grown with more TGA. This is explained by the fact that these samples were taken over much more frequent intervals, so growth between samples is much smaller. These spectrums were expected to be like those of the Nov. 11th batch. In that graph, the 1- and 2-hour samples show no increase in intensity, just a red-shift in the peak wavelength. So these dots probably are following the expected trend.

It can also be seen that the samples for 5- and 10-minutes are close to that of the initial sample. The 10-minute sample shows some presence of quantum dots, though there really is not a significant amount until the 15-minute sample. But previous trials have shown that 15 minutes is not enough time for significant growth of quantum dots to occur. However, those batches had a lower ratio of L-cys, so the increased growth observed at 15-min may be due to the faster growth from higher concentrations of L-cys.

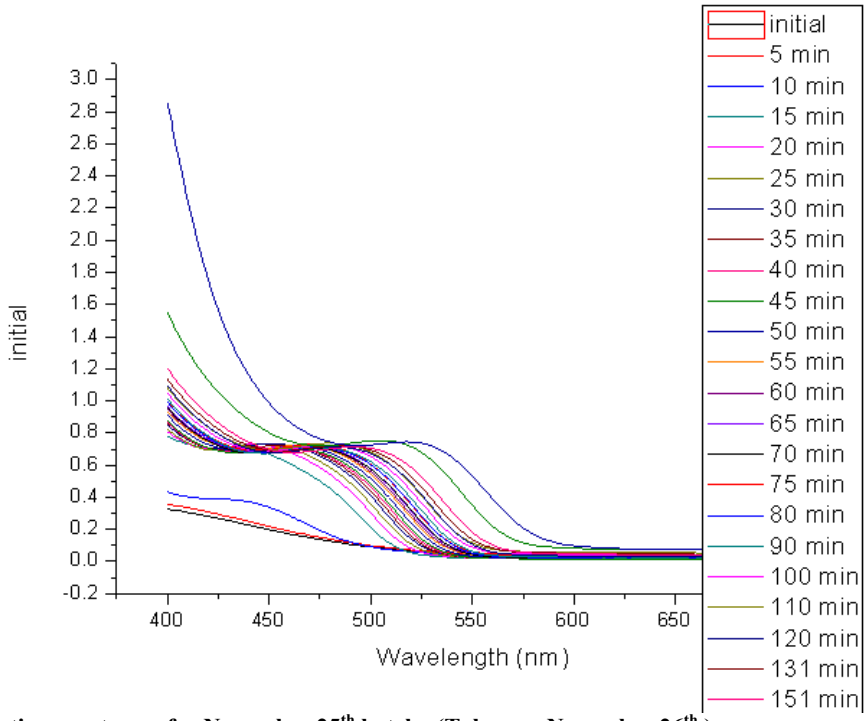

Figure 33 – Absorption spectrums for November 25th batch. (Taken on November 26th.)

The fluorescence spectrums (see **Figure 34**) show wonderfully narrow bell-shaped curves, as would be expected from quantum dots. It shows a smooth rate of growth and an increase in fluorescent intensity, though the red-shifting is perhaps not as great as was desired, but comparable to those achieved by the Nov. 11th batch. After about an hour of growth, the differences between the spectrums get sketchy, although the time between samples remains fairly consistent though it has increased from 5 minutes to 10 minutes. There is also a sizable gap between the 45- and 50-minute samples. The last few samples show a drastic decrease in fluorescent intensity, though growth of the dots continues.

It should be noted that samples were taken until the solution ran out of volume, so the intensity was probably affected by the fact that the same amount of heat was being applied to a much smaller volume. The first three samples show the results expected from the absorbance graph – that there is not a significant amount of quantum dots in this batch until about 15 minutes of growth.

Visible sample color ranged from orange to yellow and back through orange to a reddish-orange.

These spectrums all have nice tight FWHM (see **Table 12**). They start at 35 nm and go to 45 nm. This is slightly better then what has been achieved so far. It is possible that the narrower curves are because these spectrums were taken the same day. The wavelength shifts are very small, only a couple of nm. But this is to be expected as many of the samples are only 5 minutes apart, leaving little time for growth. But even towards the end, when the samples are taken 10 and 20 and 30 minutes apart, the wavelength shifts are still very small. This means that as the volume of the solution decreased, the growth of the dots slowed drastically. These dots reached

a wavelength about 10 nm larger than the Nov. 11th dots. But these dots grew for almost another hour and a half, and at 2 hours had not reached the size of the dots in the Nov. 11th batch, possibly due to the decreased growth rates as the solution volume decreased.

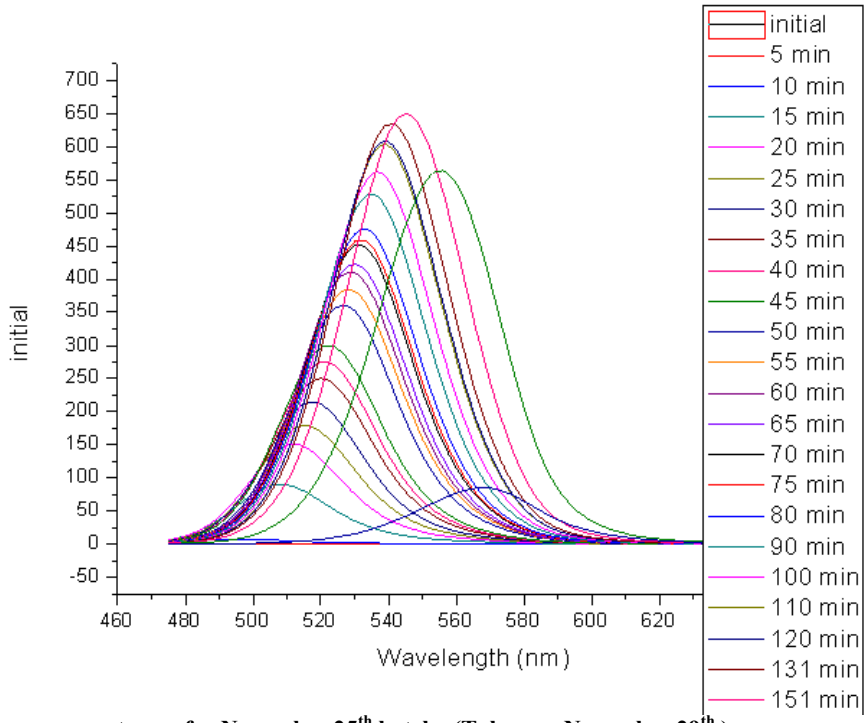

Figure 34 – Fluorescence spectrums for November 25th batch. (Taken on November 29th.)

Table 12 – FWHM for November 25th batch.

Sample	Peak Intensity	Peak Wavelength (nm)	Color	FWHM (nm)
Initial	-	-	-	-
5 min	-	-	-	-
10 min	8.1	493	Green	45
15 min	90.4	507	Green	34
20 min	150.9	512	Green	34
25 min	179.1	515	Green	35
30 min	214.6	517	Green	35
35 min	250.4	520	Green	35.5
40 min	275.3	522	Green	36
45 min	299.8	521	Green	36
50 min	360.7	527	Green	36.5
55 min	383.8	528	Green	37.2
60 min	410.1	529	Green	37
65 min	422.7	530	Green	37
70 min	452	531	Green	37.5
75 min	459.1	532	Green	37.7
80 min	475.7	533	Green	38
90 min	527.9	534	Green	38.5
100 min	561.3	537	Green	38.9

110 min	603.9	539	Green	39.5
120 min	608.4	539	Green	39
131 min	634.4	541	Green	40
151 min	648.6	545	Green	41
180 min	563.5	556	Green	42.5
211 min	85.3	567	Green	43

4.11 November 30, 2010

The trial made with just L-cys was repeated, in an attempt to replicate the results from November 5th. 1 M Te powder was used with a solution volume of ~100 mL. Samples were also taken more often, but this time it was about every 15 minutes. This way, there would be enough solution left that the results would not be affected by the change in volume, and the growth rate could still be studied.

Visible sample color ranged from golden-orange to reddish-orange to blood-orange. Samples and solution were always very dark, supporting previous conclusion that L-cys makes the visible color darker.

Unfortunately, absorbance spectrums were not taken for the samples from the second hour of growth. However, the spectrums taken seem to show the correct and expected trend (see **Figure 35**). Just as was seen in the Nov. 5th batch, these spectrums show one very pronounced hump. The difference is that these spectrums show a constant intensity after about half an hour, while the Nov. 5th trial showed increasing intensity.

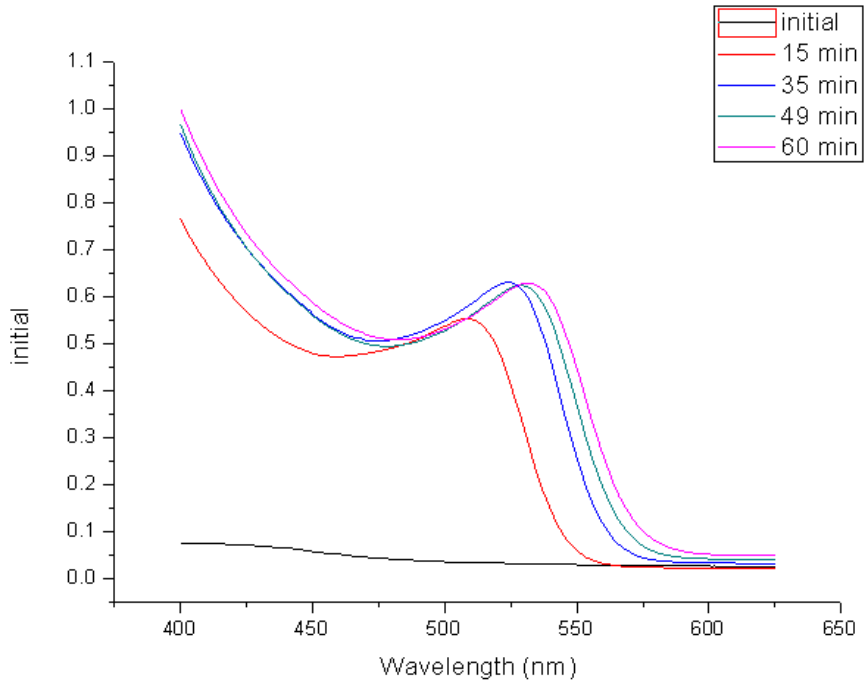

Figure 35 – Absorption spectrums for November 30th batch. (Taken on December 1st.)

The fluorescence spectrums (see **Figure 36**) show nice narrow, symmetrical spectrums. They are wider than those of the 25th. There seems to be a change in the growth rate after the first hour, The change in intensity between samples gets much smaller, though the change in peak wavelength is really about the same (3 to 5 nm) (see **Table** 13). There is an anomaly in these spectrums as well. The 78-minute sample has fluorescent intensity similar to that of the 35-minute sample, though its peak wavelength is between that of the 60- and 98-minute samples.

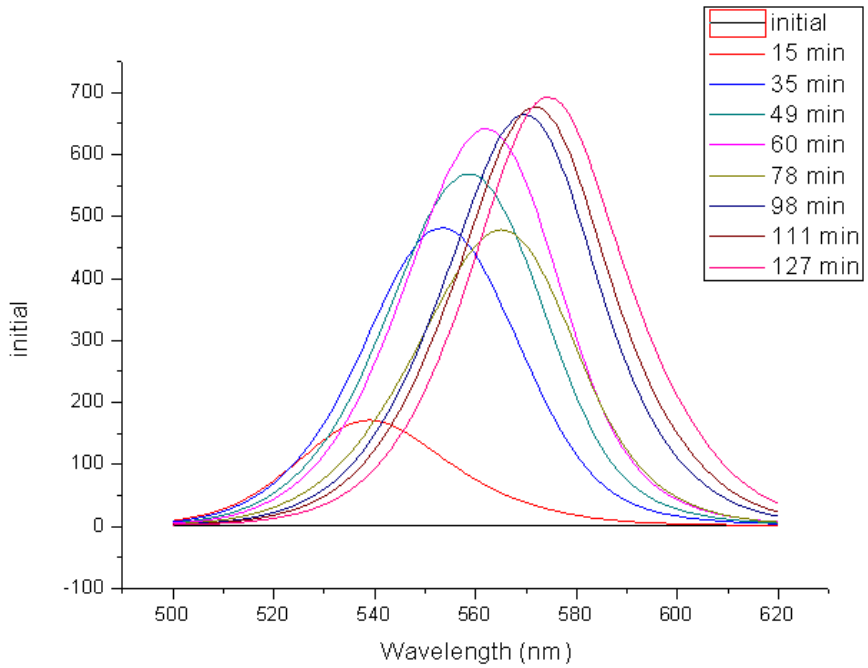

Figure 36 – Fluorescence spectrums for November 30th batch. (Taken on December 1st.)

