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Tuning Quantum Dots Optical Properties by Temperature and Concentration Modulation

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Tuning Quantum Dots Optical Properties by Temperature and Concentration Modulation

A Capstone Project Submitted in Partial Fulfillment of the Requirements
of the Renée Crown University Honors Program at Syracuse University

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and Renée Crown University Honors

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Honors Capstone Project in Chemistry

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Abstract:

Quantum dots have recently been awarded attention due to their tunable optical and spectroscopic properties. The optical and spectroscopic behavior of quantum dots was investigated as a function of mean particle size. Manipulation of the reaction conditions and constituents impact the controllability of size and surface conditions. Therefore, synthesis of CdSe and CdS semiconductor nanoparticles with tunable particle size were created using temperature, time, and composition as variables. Analytical techniques used to characterize the nanoparticles included fluorescence and electronic absorption. The effect of temperature, aside from changing the size of the particle, also eliminated defects on the surface and caused thermal annealing.

Introduction:

On August 9th, 2009 the small village of Silver Creek, NY experienced intense flashfloods that caused millions of dollars in damage and decimated much of the area with layers of mud and silt. Silver Creek, NY is prone to flooding, but this particular event denotes one of the most significant flash floods to hit the region in memory. In 2005, Hurricane Katrina was the costliest and deadliest hurricane in U.S. history in the second most active hurricane season in recorded history. The 2008 hurricane season is the most active. Floods and hurricanes are a natural occurrence and would occur even without human interference. However, the number and intensity of floods and hurricanes in recent history are happening more frequently than they statistically should.[1,2,3,4,5]

The cause seems to be a highly disputed topic called global warming. The term, global warming, was first inadvertently coined by Wallace Broecker in 1975 in a paper he published entitled *Climate Change: Are we on the Brink of a Pronounced Global Warming?* Since then the topic has been highly debated and as of 2009, just 51% of Americas believe in its existence. Whether or not global warming does exist is beyond the scope of this paper, but there is substantial proof that the average annual temperature on Earth increased over the last century causing severe environmental changes, such as floods and hurricanes.

An enhanced greenhouse effect may be responsible for global environmental change and global warming. Solar radiation passes through the atmosphere as ultra violet and visible light. The Earth absorbs this energy and reradiates it as infrared light, or heat. Gases in the atmosphere, such as water vapor (H_2O) and carbon dioxide (CO_2), absorb the outgoing energy and reradiate it back towards Earth causing the Earth's atmosphere to warm. This process is called the greenhouse effect and without it the average annual temperature on Earth would be approximately 15°C cooler and below freezing. Life as we know it would not be possible without the greenhouse effect.
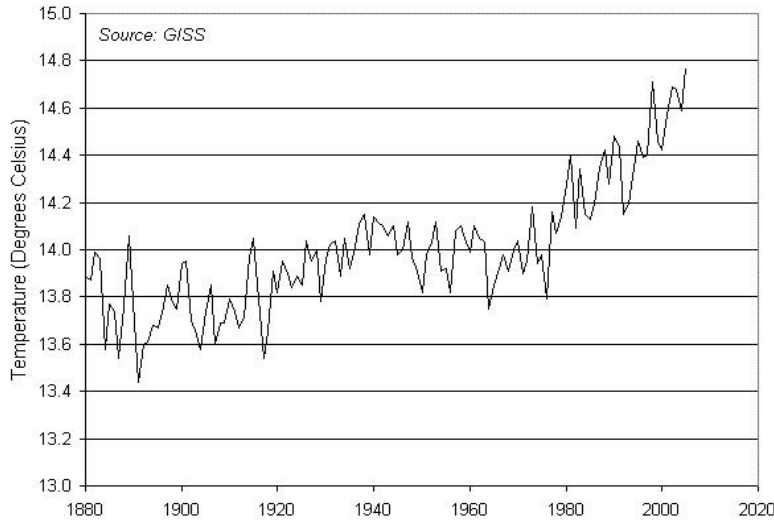
Figure 1: Average global temperature and global warming trends from 1880 to 2005. Image modified from http://www.sigthedmoon.com/?page_id=53

Since pre-industrial times, however, there has been an influx of greenhouse gases being emitted into the atmosphere including carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (NO_x) which have increased approximately 30%, 145%, and 15% respectively. The excess gases in the atmosphere are believed to enhance the greenhouse effect by preventing radiation from escaping into space leading to warmer surface temperatures. The global mean surface temperature has already increased about 0.3 to 0.6°C over the past decade (Fig. 1). Climate models project an increase in temperature between 1 and 3.5°C.[6] This change may seem small, but it can have a profound impact on Earth's systems. As Wallace Broecker once said, "We have clear evidence that different parts of the earth's climate system are linked in very subtle yet dramatic ways." A small change in one area will have rippling effects across the globe.

The effects of global warming have already been observed. Globally, the 1990s were the warmest decade of the past millennium and nine of out the ten warmest years on record occurred between 1995 and 2004.[4] Rising temperatures have caused melting glaciers, rise in sea level, coral bleaching and negative effects on agriculture. If global warming continues, the consequences lead to the loss of biodiversity, a severe strain on many agricultural areas, the spread of disease, and an increase in severe weather events (e.g. tornadoes, hurricanes, floods, etc), drought, water scarcity, and much more. These environmental changes have the ability to lead to political security issues, including war, over resources that are becoming increasingly scarce due to global warming.

The increased production of greenhouse gases that lead to environmental change is primarily the result of anthropogenic activities, in particular, the combustion of fossil fuels, such as coal and gasoline, for energy consumption. The combustion of fossil fuels, for energy related purposes (e.g. electricity, gasoline for cars, etc), is the major sources of increased levels of CO_2 by more than 30% in the last few centuries. Global CO_2 emissions are expected to increase by 1.8% annually between 2004 and 2030 according to the Energy Information Administration (2008). The demand for energy consumption will increase but the sources of fossil fuels are dwindling. Carbon free energy sources are needed not only to stabilize the amount of greenhouse gases in the atmosphere and keep them within tolerable levels with respect to their impact on global climate change, but also to meet energy demands for the future.

Alternative energy has become an increasingly popular topic since the 1973 Oil Crisis when members of the Organization of Arab Petroleum Exporting Countries (OAPEC) proclaimed an oil embargo on the United States forcing oil prices to skyrocket. Since then technology has attempted to exploit natural, renewable resources as sources of energy, such as wind, geothermal, hydroelectric, biomass, etc. Green technology has primarily been successful in the generation of electricity. There are seven fundamental methods of generating electricity: static, electromagnetic, chemical, photoelectric, nuclear, piezoelectric and thermoelectric. However there are only two ways to produce electricity commercially: electromagnetically, and via the photoelectric process.

The use of wind energy as a pollution-free means of generating electricity on a significant scale is attracting a plethora of interest and correspondingly wind power is one of the fastest growing renewable energy technologies worldwide. Wind energy produces electricity electromagnetically with a wind turbine using the same principles used for coal fired power plants, a theory based on the principles discovered by Michael Farady, an English chemist and physicist in the 19th century. Farady discovered that if a magnet is moved past a conductor, it causes electricity to flow. In a large generator, electromagnets are made by circulating direct current through loops of wire wound around stacks of magnetic steel laminations. Wind turbines work by the inflow of wind rotating the blades of the turbine converting wind energy to mechanical energy (Fig 2). The rotating blades cause spinning of a low speed shaft that in then turns the gears on a high speed shaft that runs through a generator. Inside the generator, an electrical