These FWHM (see **Table 13**) are also nice and low, like those of the previous batch. And these dots actually managed to get into the yellow fluorescence range, which not many batches did. The smaller FWHM means that the range of sizes within each sample is smaller, meaning the samples consist mostly of dots with sizes close to that of the fluorescence peak. However, the shift between the peak wavelengths is relatively small. The largest is the 20 nm shift between the 15 and 35 min samples. The rest of the shifts are only a couple of nm, resulting in only a 45 nm shift between the 15 min and 2-hour samples.

The 15-minutes spectrum shows that some quantum dots have grown by this point, but that there is still rapid growth for the remainder of the first half hour. Perhaps to get a better sense of growth, samples should be taken at 15 minutes, 30 minutes, and then on the hour from then on.

Table 13 – FWHM for November 30th batch.

Sample	Peak Intensity	Peak Wavelength (nm)	Color	FWHM (nm)
Initial	-	-	-	-
15 min	171.6	539	Green	36
35 min	481.6	554	Green	36.5
49 min	568.5	558	Green	37
60 min	642.0	562	Green	36.3
78 min	479.1	565	Green	37.5

98 min	664.4	570	Yellow	35.8
111 min	677.2	572	Yellow	36.2
127 min	693.6	574	Yellow	36.3

4.12 December 11, 2010

This batch was a repeat of the TGA:L-cys = 1:1 ratio, as analysis indicated that this was probably the best of the buffer ratios. This was because while L-cys gave fast growth and a larger color range, a precipitate was often seen, and seen quickly, meaning growth of the dots could not reach the red spectrum. TGA significantly slowed the growth, but seemed to yield higher fluorescent intensities, and no precipitate. The batches grown with 1:1 and 1:2 both seemed to have very good results, with the 1:1 batches less likely to yield a precipitate. This particular test was an effort to replicate the results from November 12th. 1 M Te powder was used. Samples were taken every half hour, as the growth rate was expected to be slower than that of the Nov. 30th batch, so samples every 15 minutes would not be needed.

Visible sample color began at a golden-orange, lightened to pale yellow, and then darkened to orange. Growth was stopped after three hours because a precipitate was observed in the solution and samples. This was unusual, as normally the batches with an even or higher amount of TGA did not form a precipitate. The Nov. 12th batch ran for 8 hours with no precipitate. The precipitate occurring in this batch was different then that usually found in the L-cys batches, being a whitish-grey instead of black.

The absorption spectrums (see **Figure 37**) seem to be very like those of Nov. 12th. They show the bump, much more pronounced this time, and they also do not asymptote at 0 intensity. Curiously, though intensity increases with each sample, the peak wavelength shifts very little. This means the fluorescence peak wavelengths are probably all very close as well.

The fluorescence spectrums (see **Figure 38**) show the expected results. Fluorescent intensity gets very high, and the spectrums are narrow and bell-shaped. And the red-shifts between each sample are small, as expected from the absorption spectrums. The 1.5-hour sample seems to be another anomaly, with an intensity lower than it would be expected to be, but the peak wavelength still in sequence with the other samples.

These dots have reasonably small FWHM (see **Table 14**). At 37 to 40 nm they are about normal for the dots produced using this method. The wavelength shifts are large for the first hour and a half, and then become very small for the next. This rapid growth at the beginning is supported by the graph of the fluorescence spectrums.

Table 14 – FWHM for December 30th batch.

Sample	Peak Intensity	Peak Wavelength (nm)	Color	FWHM (nm)
Initial	-	-	-	-
0.5 hr	86.6	514	Green	37
1 hr	204.1	527	Green	37.5
1.5 hr	234.6	535	Green	39.5
2 hr	326.4	539	Green	39

2.5 hr	388.9	542	Green	40
3 hr	457.1	544	Green	40.3

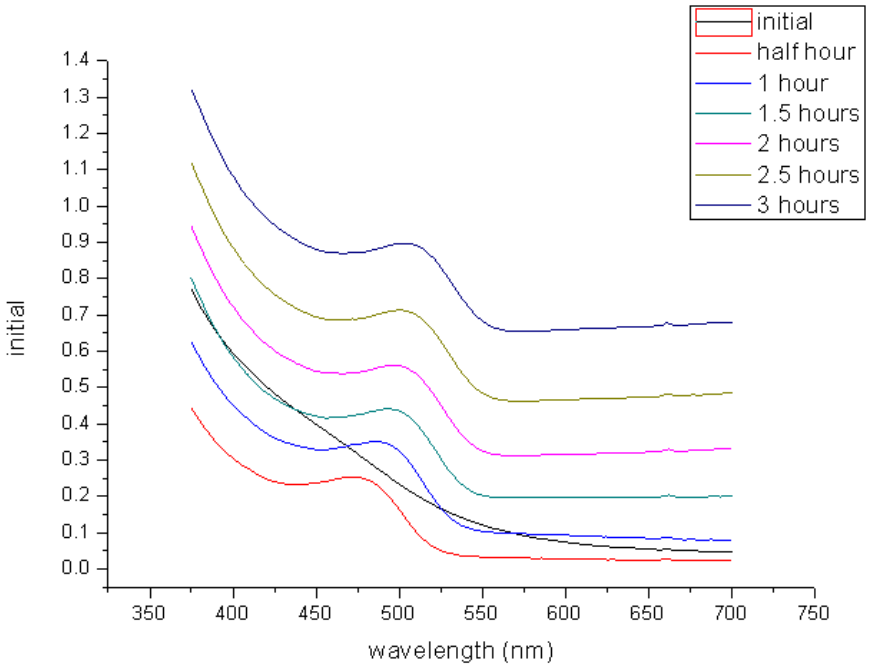

Figure 37 – Absorption spectrums for December 11th batch. (Taken on December 11th.)

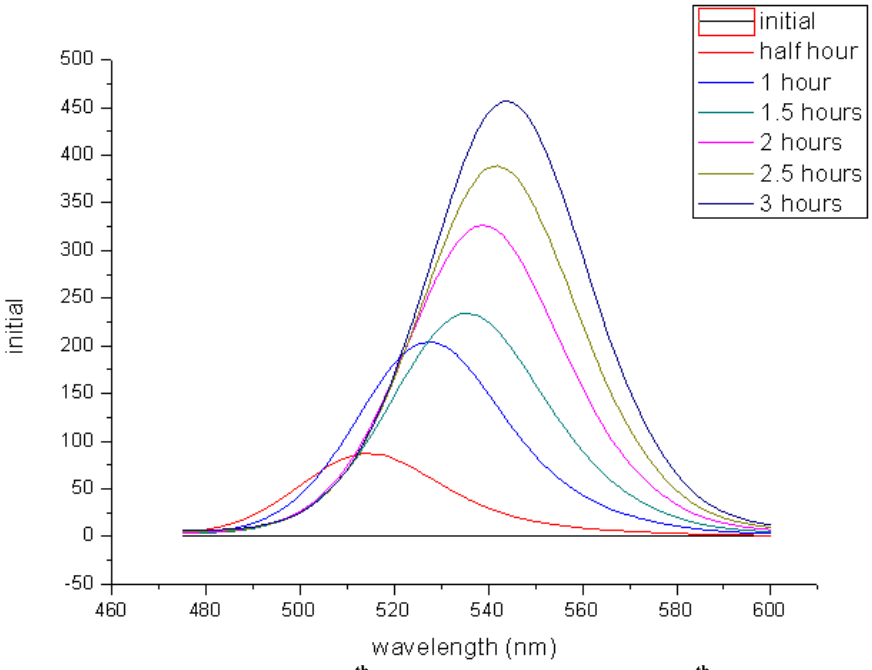

Figure 38 – Fluorescence spectrums for December 11th batch. (Taken on December 11th.)

4.13 December 13, 2010

This trial was again a repeat of the TGA:L-cys = 1:1 ratio. This time, the pH was adjusted to ~11, instead of ~10, to see how a more basic pH affected the growth of the dots. This trial can be compared with those of both Nov. 12th and Dec. 11th. 1 M Te powder was used. Samples were again taken every half hour until the third hour, after which they were supposed to be taken on the hour.

Visible sample color was initially a golden-yellow, then darkened to orange and continued to darken to a reddish-orange. Growth was stopped after six hours of growth, as again, a precipitate was seen in the solution. This precipitate was greyish-white, and on Dec. 14th the samples up to the third hour of growth were observed to contain black sediment after they had settled.

This is a bit of a mystery, both what the sediments are, and why they are forming in the solutions. It is possible that the black sediment is unreacted chemicals, which would explain why it eventually disappeared, or it could be sediment from the NaHTe vial that was accidentally transferred with the NaHTe solution. But the precipitate at the end, and why it is forming in batches that do not have higher amounts of L-cys, is unknown.

The absorption spectrums (see **Figure 39**) are dissimilar to those of Nov. 12th and Dec. 11th in that the majority of the spectrums appear to asymptote at an intensity of 0. However, otherwise they do show roughly the same trends, with very little shift between the peak wavelength of samples.

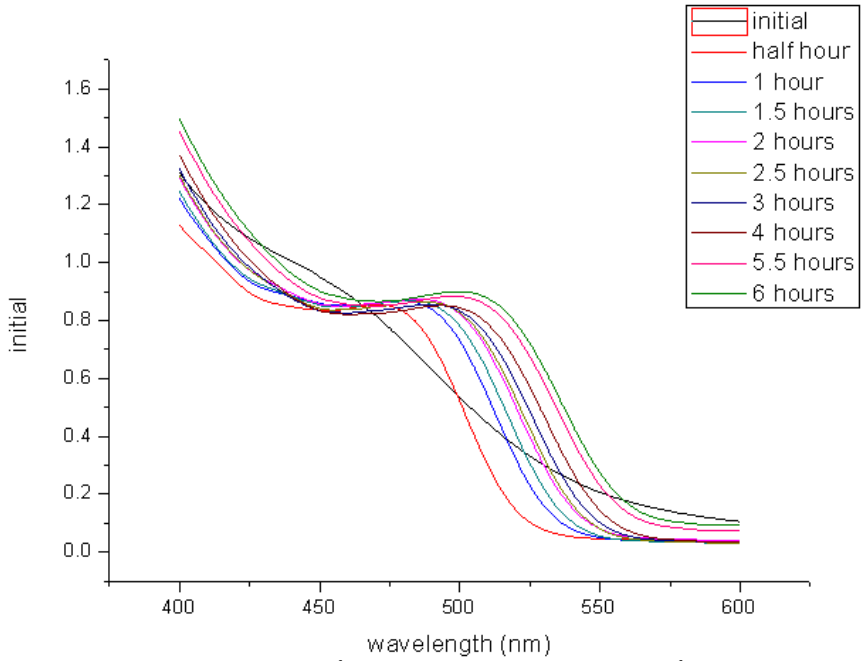

Figure 39 – Absorption spectrums for December 13th batch. (Taken on December 13th).

The fluorescence results (see **Figure 40**) are very similar to those of the Dec. 11th and Nov. 12th batches. Narrow, bell-shaped spectrums with increasing intensity. However, the growth rate appears to be faster towards the beginning. A precipitate was also observed in this batch,

appearing sometime around the 5.5 or 6 hour mark. This differs from the others in that the Nov. 12th batch had no precipitate, and the Dec. 11th batch had a precipitate after 3 hours.

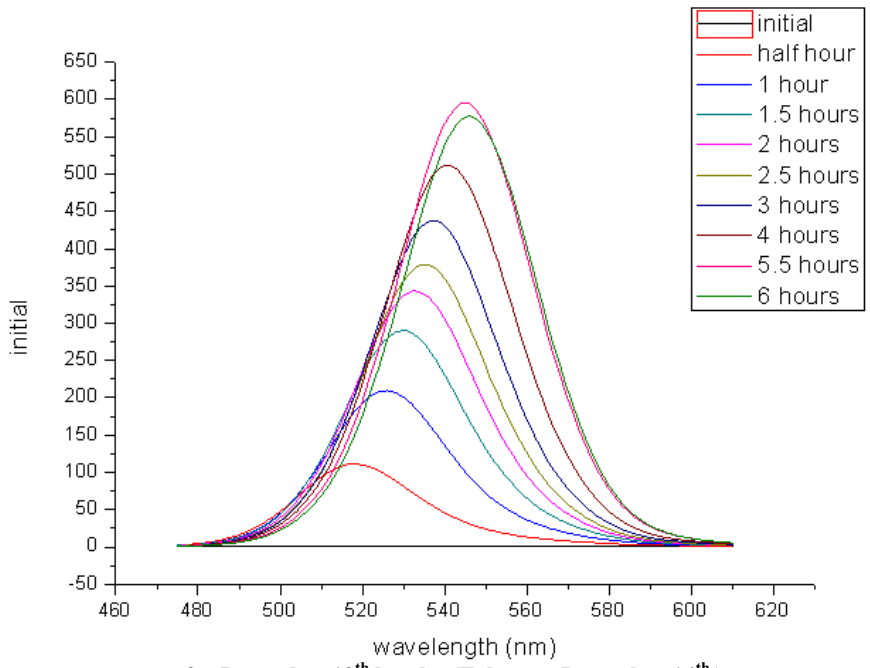

Figure 40 – Fluorescence spectrums for December 13th batch. (Taken on December 14th.)

These dots also show very small FWHM (see **Table 15**). All are below 40 nm. This is better than average for this method of making dots. Or it could be because these fluorescence spectrums were taken very soon after taking the samples. Wavelength shift is 5 nm between the half hour and 1-hour samples, and decreases quickly after that. This is not a fantastic wavelength shift, but is to be expected from the absorption spectrums (see **Figure 39**). The wavelength shifts means that growth was quick within the first hour and then fairly slow and constant after that.

So, it is probable that a lower pH will allow the quantum dots to grow for longer and reach a higher fluorescent intensity, with narrow FWHM but relatively small peak wavelength shifts.

Table 15 – FWHM for December 13th batch.

Sample	Peak Intensity	Peak Wavelength (nm)	Color	FWHM (nm)
Initial	-	-	-	-
0.5 hr	111.1	517	Green	36
1 hr	209.6	526	Green	35
1.5 hr	290.0	530	Green	36
2 hr	343.2	533	Green	36.5
2.5 hr	378.9	535	Green	37
3 hr	437.7	537	Green	37.5
4 hr	511.4	540	Green	38
5.5 hr	595.4	545	Green	39
6 hr	577.9	546	Green	39

4.14 Rhodamine 6G

Figure 41 shows the full absorption spectrum of rhodamine 6G. The purpose was to highlight the difference between a fluorescent dye and the quantum dots, mainly through analysis of the quantum fluorescent yield.

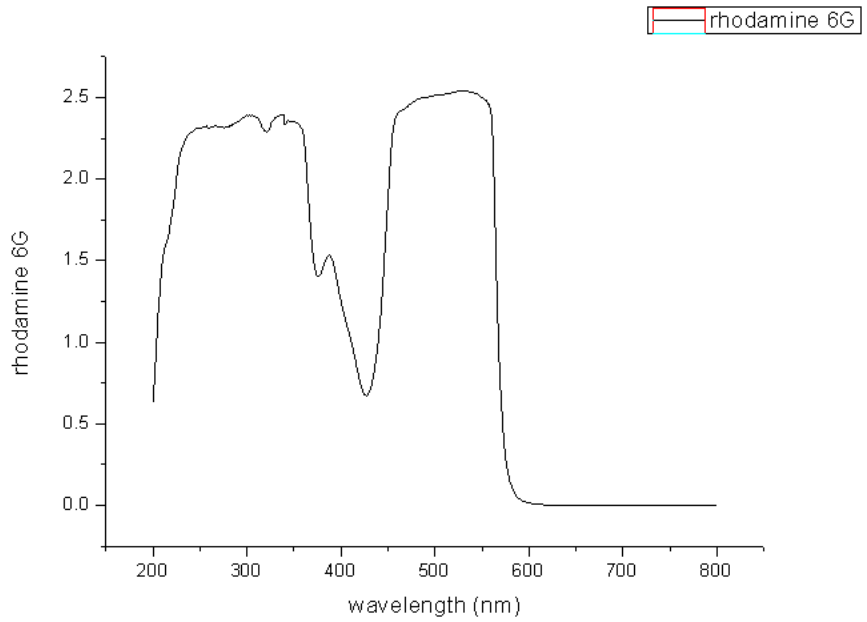

Figure 41 – Absorption spectrum for rhodamine 6G. (Taken on December 7th.)

The R6G solution was prepared on December 7th, and this absorption spectrum was taken the same day. The rhodamine was stored in the refrigerator in an effort to keep it from photobleaching.

This spectrum (see **Figure 41**) proved to be vastly different from that of the quantum dot spectrums. The quantum dots absorbance spectrums show the effects of TGA between 200 and 300 nm and then show a single bump as they quickly asymptote to 0 by about 600 nm. Rhodamine 6G shows a much different shape, including a high absorption plateau from ~475 to ~550 nm.

Figure 42 is a typical fluorescence spectrum for a fluorescent dye. The A-symmetry can be seen very clearly, along with the tail into the red region. It is this tail that makes the dyes have a larger FWHM, and makes fluorescent dyes more difficult indicators to analyze then quantum dots.

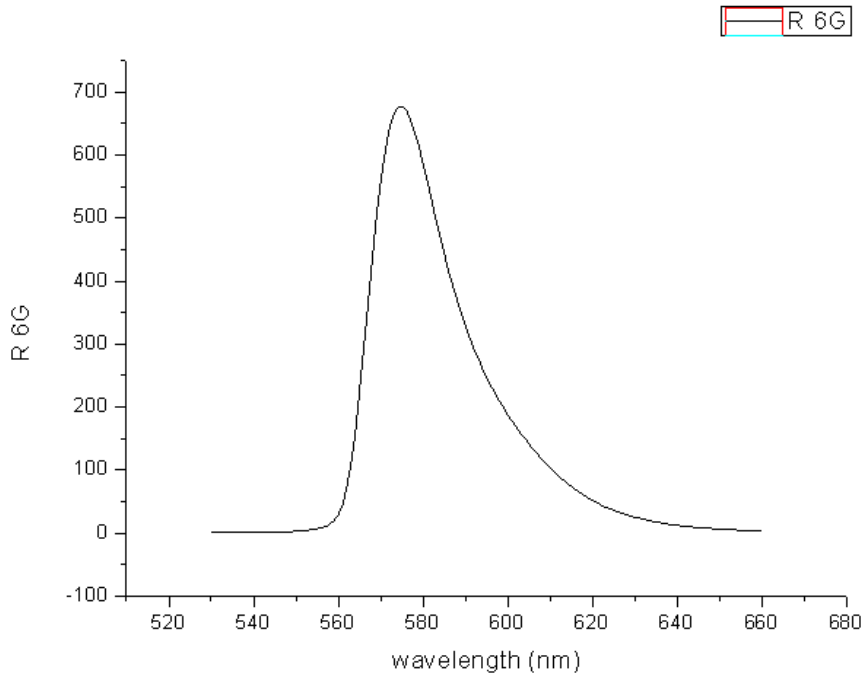

Figure 42 – Fluorescence spectrum of rhodamine 6G. (Taken on December 9th.)

4.15 Quantum Yield

The quantum yield is a measure of how bright the dots are. Bruchez et al. report green CdSe quantum dots coated in a layer of CdS and used in an immunoassay to have a 15% quantum yield, and red dots to have a QY of 6%. They also report nanocrystals having a QY above 50% (Bruchez, et al. 1998). While quantum yield for quantum dots has been reported as high as 80% (Qu and Peng), dots made aqueously typically have much lower quantum yield (Chen, et al. 2007). Quantum yield was calculated as follows:

$$Y_u = Y_s \cdot \frac{F_u}{F_s} \cdot \frac{A_s}{A_u} \cdot \frac{{G_u}^2}{{G_s}^2}$$

Subscript 's' refers to rhodamine 6G, and subscript 'u' refers to the quantum dot samples. 'Y' is the yield, 'F' is the intensity at the fluorescence peak, 'A' is the absorbance (which needed to be <0.1) at the excitation wavelength, and 'G' is the reference index. Water was the reference for the quantum dots, with a G_u = 1.3329 and ethanol was the reference used for the rhodamine, with a G_s= 1.3611. Complete calculations can be seen in Appendix A.

Theoretically, the QDs should have a higher quantum yield then rhodamine. As time was short, quantum yield was calculated for the dots that appeared to be the best from analysis of the absorbance and fluorescence spectrums. These were the dots made on November 10th, 12th, and 16th, which have TGA:L-cys ratios of 1:1, 1:1, and 1:2, respectively. The Nov. 10th dots were made with 2 M Te, while the other two batches were made with 1 M Te.

In order to get absorption values that fit the requirements of the equation the samples had to be diluted and rescanned, both absorption and fluorescence. Since this dilution was not done for the

other batches, their quantum yield cannot be analyzed. Dilution of the samples was not uniform, as the tubes and sample volumes were not uniform. But the important thing was to get the absorption below 0.1 at the excitation wavelength. The original absorption spectrums were completed using an excitation wavelength of 380 nm. It was decided to use a wavelength between 400 and 500 nm for the diluted spectrums as it would be very difficult to get the absorption below 0.1 at 380 nm. The excitation wavelength of 430 nm was used for the spectrums used in these calculations.

After the samples were diluted, the fluorescent spectrums also had to be retaken in order to avoid errors due to different concentrations in the absorption and fluorescence spectrums.

The rhodamine 6G solution also had to be diluted so that the absorption at 430 nm was <0.1. On December 9th, a 5 mL sample of the r6G solution made on Dec. 7th was cut with a total of 40 mL of ethanol, for a final r6G:ethOH ratio of 1:8. The fluorescence for the diluted rhodamine was also rescanned.

Results are shown in **Tables 16-18**. In these tables, the values in italics are the ones that did not quite fit the requirements of the equations. Either the absorption was not <0.1, or the fluorescence did not have a peak, as was the case with some of the initial samples.

Table 16 – Quantum yield for November 10th dots.

Sample	Initial	0.5 hr	1.5 hr	2 hr	3hr	4hr	5 hr	6 hr	7 hr	8 hr	9 hr
Yield (%)	*0.1*	3.4	10.1	10.4	11.5	13.2	*3.5*	5.4	14.1	17.2	13.5

Table 17 – Quantum yield for November 12th dots.

Sample	Initial	10 min	1 hr	2 hr	3 hr	4 hr	5 hr	6 hr	7 hr	8 hr
Yield (%)	2.1	*0.3*	7.3	15.4	13.6	14.6	15.9	14.2	14.8	14.3

Table 18 – Quantum yield for November 16th dots.

Sample	Initial	15 min	1.25 hr	2 hr	3 hr	4 hr	5 hr	6 hr	7 hr	8 hr	10.5 hr
Yield (%)	0.2	0.1	4.8	6.3	6.6	*7.1*	*8.7*	13.0	*6.6*	*8.7*	*4.2*

4.16 Environmental testing

These tests were performed on December 14, 2010. The dots from December 11th were used. The November 12th dots (TGA:L-cys = 1:1) had proved by this point to be the best. But some of the other samples had shown signs of precipitation and a slight degradation over time, so it was decided that a more recent batch would be used. The Dec. 11th dots were made with the same ratios and concentrations as the Nov. 12th dots, and had showed similar results, so it was felt that they would be the best dots to use in these tests.

The quantum dots were not conjugated to either the polychlorinated biphenyls (PCBs) or the bovine serum albumin (BSA). Tests were performed to see if the dots reacted to the presence of the contaminates.

4.16.1 PCBs

PCB was tested in very small amounts at five different concentrations, with a blank as a control. The results shown in **Figure 43** clearly indicate that the dots are affected by the presence of the PCBs. Intensity decreased from the blank for the sample with 0.2 mL PCBs, and increased for all the others. The highest intensity is from the sample with 0.6 mL PCBs.

Though the quantum dots are clearly affected by the presence of the PCBs (see **Figure 43**), there is no trend in this effect. The dots neither increase nor decrease proportionally to the amount of PCBs present, so the test is inconclusive. These tests show the dots could be used to test for the presence of PCBs, but not for the amount of PCBs.