current is generated when a magnetic rotor on the high speed shaft spins inside loops of copper wire that are wound around a copper core causing electromagnetic induction through the coils. Though wind energy is becoming increasingly popular, there are consequences to using wind energy. It cannot be transferred long distance, wind energy is harmful and fatal to many species of birds, and many people complain that wind turbines are an eye sore. It is also more expensive than coal fired power plants due to the fact that the technology is still new and is not massed produced which raises costs.
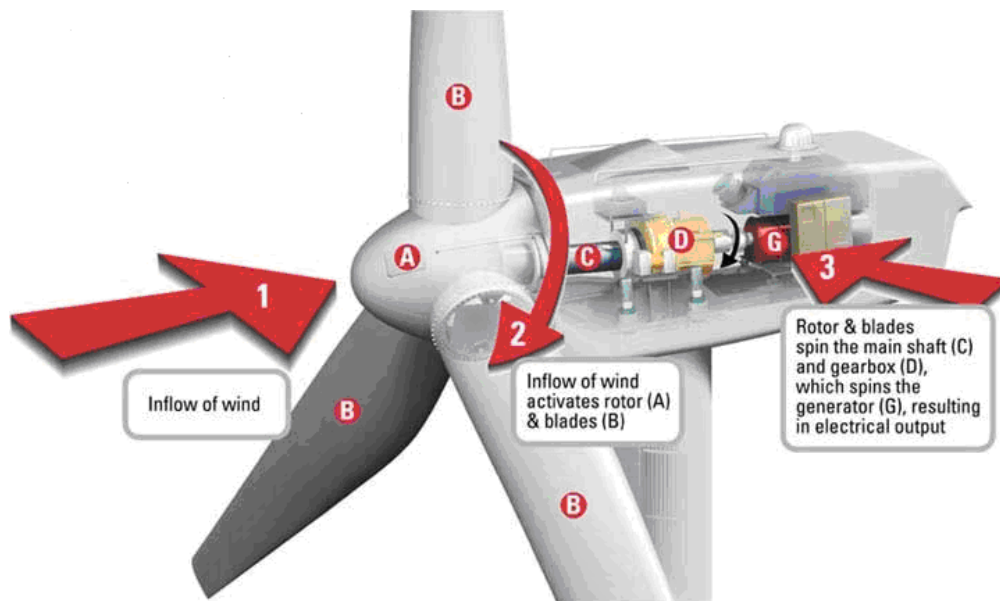

Figure 2: Generic Wind Turbine. Image modified from http://renewable-sources-of-energy.com/

Hydroelectric energy has been a source of energy for centuries and it is generated in a similar manner to wind energy. In order to harness hydroelectric energy a dam must first be built on a river. Water is then stored behind the dam and channeled through an intake near the bottom of the well. The moving water rotates a turbine that generates electricity in the same manner as a wind turbine.

The consequences of hydroelectricity are far more damaging than wind. The process of building a dam and the water that is trapped behind it, destroy large tracts of land and can displace or destroy entire ecosystems. The dam also stops the movement of fish species to spawning pools. While it is economically feasible to build hydroelectric plants, they are expensive to maintain and facilities do not last forever and must undergo repairs or be dismantled.

The most promising source of green energy, however, is solar energy. Solar energy is the most abundant renewable form of energy on Earth and the current amount of solar energy incident on the planet is enough to meet global energy demands. Solar energy is not produced electromagnetically, rather it employs the principles of the photoelectric effect, or the second way to viably produce energy for commercial use. The photoelectric effect occurs when electrons are emitted from matter as a result of absorption of electromagnetic radiation, or light energy, creating a current (Fig 3). In 1887, Heinrich Hertz was the first person to observe the photoelectric effect, but he declined to attempt to describe a theory that would explain his experiment. In 1905, Albert Einstein proposed a simple theory to explain the phenomena. Light, he realized, was quantized and transferred all of its energy to an electron during a collision causing the electron to be emitted from matter (Fig 3). Robert Millikan worked for ten years to disprove Einstein's theory only to provide experimental proof in favor of Einstein in 1916. The photoelectric effect is the driving force behind photovoltaics (PV).
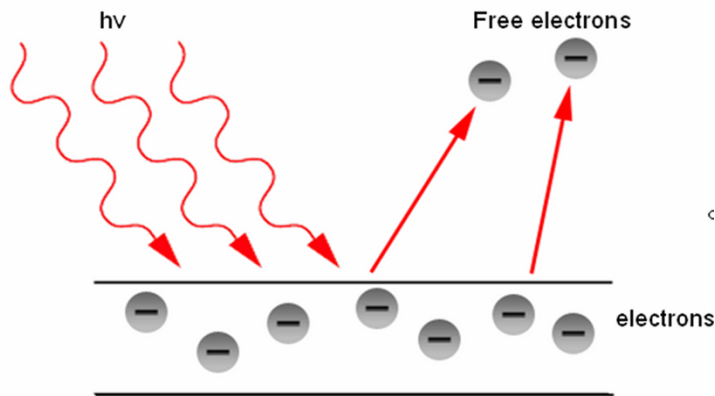
Figure 3: Visual representation of the Photoelectric effect. Image modified from http://physweb.bgu.ac.il/COURSES/PHYSICS3_ChemMatr/index_files/