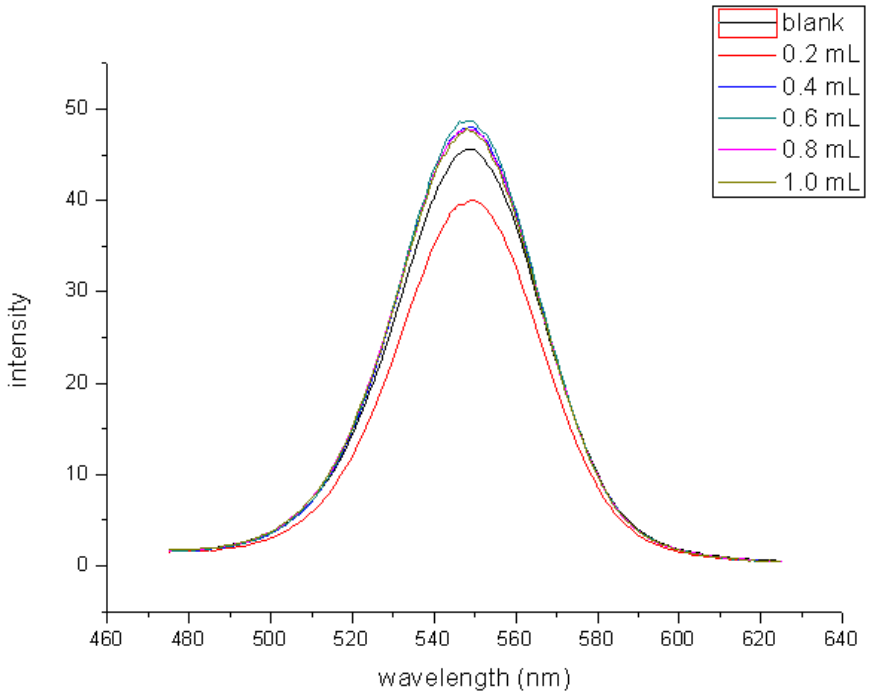

Figure 43 – Fluorescence spectrums for dots tested against PCBs. (Taken on December 14th.)

4.16.2 BSA

When the PCBs proved to be inconclusive, BSA was tested. BSA is a substance commonly used in immunoassays, and it is known that quantum dots respond to them (Chan and Nie 1998).

The results (see **Figure 44**) clearly show a trend. All of the dots show decreased fluorescence intensity in the presence of BSA. And the intensity continues to decrease as the concentration of BSA increases. This means that these quantum dots can be used to test for the presence and concentration of BSA.

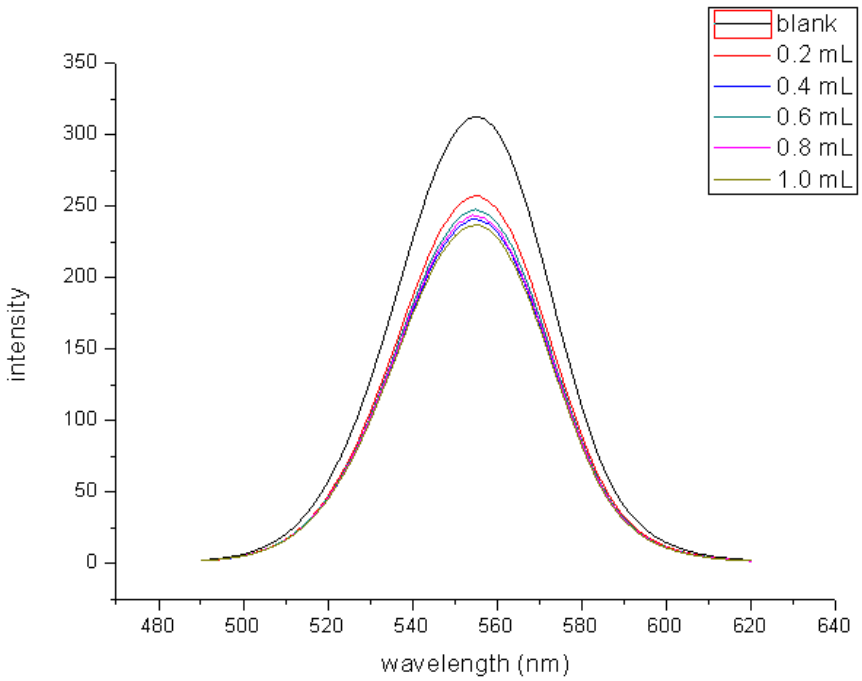

Figure 44 – Fluorescence spectrums for dots tested against BSA. (Taken December 14th.)

5.0 Discussion

Several characteristics of the dots are discussed below, including growth rate and time, size, and fluorescent quantum yield, in order to determine which is the best method for growing CdTe quantum dots for environmental use. Comparison of repeat trials is included to determine the accuracy of the trials. Evaluation of the full width half maximum (FWHM) shows how narrow the fluorescent spectrums of the quantum dots are.

5.1 Peak Fluorescent Wavelength Vs. Time

There are several characteristics of quantum dots that can be analyzed. The easiest ones are growth rate and particle size.

For quantum dots, fluorescent wavelength is a direct indication of size. As the quantum dot grows, its size increases, as does the peak fluorescent wavelength. Therefore size of the quantum dot can be directly analyzed by measuring the wavelength. The largest size range possible is desired, as that means the largest fluorescent color range possible. If multiple tests using quantum dots are to be performed at once, it is important that the different dots can be differentiated, and convenient if this can be done by the human eye instead of relying on a spectroscope. This means different colors, like green, yellow, and red, are needed.

Growth rate can be seen very easily by looking at a graph of peak wavelength over time and seeing which has the steepest slope.

Figure 45 shows many things. The first is that some of the batches grew for several hours, while others only lasted 2 or 3. The batches that grew for fewer hours are also the batches that grew very fast, and tended to contain higher ratios of L-cys and develop a precipitate after two or three hours of growth.

The batches that reached the highest size are those of Nov. 5th (just L-cys), Nov. 30th (just L-cys), Nov. 16th (TGA:L-cys = 1:2), and Nov. 25th (1:3). Unfortunately, many of these batches also saw precipitates form, meaning they would not be able to get farther than these sizes, which have just barely reached yellow.

The longest growing batches are those of Nov. 16th (1:2), Nov. 18th (2:1), Nov. 23rd (3:1), and Nov. 10th (1:1). Although to be honest, this may not be an accurate measure of which batches grew longest, because these and several others could have kept growing past these times, if only the heater could be left on over-night. It can be safely assumed that any batch grown with a higher ratio of TGA grows for a long time period, and a precipitate is unlikely to occur.

The longer the dots are able to grow, the larger they grow. This means that the longer growing dots are more likely to reach the red color range then the faster growing dots. This can be seen in that the Nov. 16th (1:2) dots were able to be one of the longest growing in addition to yielding some of the largest dots. For this reason, it was determined that the 1:1 and 1:2 batches were the best.

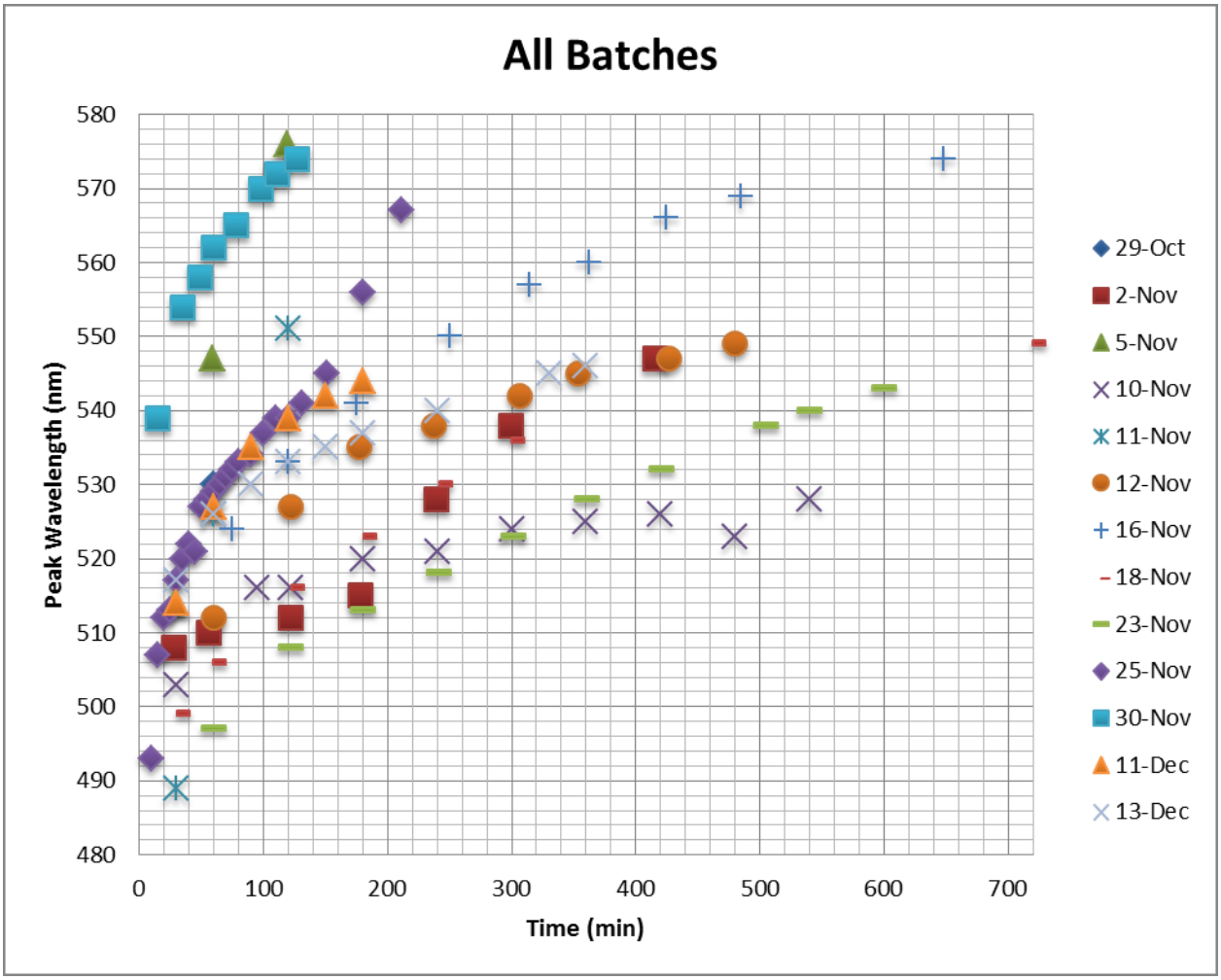

Figure 45 – Peak fluorescent wavelength over time (all quantum dot batches).

5.2 Just TGA

The batches grown on October 29th and November 2nd use only thioglycolic acid as the buffer. The Oct. 29th batch has only one sample besides the initial and was made with 1 M Te powder, while the Nov. 2nd batch was made using 2 M Te powder and samples were taken over a period of 7 hours.

From the trendline in **Figure 46**, it is clear that the growth of the size of the dots grown on Nov. 2nd is roughly linear and relatively constant. The size of the 2- and 3-hour samples is smaller than would be expected, given this linear growth. Also, the dots should be growing faster at the beginning of the time period, as that is when there are the most raw materials available. So the drop in growth rate after the first hour is unexpected, but not entirely deviant from the general growth trend. The Nov. 2nd batch was the second batch grown, and it is possible that there were errors in the growth method due to it not being completely refined at that point in time.

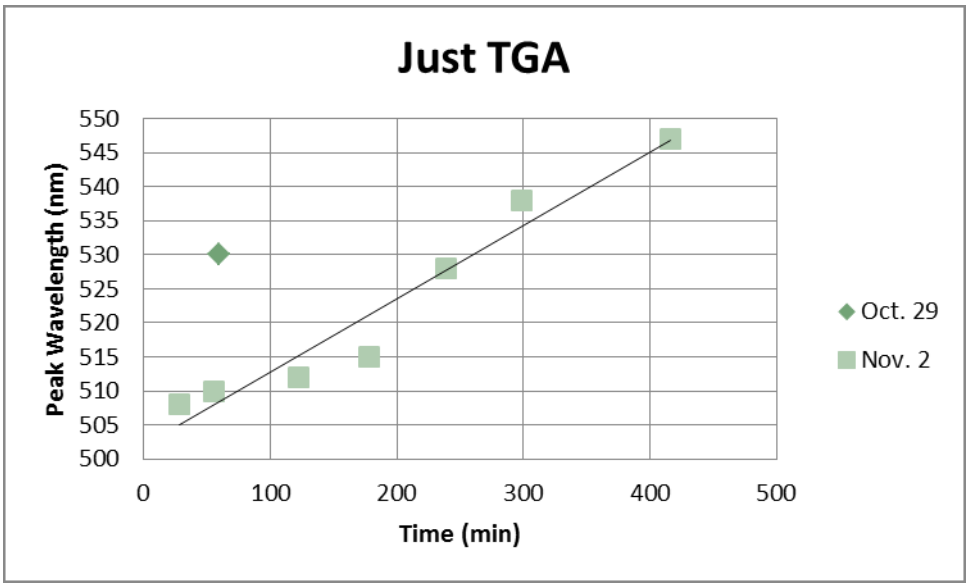

Figure 46 – Peak wavelength over time for batches grown using only thioglycolic acid. Data for the initial samples is not included as they did not have fluorescent peaks.

What does not make all that much sense, is that the peak wavelength for the 1-hour sample from October 29th is at a much higher wavelength then the 1-hour sample from November 2nd. The Nov. 2nd samples do not reach this size until the fourth hour of growth. It's possible this difference is due to the molar amounts of starting ingredients. But the Oct. 29th dots were also made with more cadmium then any of the other batches. These results suggest that perhaps a higher ratio of cadmium to tellurium causes a faster growth rate in the quantum dots.

5.3 Just L-cys

The batches from November 5th and November 30th were made using just L-cys as a buffer. The difference is that the Nov. 5th dots were made with 2 M Te, while the Nov. 30th dots were made with 1 M Te.

Data for the initial sample from Nov. 30th is not included in **Figure 47**, as there was no peak. However, the initial sample for the Nov. 5th batch *did* have a peak, and it is shown on the graph.

Both batches went for about 2 hours before a precipitate was seen. However, the growth rates appear to be a bit different. The Nov. 5th batch has a very constant growth rate through the first hour, which then decreases between the first and second hour. The Nov. 30th batch shows a more constant growth over the whole time period, with a brief section of rapid growth in the first half hour. This would imply that the longer period of rapid growth in the Nov. 5th dots is due to that solution being 2 M Te and that the dots were able to grow rapidly for longer simply because there were more dots that could grow.

Size of the Nov. 5th dots is also smaller in the first hour. This is probably because more dots were forming, rather than growing, in the solution during this time period. It is curious to note that the final size of the dots is just about the same. This would imply that though dots in higher concentration solutions take a bit longer to form, ultimately the same dots are formed, not matter the concentration.

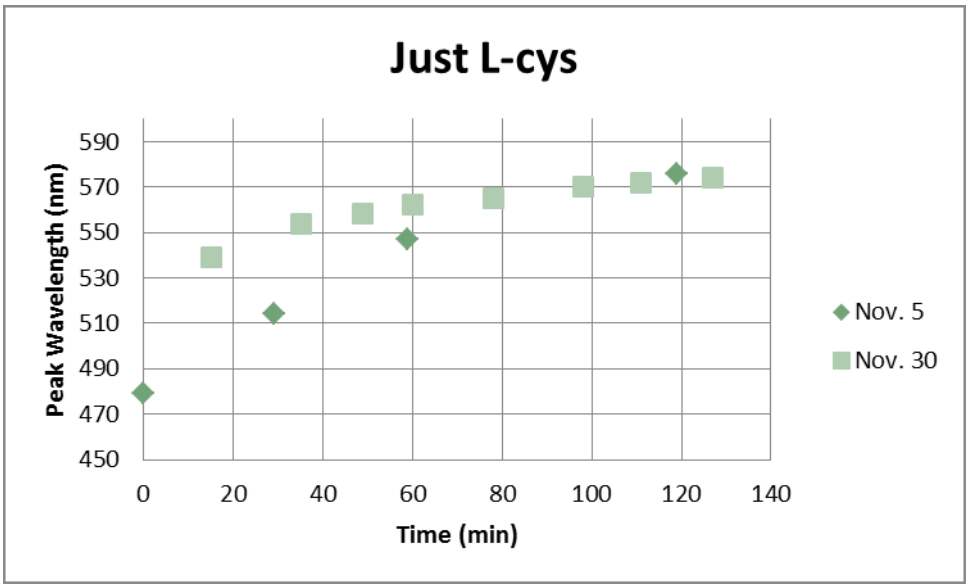

Figure 47 – Peak wavelength over time for batches grown using only L-cysteine.

5.4 TGA:L-cys = 1:1

There were four batches made with the TGA:L-cys ratio 1:1. These are: November 10th, November 12th, December 11th, and December 13th. It was determined after examining the absorbance and fluorescence spectrums partway through the experiments that this ratio was one of the best, which is why it was repeated so many times. The Nov. 10th batch is 2 M Te while the other three are 1 M Te. The Dec. 13th batch was adjusted to a pH of ~11, while the other three were adjusted to ~10. The Dec. 11th trial was a straight repeat of the Nov. 12th trial, only with samples taken more often.

Again, data for initial samples could not be included in **Figure 48**. All batches show a period of rapid size growth for the first hour and a half or two hours. After that, growth slows, but remains relatively constant.

In some ways, this data does not support the conclusion of the last section that higher molarity ultimately yields the same size dots. The Nov. 10th dots were grown with 2 M Te, and the smaller sizes outlast the rapid growth period that all the batches show. However, it is possible that the Nov. 10th batch would eventually reach the same size as the other batches. The growth time for these dots (when no precipitate appeared) was very long. In most of the batches, the dots would have continued growing past when the last sample was taken, except that the heater had to be turned off as it could not be left unattended over-night, meaning these experiments were stopped early. So it is possible and perhaps even probable that the 2 M dots eventually catch up with the 1 M dots, supporting previous conclusions.

The Dec. 11th batch was odd, because a precipitate was observed after 3 hours, while all the other batches continued to grow long after that time. It is possible that there was some contaminate in the solutions or glasswear which could explain both the higher growth rate and the precipitate.

The Dec. 11th trial has the same general trends as the Nov. 12th trial, the size growth rates are just higher. This makes the Dec. 13th batch appear to be a better match to the Nov. 12th batch.

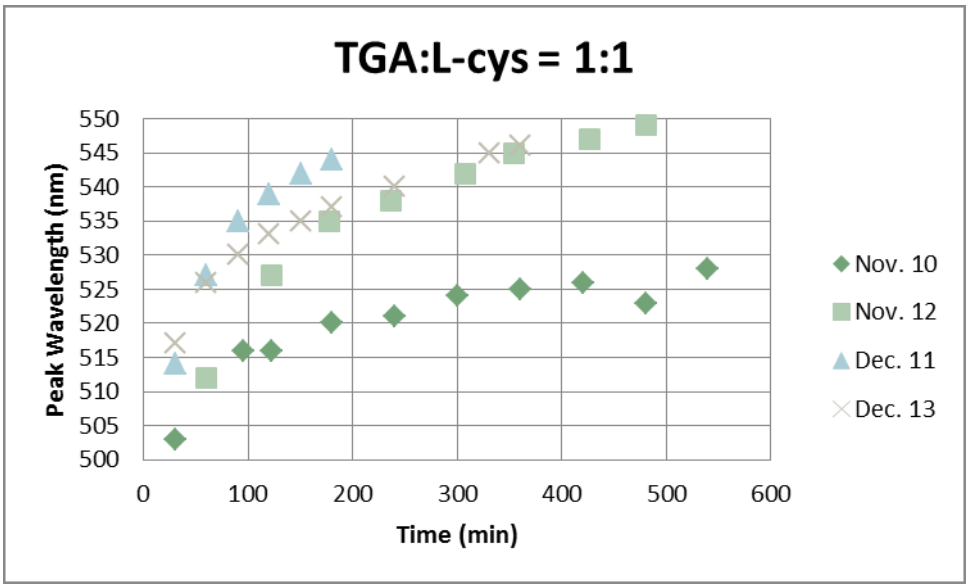

Figure 48 – Peak wavelength over time for batches grown with a TGA:L-cys ratio of 1:1.

The points for the Dec. 13th batch are almost on top of those of the Nov. 12th batch, though they are a little above. They are much more noticeably higher in the first two hour period. This would imply that a more basic pH gives the dots a faster initial growth rate, but ultimately the results are about the same. It is possible that the difference in pH between 10 and 11 is simply not enough to see the effects over a long time period. This suggests that getting quantum dots that fluoresce red is simply a waiting game, while quickly growing dots in the green to yellow spectrum can be achieved by making the pH more basic.

5.5 TGA:L-cys = 1:3

Two batches were made that had a TGA:L-cys ratio of 1:3. Both are slightly off from the norm. The November 11th batch was one of the four made using 2 M Te, while the November 25th batch was the one with samples taken every five minutes, drastically changing the solution size and ultimately affecting the growth of the dots.

Data for samples taken before 10 minutes of growth is not shown in **Figure 49**, as there were no peaks.

The November 25th trial was meant to be a repeat of the November 11th trial, with samples taken more often to better show the growth trends within the first hour, when the fastest growth occurs. The growth trends can be seen very clearly. The change in size is logarithmic for the first hour and a half, and then different linear trends after that. Again, it is believed that the later samples were affected by the drastic reduction in solution volume. Curiously, this seems to have increased the growth rate at the end. This would imply that higher heat flux cause more rapid growth.

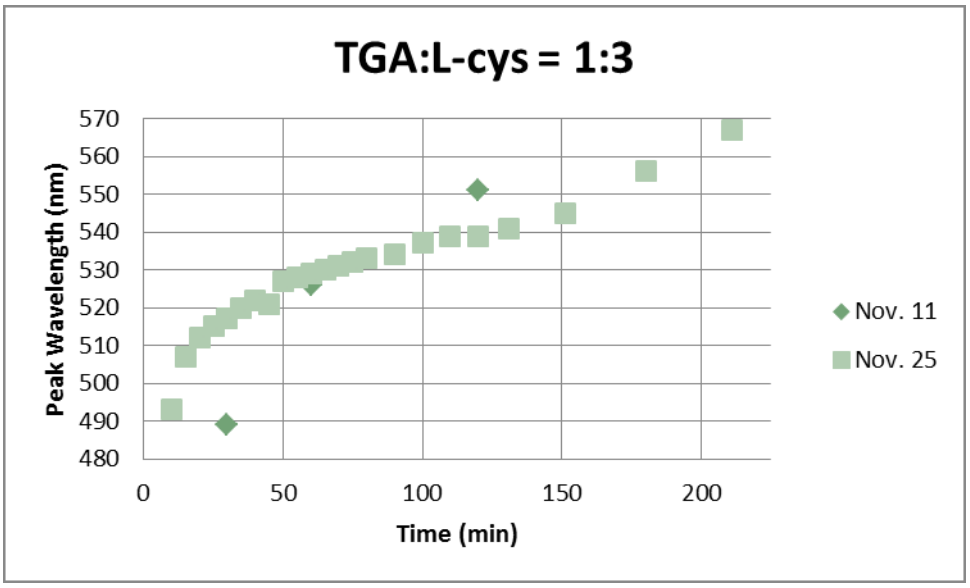

Figure 49 – Peak wavelength over time for samples grown with a TGA:L-cys ratio of 1:3.

Also, the sizes of the dots do not match. In some sense this is to be expected, as previous comparisons of 2 M Te solutions with 1 M Te solutions show differences. But these are not quite the differences expected. The graphs of both the dots grown with just L-cys and the dots grown with a 1:1 ratio (**Figures 47 and 48**) show the 2 M samples as always having smaller sizes then the 1 M samples from the same time. In this graph, that is true for the first two samples from Nov. 11th, but not the last one. Previous analysis has also shown a slower initial growth rate for higher molarity batches, which is seen here, and has indicated that the overall size growth rate of 2 M batches is slower. This is why it is curious that the 2-hour sample from Nov. 11 is so large compared to the Nov. 25th samples.