Solar energy is harvested using photovoltaics. The photovoltaic effect was discovered in the late 19th century, but it was not until the 1950s that the breakthrough occurred that set in motion the development of modern, high-efficiency solar cells. The breakthrough occurred in Bell Telephone Laboratories in New Jersey and came in the form of semiconductors. Semiconductors are a non-metallic material whose properties lie between metals that offer little resistance to the flow of electric current and insulators which block the flow of current. Semiconductors are separated from metals or insulators by the size of their bandgap which will be explained later in further detail.

The basic and most common PV consists of a junction between p-type and n-type semiconductors and are usually made of silicon (Si). An n-type, or negative, semiconductor is made from crystalline Si that has been doped with small amounts of impurities, such as phosphorous, that cause a relative surplus of free electrons. A p-type, or positive, semiconductor, on the other hand is usually made from crystalline Si that has been doped with small amounts of impurities, usually boron, so that there is a relative deficit of free electrons, or

'holes.' The joining of these two types of semiconductors creates a p-n junction that sets up an electrical field.

When light falls on the p-n junction, the photons transfer their energy to some of the electrons and promote them to a higher energy level. The photovoltaic effect, however, generates electricity. The excited electrons become 'free' to conduct electric current by moving through the material leaving a hole behind, which can also move. Holes, in the p-type, and electrons, in the n-type, are attracted to combine with one other. The net effect is to set up a junction with a layer on the n-type more positively charged than usual, and a layer on the p-type that is more negatively charged than usual forming a reverse electric field. When an electron in the junction is stimulated by a photon, the excited electron goes to the conduction band leaving a hole in the valence band creating an electron-hole pair. The electrons are attracted to the n-region due to the reverse electric field. The flow of electrons to the n-region is an electrical current generating a potential difference or electromotive force. This force drives the electrons through a load in an external circuit to do electrical work.

Solar energy is relatively abundant depending on the time of year and latitude and the generation of electricity does not produce CO_2 or any other greenhouse gases. Despite its advantages, there are three major reasons that PVs are not more widely used for the production of electricity: cost, inability to store it, and inefficiency. The major component, Si, of the most common type of PV is expensive and there is a worldwide effort to minimize Si usage.[7]Not only is Si expensive, but so are the materials for the infrastructure and the production.

Solar cells, like wind turbines, are not massed produced which raises costs as well. Photovoltaics are obviously dependent on the sun in order to generate electricity and the sun is not available at all latitudes 24 hours a day. The technology to store solar energy is severely lacking. This deficiency may be directly tied to the inefficiency of solar cells. The most efficient crystalline Si solar cell can only hope to be 24.7% efficient, but the cheaper and more widely used amorphous Si solar cells are a measly 10.1% efficient.[7]

The Shockley–Queisser approximation was first calculated by William Shockley and Hans Queisser at Shockley Semiconductor in 1961. Shockley and Queisser assumed that an electron-hole pair must annihilate at some point and that during this annihilation light would be emitted. However, that is the ideal case and does not always happen. Generally the extra energy of the excited electron is wasted as heat. They also postulated that only electrons of a certain energy would be able to produce power. As such a vast amount of energy is wasted. The Shockley-Queisser limit is then calculated by examining the amount of electrical energy that is extracted per photon of incoming sunlight. Shockley and Queisser calculated a limit of only 31%. This limit is fundamental to solar energy production and has promoted research of Quantum Dots.