It is possible that by this time the Nov. 25th samples had been affected by the reduced solution size, and following the trend of the samples from between about 50 and 90 minutes of growth would indicate a slightly higher rate of growth than the one observed in the graph at the 120 minute mark. But even that would not be enough to make the Nov. 25th samples as large as the Nov. 11th 2-hour sample. It is tempting to say that the larger ratio of L-cys has made the dots grow faster, but the graph of dots grown with just L-cys (**Figure 47**) would suggest otherwise. A black precipitate was observed in the Nov. 5th 2-hour sample, while the Nov. 25th batch ran until solution volume was exhausted about an hour and 20 minutes after that. This would suggest differences in the growth of the quantum dots. Perhaps these two batches simply have too many variables to be effectively compared.

5.6 Complete Spectrum of Buffer Ratios

One of the goals of these experiments was to find the best TGA:L-cys ratio for the growth of aqueous CdTe quantum dots. In determining the best, the wavelength range and growth rate were analyzed, in addition to fluorescence intensity.

Figure 50 shows peak fluorescent wavelength over time for one batch at each ratio.

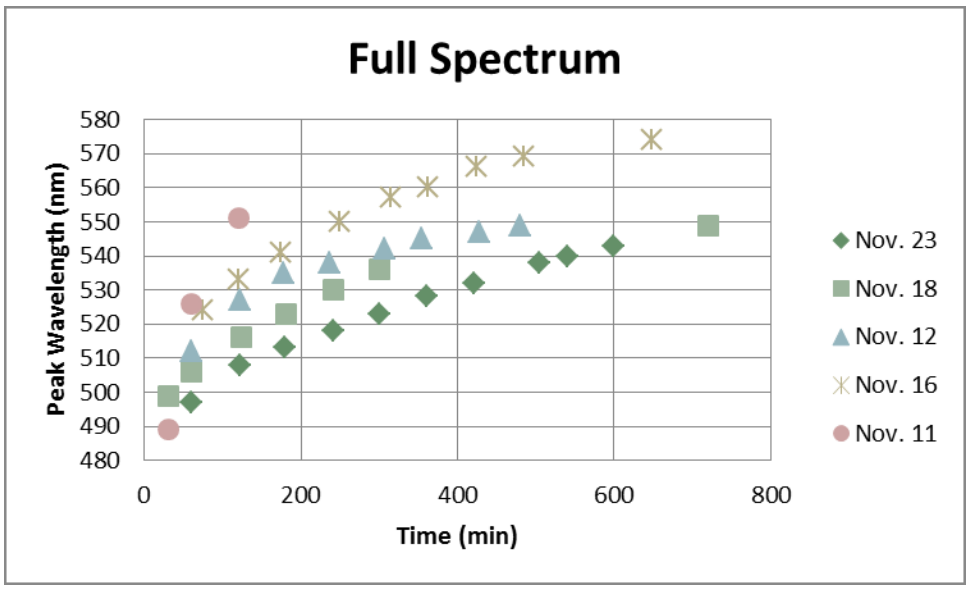

Figure 50 – Peak wavelength over time for one batch from each TGA:L-cys ratio. Only-TGA and only-L-cys are not included.

Table 19 lists the ratios used for each batch used in **Figure 50**.

Table 19 – Batches and their respective TGA:L-cys ratios.

Batch	TGA:L-cys
Nov. 23rd	3:1
Nov. 18th	2:1
Nov. 12th	1:1
Nov. 16th	1:2
Nov. 11th	1:3

All the batches were made using 1 M Te, except for the November 11th trial, which was made using 2 M Te. This batch was used instead of the Nov. 25th batch because it was more consistent with the results of other trials grown with high amounts of L-cys, and it was felt that the Nov. 25th results were affected by the frequent sampling.

In the graph it can be seen clearly that as the ratio changes from 3:1 to 1:3 the growth rate increases. This supports previous conclusions made during the experiments that dots with more TGA grow slower than dots with more L-cys.

The Nov. 5th (1:3) half hour sample is about 10 nm towards blue from the Nov. 18th (2:1) half-hour sample. This would suggest that batches grown with more TGA have faster initial growth rates then batches grown with more L-cys. Unfortunately, many of the batches grown with more TGA grew so slowly that the earlier samples did not have fluorescent peaks, making this conclusion difficult to verify. And the Nov. 25th batch was at 517 nm after a half-hour of growth, suggesting the opposite and making this conclusion more difficult to compare. Clearly, more analysis of the initial growth rate within the first hour and a half is needed.

The 1:1 and 1:2 ratios appeared to be the best based on fluorescence and absorption alone. This chart appears to support that conclusion. The Nov. 12th (1:1) and Nov. 16th (1:2) dots were able to reach relatively large peak wavelengths, and grow for long periods of time before a precipitate would appear in solution. The Nov. 12th dots reached a size comparable to those of the Nov. 5th (1:3) dots, and the Nov. 16th dots surpassed them both. This means that with these two ratios, the dots grown would have the largest possible wavelength spectrum. What determines which is best would be the quantum yield analysis.

5.7 Fluorescent Quantum Yield

The quantum yield was analyzed for three batches of quantum dots, those from November 10th (TGA:L-cys = 1:1), November 12th (1:1), and November 16th (1:2). This was an attempt to determine exactly which of the two ratios is best, and also to see the effect of a 2 M solution (Nov. 10th).

The calculations for the quantum yield can be seen in section 4.15, as well as Appendix A. The highest quantum yield is for the 8-hour sample from Nov. 10th at 17.2 %. But the dots from Nov. 12th are consistently higher, as can be seen in the **Figure 51**.

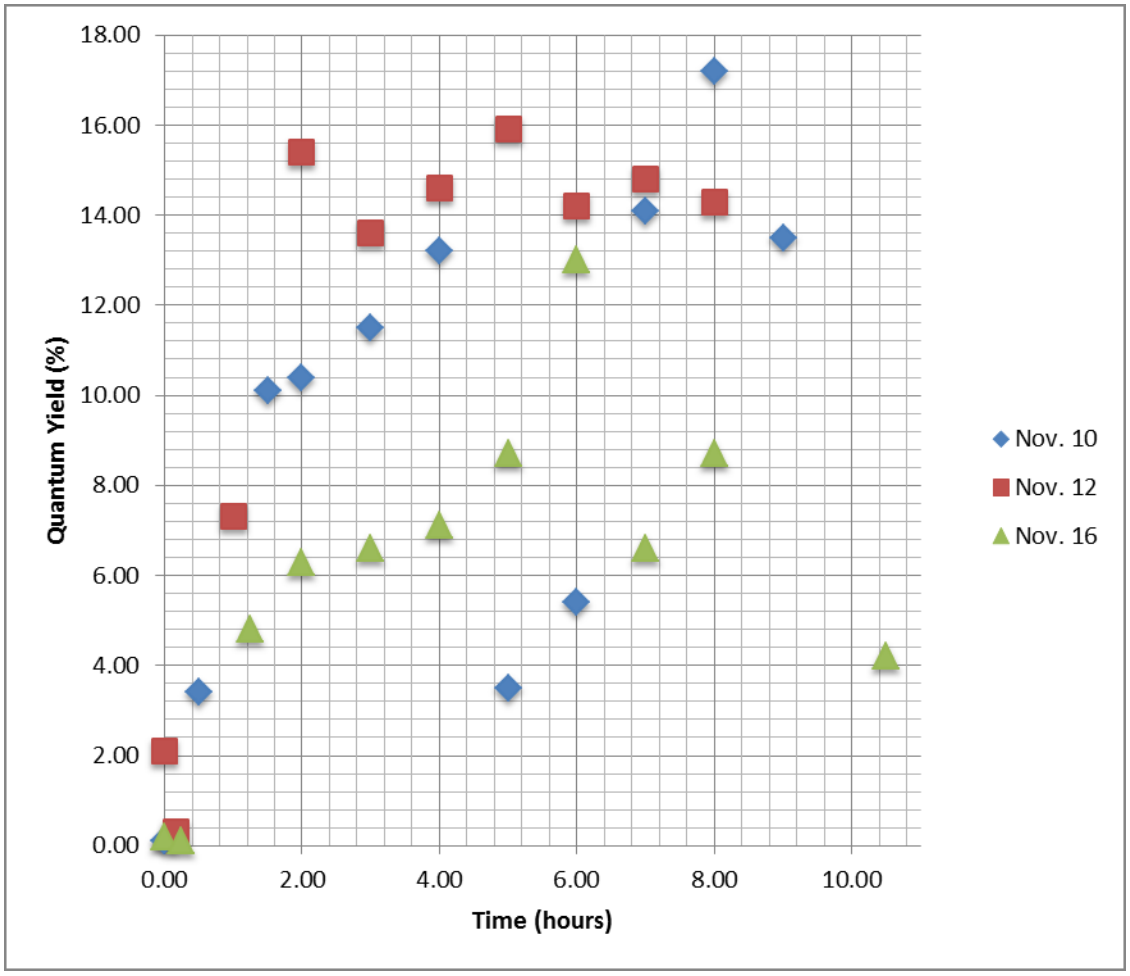

Figure 51 – Quantum yield over time.

The Nov. 16th (1:2) quantum yields are consistently below those of the other two batches. This means dots grown with 1:2 have lower fluorescent quantum yield then those grown with 1:1. This supports earlier beliefs that higher ratios of TGA yield higher fluorescence.

Next the two 1:1 batches need to be analyzed. Though the highest QY is from the Nov. 10th batch, the Nov. 12th batch is consistently higher (and has fewer errors) then the Nov. 10th batch. This would imply that the 1 M solutions have better QY then the 2 M solutions. But previous analysis has shown that these experiments did not really yield enough data to effectively test the effects of concentration within the solution. And the buffer ratio is really the important bit. Analysis of fluorescent quantum yield shows that the best TGA:L-cys ratio is 1:1.

5.8 Full Width Half Maximum

Full width half maximum is a way of telling how wide or narrow the fluorescent spectrum is. Calculation of the FWHM can be seen in **Tables 3-15** as well as in Appendix B. **Figure 51** shows a graph comparing all of the FWHM.

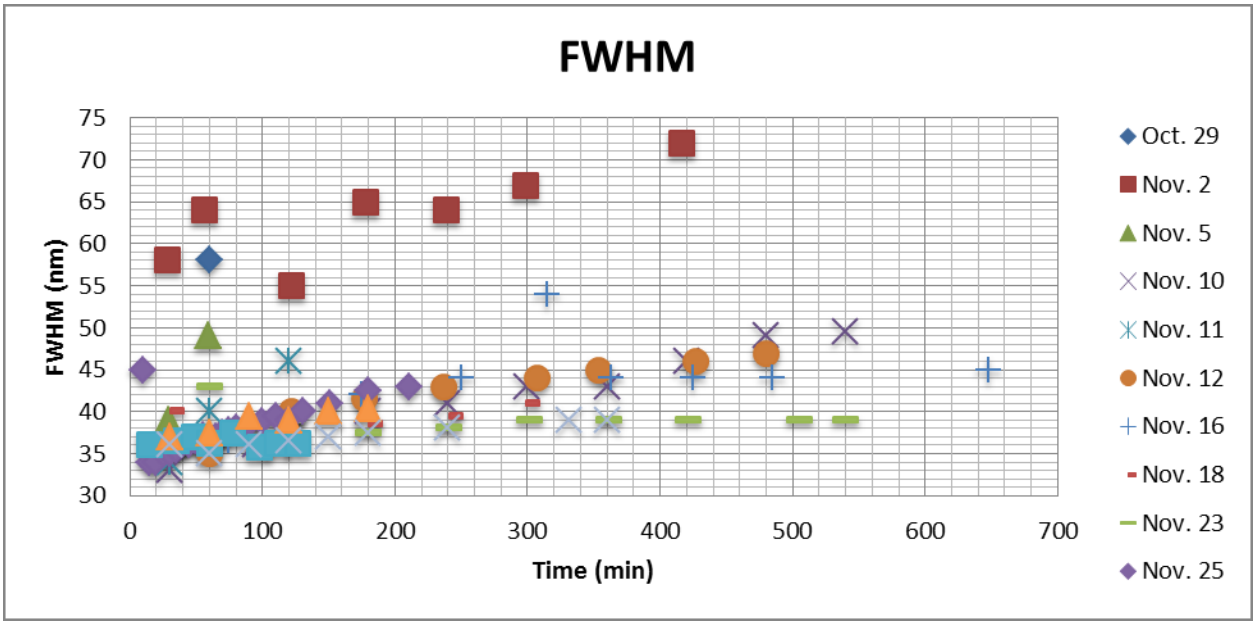

Figure 52 – Full width half maximum against sample time for all batches.

The earliest batches have comparatively high FWHM. These values are still acceptable for quantum dots, but a little larger then desired. However, once you get past the first three batches made, the FWHM becomes very consistent. The FWHM range for the majority of the batches is between 35 and 50 nm. This range is very narrow, and very good for quantum dots.

6.0 Conclusions and Recommendations

6.1 Conclusions

The aqueous synthesis method described in this paper successfully produces CdTe quantum dots capped with TGA, L-cys, or both that are functional and can be used in environmental and biological applications.

Batches grown with more L-cys were observed to grow faster, and thus reach a higher wavelength range faster. But these batches also tend to form precipitates, meaning growth has to stop. Batches grown with higher amounts of TGA were observed to grow much slower, though probably with the potential to reach wavelength ranges comparable to or exceeding those of the high L-cys batches. Dots with more TGA also tend to have higher fluorescence. This means both buffers are desired, as they both have desirable characteristics.

Analysis of absorption and fluorescence spectrums, as well as the fluorescent quantum yield, indicate that the TGA:L-cys ratio of 1:1 produces quantum dots with the a large florescent color range and high fluorescent intensity.

6.2 Recommendations

Time for experimentation on this topic was limited to eight weeks. As such, it is felt that there is much work left to be done in several areas.

Additional repetition of the different buffer ratios should be performed to ensure that the conclusions drawn are correct. The quantum dots should be grown to completion, either until red fluorescence is reached or until a precipitate appears. The fluorescence and absorption spectrums should be taken as quickly as possible, and at least the same day, in order to eliminate errors in analysis due to the samples degrading or continuing to react over time.

More pH values should be tested. Almost all of these tests involved the dots growing from an initial pH of ~10. The one batch grown at a different pH seemed to imply that a more basic pH yields faster initial growth, which can be useful if trying to get smaller quantum dots quickly. Some studies have shown that a higher or lower pH is better for growth rates or fluorescent intensity, so test should be carried out to see if *these* quantum dots grow better at a higher or lower pH.

Different Cd^{2+}:Te:buffer ratios should be tested. Virtually all of the tests were performed using the same 3:1:6 ratio, and it's possible that the dots grow more efficiently or have a longer range or a higher quantum yield with a different ratio. Results from the two batches made with just TGA (Oct. 29th and Nov. 2nd) suggest that higher ratios of cadmium to tellurium may increase the fluorescence. In fact, Qu and Peng suggest that a higher ratio of the VI element (Te in this case) to the II element (Cd) increases fluorescence, which is the opposite of what has been tested here.

The effects of batch size and molarity should be tested. If the dots grow differently in a larger batch, then that needs to be known and understood.

The effects of heat flux during growth should be tested. Heat was not a variable that was considered in these experiments, but some of the data suggests that it should be, as higher heat flux could increase growth.

Closer examination of the rapid growth at the beginning should be performed. Analysis showed very different growth rates within the first hour and a half of growth. Studies should be performed, carefully, to study the growth in this time period.

Further environmental testing should be performed. Tests of other materials should be carried out, to show that these CdTe quantum dots can be used in many applications.

Conjugating the dots should be tested. This is what will need to be used in immunoassays and other medical and biological tests. The ability for these particular quantum dots to attach to particles and perform as expected is currently untested.

7.0 References

Bruchez, Marcel, et al. "Semiconductor Nanocrystals as Fluorescent Biological Labels." Science (1998): 2013-2016.

Chan, Warren C. and Shuming Nie. "Quantum Dot Bioconjugates for Ultrasensitive Nonisotopic Detection." Science (1998): 2016-2018.

Chen, Qi-Fan, et al. "Direct Aqueous Synthesis of cysteamine-Stabilized CdTe Quantum Dots and Its Deoxyribonucleic Acid Bioconjugates." Chinese Journal of Analytical Chemistry (2007): 135-138.

Chen, X., et al. "Photoluminescence from single CdSe quantum rods." Journal of Luminescence (2002): 205-211.

Danek, M., et al. "Preparation of II-VI quantum dot composites by electrospray organometallic chemical vapor deposition." Journal of Crystal Growth (1994): 714-720.

Goldman, Ellen R., et al. "Avidin: A Natural Bridge for Quantum Dot-Antibody Conjugates." Journal of the American Chemical Society (2002): 6378-6382.

Hu, Ye, et al. "Nanodevices in diagnostics." Wiley Inderdisciplinary Reviews: Nanomedicine and Nanobiotechnology (2010): 11-32.

Idowu, Mopelola, Emmanuel Lamprecht and Tebello Nyokong. "Interaction of water-soluble thiol capped CdTe quantum dots and bovine serum albumin." Journal of Photochemistry and Photobiology A: Chemistry (2008): 7-12.

Mallinckrodt Baker Inc. Bovine Serum Albumin. 20 August 2008. March 2011 <http://www.jtbaker.com/msds/englishhtml/a2010.htm>.
—. Mercaptoacetic Acid. 20 August 2008. December 2010 <http://www.jtbaker.com/msds/englishhtml/m1157.htm>.
—. N,N-Dimethylformamide. 16 September 2009. December 2010 <http://www.jtbaker.com/msds/englishhtml/d6408.htm>.
—. Sodium Borohydrate. 21 November 2008. December 2010 <http://www.jtbaker.com/msds/englishhtml/s3146.htm>.

Murray, C. B., D. J. Norris and M. B. Bawendi. "Synthesis and Characterization of Nerally Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites." Journal of the American Chemical Society (1993): 8706-8715.

Nose, Katsuhiro, et al. "Chemical role of amines in the colloidal synthesis of CdSe quantum dots and their luminescence properties." Journal of Luminescence (2006): 21-26.

Ooba, Hideki. "Synthesis of Unique High Quality Fluorescence Quantum Dots for the Biochemical Measurements." AIST Today (2006): 27.

Oxford University. Safety data for aroclor 1254. 18 February 2005. December 2010 <http://msds.chem.ox.ac.uk/AR/aroclor_1254.html>.
—. Safety data for cadmium chloride, anhydrous. 26 August 2010. December 2010 <http://msds.chem.ox.ac.uk/CA/cadmium_chloride_anhydrous.html>.
—. Safety data for L-cysteine. 15 February 2008. December 2010 <http://msds.chem.ox.ac.uk/CY/l-cysteine.html>.

Peng, Xiaogang, et al. "Shape control of CdSe nanocrystals." Nature (2000): 59-61.

Persistent Organic Pollutant. 2011. 4 2011 <http://en.wikipedia.org/wiki/Persistent_organic_pollutant>.

Polychlorinated Biphenyl. 2011. 4 2011 <http://en.wikipedia.org/wiki/PCBs>.

Qu, Lianhua and Xiaogang Peng. "Control of Photoluminescence Properties of CdSe Nanocrystals in Growth." Journal of the American Chemical Society (2002): 2049-2055.

Reiss, P., et al. "Low polydispersity core/shell nanocrystals of CdSe/ZnSe and CdSe/ZnSe/ZnS type: preparation and optical studies." Synthetic Metals (2003): 649-652.

Rzigalinski, Beverly A. and Jeannine S. Strobl. "Cadmium-containing nanoparticles: Perspectives on pharmacology and toxicology of quantum dots." Toxicology and Applied Pharmocology (2009): 280-288.

Talapin, Dmitri V., et al. "Highly Luminescent Monodisperse CdSe and CdSe/ZnS Nanocrystals Synthesized in a Hexadecylamine-Trioctylphosphine Oxide-Trioctylphospine Mixture." American Chemical Society (2001): 207-211.

Testbourne Ltd. Safety Data Sheet: Tellurium, Te. 30 July 2008. December 2010 <http://www.testbourne.com/im/pdf/material-safety-data-sheets/Tellurium-Te-powder.pdf>.

Tian, Jianniao, et al. "Controllable synthesis and cell-imaging studies on CdTe quantum dots together capped by glutathione and thioglycolic acid." Journal of Colloid and Interface Science (2009): 504-509.

8.0 Appendix

A: Fluorescent Quantum Yield

Quantum yield was calculated on December 9, 2010 using diluted samples from November 10, November 12, and November 16, 2010 and the rhodamine 6G solution made on December 7, 2010.

It was noted that at this time some of the samples from other batches had degraded. This included fading of visible color and precipitation out of solution. It was felt that the samples used in this calculation had not degraded too terribly at this point, though it is possible that the fluorescence (and so the yield) had decreased.

Quantum Yield was calculated using the following equation:

$$Y_u = Y_s \cdot \frac{F_u}{F_s} \cdot \frac{A_s}{A_u} \cdot \frac{{G_u}^2}{{G_s}^2}$$

Y_u = Yield of the sample
Y_s = Yield of the reference, which was known as 0.95(or 95%) (Qu and Peng)
F_u = Peak fluorescence intensity of the sample
F_s= Peak fluorescence intensity of the reference, measured as 234.4169
A_s = Absorption of the reference at the excitation wavelength (must be <0.1), measured as 0.089358
A_u = Absorption of the sample at the excitation wavelength (must be <0.1)
G_u = Index of the reference material of the sample; water was used, and the index is 1.3329
G_s = Index of the reference material of the reference; ethanol was used, and the index is 1.3611

Calculations were carried out in Microsoft Excel as follows.

Table 20 – Calculations of quantum yield for diluted samples from November 10th, 12th, and 16th.

Sample	Fu	Au	Fu/Fs	As/Au	Gu2/Gs2	Yu
10-Nov						
1	***0.05***	0.011969	*0.000213*	7.465787	0.958992	*0.001451*
2	5.105	0.052086	0.021777	1.715586	0.958992	**0.034038**
3	20.182	0.069609	0.086094	1.283713	0.958992	**0.100689**
4	21.452	0.071425	0.091512	1.251075	0.958992	**0.104304**
5	27.185	0.082031	0.115969	1.08932	0.958992	**0.115089**
6	31.982	0.083996	0.136432	1.063836	0.958992	**0.13223**
7	26.715	***0.266009***	0.113964	*0.335921*	0.958992	*0.034877*
8	13.994	0.090462	0.059697	0.987796	0.958992	**0.053723**
9	25.161	0.06191	0.107334	1.443353	0.958992	**0.14114**

10	25.911	0.052419	0.110534	1.704687	0.958992	**0.171664**
11	27.755	0.071198	0.1184	1.255063	0.958992	**0.135381**
12-Nov						
1	0.167	0.002699	0.000712	33.10782	0.958992	**0.021488**
2	***0.058***	0.006577	*0.000247*	13.58644	0.958992	*0.003063*
3	7.259	0.034627	0.030966	2.580587	0.958992	**0.072802**
4	17.306	0.039001	0.073826	2.291172	0.958992	**0.154101**
5	27.244	0.069369	0.11622	1.288155	0.958992	**0.136392**
6	31.668	0.07535	0.135093	1.185906	0.958992	**0.145956**
7	31.502	0.068944	0.134385	1.296095	0.958992	**0.158681**
8	25.498	0.062237	0.108772	1.43577	0.958992	**0.142279**
9	29.646	0.069369	0.126467	1.288155	0.958992	**0.148417**
10	29.176	0.07073	0.124462	1.263368	0.958992	**0.143254**
16-Nov						
1	***0.07***	0.010634	*0.000299*	8.403047	0.958992	*0.002286*
2	***0.05***	0.028343	*0.000213*	3.152736	0.958992	*0.000613*
3	7.742	0.055946	0.033027	1.597219	0.958992	**0.048058**
4	11.99	0.066622	0.051148	1.341269	0.958992	**0.062501**
5	17.1	0.08965	0.072947	0.996743	0.958992	**0.066241**
6	21.884	***0.107346***	0.093355	*0.83243*	0.958992	*0.070798*
7	28.112	***0.112502***	0.119923	*0.794279*	0.958992	*0.086779*
8	22.852	0.061008	0.097484	1.464693	0.958992	**0.130083**
9	28.248	***0.14797***	0.120503	*0.603893*	0.958992	*0.066298*
10	26.647	***0.10583***	0.113674	*0.844354*	0.958992	*0.087443*
11	24.916	***0.204428***	0.106289	*0.437112*	0.958992	*0.042327*

The results in italics are those that do not fit the requirements of the equation. It turns out some of the samples were not diluted enough, resulting in an absorption >0.1 at 430 nm. And some of the initial samples simply do not have a fluorescent peak, so a relative high for the spectrum was used.

These errors would affect the calculation in the following ways:

A sample absorption that is too high would decrease the A_s/A_u fraction, resulting in a lower QY. But at the same time, the absorption is too high because the sample was not diluted enough, meaning the fluorescence will be higher too. This means the F_u/F_s fraction would be increased. It appears that the yields with this error are much lower than they should be, implying that the decrease in the absorption ratio is much greater than the increase in the fluorescence ratio.

The samples without a peak are the samples in which almost no quantum dots have grown. It is possible that these calculated yields are entirely correct. They are just very small. Then again, if there are no quantum dots there is not much point to calculating the yield.

B: Full Width Half Maximum

FWHM was found by taking the peak fluorescent intensity, cutting it in half, and then finding the wavelengths at which the fluorescent spectrum is at this half-intensity. The difference between these two points is the FWHM. The two wavelengths are not always an equal distance from the peak fluorescent wavelength, meaning that these spectrums are not perfectly symmetrical. **Table 21** shows the calculation, performed in Excel, of the FWHM based on the fluorescent spectrums of the samples.

In the table, data for Nov. 10th, 11th, and 12th is shown for both the light intensities the other batches were measured at and the lower light intensities, labeled 'less light.' This is so that these batches might be compared to the other batches for the samples for which peak wavelengths could be measured at the higher light intensity. **Look up the light intensities and wavelengths used for the fluorescent spectrums.**

Table 21 – FWHM calculation.

Date	Sample	Peak Intensity	Peak Wavelength	Color	FWHM Intensity	start	finish	FWHM	left half	right half
	(min)		***(nm)***			*(nm)*	*(nm)*	***(nm)***	*(nm)*	*(nm)*
10/29/2010	0	-	**-**	-	-	-	-	**-**		
	60	54	**530**	green	27	504	562	**58**	26	32
11/2/2010	0	-	**-**	-	-	-	-	**-**		
	28	13.5	**508**	green	6.75	477	535	**58**	31	27
	56	37.5	**510**	green	18.75	475	539	**64**	35	29
	122	173.3	**512**	green	96.65	489	544	**55**	23	32
	178	243.6	**515**	green	121.8	490	555	**65**	25	40
	239	498.9	**528**	green	249	498	562	**64**	30	34
	299	576.8	**538**	green	288	503	570	**67**	35	32
	416	395.8	**547**	green	197.9	506	578	**72**	41	31
11/5/2010	0	49.2	**479**	cyan	25	450	540	**90**	29	61
	29	161.2	**514**	green	80.6	495	534	**39**	19	20
	59	214	**547**	green	107	519	568	**49**	28	21
	119	59.8	**576**	yellow	30	554	593	**39**	22	17

11/10/2010	0	-		**-**		-	-		-	-	**-**			
	30		298		**504**	green		150	489	521.5	**32.5**	15	17.5
	95		709		**516**	green		355	500	536	**36**	16	20
	122		759		**518**	green		380	500	537	**37**	18	19
	180		881		**521**	green		440	502	541	**39**	19	20
	240		945		**523**	green		472	503	544	**41**	20	21
	300		1014		**525**	green		507	504	547	**43**	21	22
	360	plateau									**0**	0	0
	420	plateau									**0**	0	0
	480		921		**524**	green		460	502	550	**48**	22	26
	540	plateau									**0**	0	0
11/10/2010	0	-		**-**		-	-		-	-	**-**			
less	30		57.3		**503**	green		28.65	488	521	**33**	15	18
light	95		140.8		**516**	green		70.4	499	535	**36**	17	19
	122		153.5		**516**	green		76.75	499	537	**38**	17	21
	180		177.2		**520**	green		88.6	501	541	**40**	19	21
	240		189		**521**	green		94.5	502	543	**41**	19	22
	300		199.7		**524**	green		99.85	503	546	**43**	21	22
	360		205.3		**525**	green		102.65	504	547	**43**	21	22
	420		203.4		**526**	green		101.7	504	550	**46**	22	24
	480		177.7		**523**	green		88.85	500	549	**49**	23	26
	540		203.6		**528**	green		101.8	504	553.5	**49.5**	24	25.5
11/11/2010	0	-		**-**		-	-		-	-	**-**			
	30		82		**492**	cyan		41	477	508	**31**	15	16
	60	plateau									**0**	0	0
	120		799		**555**	green		400	530	575	**45**	25	20
11/11/2010	0	-		**-**		-	-		-	-	**-**			
less	30		13.4		**489**	cyan		6.7	474	508	**34**	15	19

light	60		209.4		**526**	green		104.7	507	547	**40**	19	21
	120		139.2		**551**	green		69.6	528	574	**46**	23	23
11/12/2010	0	-		**-**		-	-		-	-	**-**		
	10	-		**-**		-	-		-	-	**-**		
	60		294		**514**	green		147	497	533	**36**	17	19
	122		610		**528**	green		305	509	549	**40**	19	21
	177		750		**536**	green		375	516	557	**41**	20	21
	237		842		**540**	green		421	520	562	**42**	20	22
	307		960		**545**	green		480	522	567	**45**	23	22
	354		1004		**547**	green		502	524.5	568.5	**44**	22.5	21.5
	427	plateau									**0**	0	0
	480	plateau									**0**	0	0
11/12/2010	0	-		**-**		-	-		-	-	**-**		
less	10	-		**-**		-	-		-	-	**-**		
light	60		59.3		**512**	green		29.65	496	531	**35**	16	19
	122		120.9		**527**	green		60.45	507	547	**40**	20	20
	177		154.7		**535**	green		77.35	514	555.5	**41.5**	21	20.5
	237		173.6		**538**	green		86.8	518	561	**43**	20	23
	307		193.1		**542**	green		96.55	521	565	**44**	21	23
	354		197.5		**545**	green		98.75	522	567	**45**	23	22
	427		206.6		**547**	green		103.3	524	570	**46**	23	23
	480		209.1		**549**	green		104.55	524.6	571.5	**46.9**	24.4	22.5
11/16/2010	0	-		**-**		-	-		-	-	**-**		
	15	-		**-**		-	-		-	-	**-**		
	75		530.5		**524**	green		265.25	507	543.5	**36.5**	17	19.5
	120		704.5		**533**	green		352.25	514	553	**39**	19	20
	175		797		**541**	green		398.5	520	562	**42**	21	21
	250		814.8		**550**	green		407.4	527.5	571.5	**44**	22.5	21.5

	315	757	**557**	green	378.5	523.5	577.5	**54**	33.5	20.5
	363	702	**560**	green	351	536.5	580.5	**44**	23.5	20.5
	425	565	**566**	green	282.5	541	585	**44**	25	19
	485	468	**569**	green	234	545	589	**44**	24	20
	648	116	**574**	yellow	58	552	597	**45**	22	23
11/18/2010	5	-	**-**	-	-	-	-	**-**		
	31	20	**499**	green	10	482	522	**40**	17	23
	60	58	**506**	green	29	490	526	**36**	16	20
	123	130	**516**	green	65	499	536	**37**	17	20
	181	192	**523**	green	96	504.5	543	**38.5**	18.5	20
	242	253	**530**	green	126.5	511	550.5	**39.5**	19	20.5
	300	284	**536**	green	142	516	557	**41**	20	21
	720	201	**549**	green	100.5	526	571	**45**	23	22
11/23/2010	0	-	**-**	-	-	-	-	**-**		
	31	-	**-**	-	-	-	-	**-**		
	60	11.9	**497**	green	5.95	478	521	**43**	19	24
	122	53.4	**508**	green	26.7	490	529	**39**	18	21
	180	89	**513**	green	44.5	496	533.5	**37.5**	17	20.5
	241	126	**518**	green	63	501	539	**38**	17	21
	301	165	**523**	green	82.5	505	544	**39**	18	21
	361	196	**528**	green	98	509	548	**39**	19	20
	421	226	**532**	green	113	513	552	**39**	19	20
	505	299.2	**538**	green	149.6	519	558	**39**	19	20
	540	289.2	**540**	green	144.6	522	561	**39**	18	21
	600	368	**543**	green	184	524	564	**40**	19	21
11/25/2010	0	-	**-**	-	-	-	-	**-**		
	5	-	**-**	-	-	-	-	**-**		
	10	8.1	**493**	cyan	4.05	472	517	**45**	21	24

	15	90.4	**507**	green	45.2	492	526	**34**	15	19
	20	150.9	**512**	green	75.45	496	530	**34**	16	18
	25	179.1	**515**	green	89.55	499	534	**35**	16	19
	30	214.6	**517**	green	107.3	501	536	**35**	16	19
	35	250.4	**520**	green	125.2	503	538.5	**35.5**	17	18.5
	40	275.3	**522**	green	137.65	504	540	**36**	18	18
	45	299.8	**521**	green	149.9	505	541	**36**	16	20
	50	360.7	**527**	green	180.35	509	545.5	**36.5**	18	18.5
	55	383.8	**528**	green	191.9	510.3	547.5	**37.2**	17.7	19.5
	60	410.1	**529**	green	205.05	511	548	**37**	18	19
	65	422.7	**530**	green	211.35	512	549	**37**	18	19
	70	452	**531**	green	226	513	550.5	**37.5**	18	19.5
	75	459.1	**532**	green	229.55	513.3	551	**37.7**	18.7	19
	80	475.7	**533**	green	237.85	514	552	**38**	19	19
	90	527.9	**534**	green	263.95	516	554.5	**38.5**	18	20.5
	100	561.3	**537**	green	280.65	517.6	556.5	**38.9**	19.4	19.5
	110	603.9	**539**	green	301.95	519.5	559	**39.5**	19.5	20
	120	608.4	**539**	green	304.2	520	559	**39**	19	20
	131	634.4	**541**	green	317.2	521	561	**40**	20	20
	151	648.6	**545**	green	324.3	525	566	**41**	20	21
	180	563.5	**556**	green	281.75	533.5	576	**42.5**	22.5	20
	211	85.3	**567**	green	42.65	545	588	**43**	22	21
11/30/2010	0	-	**-**	-	-	-	-	**-**	-	-
	15	171.601	**539**	green	85.8005	522	558	**36**	17	19
	35	481.643	**554**	green	240.8215	535	571.5	**36.5**	19	17.5
	49	568.47	**558**	green	284.235	539.5	576.5	**37**	18.5	18.5
	60	641.96	**562**	green	320.98	543	579.3	**36.3**	19	17.3
	78	479.125	**565**	green	239.5625	545	582.5	**37.5**	20	17.5
	98	664.401	**570**	yellow	332.2005	551	586.8	**35.8**	19	16.8
	111	677.21	**572**	yellow	338.605	553	589.2	**36.2**	19	17.2

	127	693.589	**574**	yellow	346.7945	556.3	592.6	**36.3**	17.7	18.6
12/11/2010	0	-	**-**	-	-	-	-	**-**		
	30	86.6	**514**	green	43.3	497	534	**37**	17	20
	60	204.1	**527**	green	102.05	509.5	547	**37.5**	17.5	20
	90	234.6	**535**	green	117.3	516.5	556	**39.5**	18.5	21
	120	326.4	**539**	green	163.2	520	559	**39**	19	20
	150	388.9	**542**	green	194.45	522	562	**40**	20	20
	180	457.1	**544**	green	228.55	524	564.3	**40.3**	20	20.3
12/13/2010	0	-	**-**	-	-	-	-	**-**		
	30	111.1	**517**	green	55.55	502	538	**36**	15	21
	60	209.6	**526**	green	104.8	509	544	**35**	17	18
	90	290	**530**	green	145	512.5	548.5	**36**	17.5	18.5
	120	343.2	**533**	green	171.6	515	551.5	**36.5**	18	18.5
	150	378.9	**535**	green	189.45	517	554	**37**	18	19
	180	437.7	**537**	green	218.85	519	556.5	**37.5**	18	19.5
	240	511.4	**540**	green	255.7	522	560	**38**	18	20
	331	595.4	**545**	green	297.7	525.5	564.5	**39**	19.5	19.5
	360	577.9	**546**	green	288.95	526.5	565.5	**39**	19.5	19.5