Quantum Dots are colloidal crystalline molecular sized semiconductor nanocrystals that are confined in three dimensions.[8,9] Semiconductor nanocrystals are tiny light-emitting particles on the nanometer scale.[10] The QD core is made up of semiconductor elements from the II-IV (e.g. CdSe, CdTe, CdS, ZnSe), III-V (e.g. InP, InAsO), or IV-VI (e.g. PbSe) group. Research into

Quantum Dots (QDs) has recently gained momentum because they posses unique optical properties due to quantum confinement effects.[11]

At a molecular level, atomic orbitals interact constructively or destructively to create distinct energy levels (Fig 4). As opposed to the case of atoms and molecules, the energy structure of a solid no longer consists of discrete energy levels, but rather broad energy bands because molecular orbitals become indistinguishable from one another in a bulk material (Fig 4). Semiconductor nanocrystals, however, despite containing multiple molecules, have optical and electronic properties that deviate substantially from those of a bulk material. Quantum dots bridge the gap between molecules and large crystals and display discrete electronic transitions that are similar to those of molecules or atoms (Fig 4).[10]

Molecule   **Semiconductor Quantum Dots**   **Bulk Semiconductor**

LUMO

Conduction Band
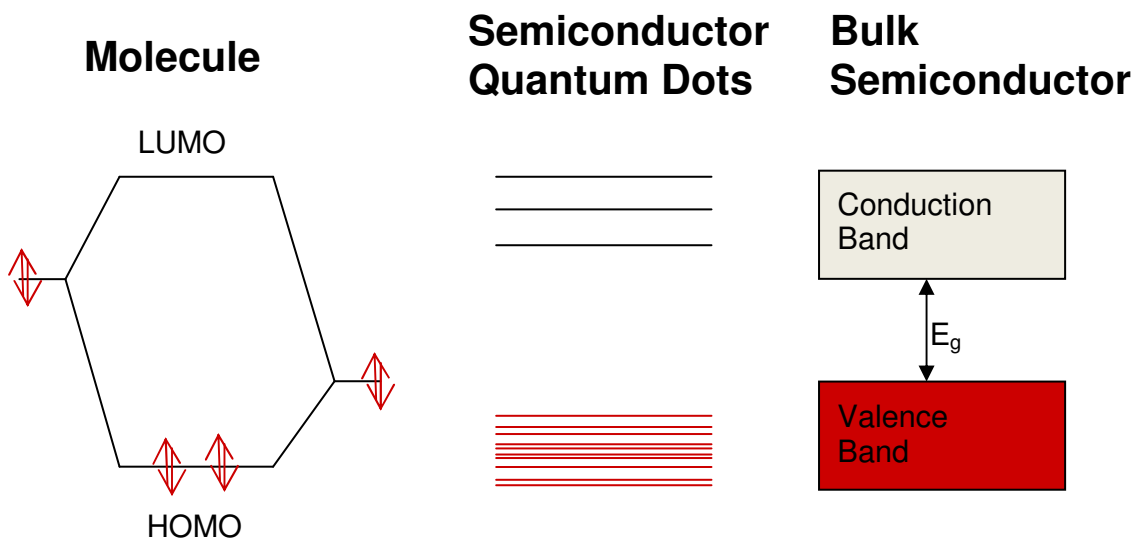
E_g

Valence Band

HOMO

Figure 4: Energy levels of a molecule, semiconductor, and bulk material.

These discrete energy levels can be explained by the particle in the box theory. A particle in a box is a quantum mechanical system that describes a particle that is confined within a region. The particle is free to move anywhere

within that region, but is trapped inside of a certain space. For the particle to be trapped it is surrounded by impenetrable walls and it is assumed that the potential energy is zero inside the box, but the potential energy at the borders is assumed to be infinite. In a Quantum Dot the theoretical particle is confined in three dimensions resulting in a quantization of energy that leads to the discrete energy levels indicated in Figure 4. Only discrete energy levels are allowed for quantum dots. Quantum confinement, therefore, is the three dimensional confinement of particles that results in discrete energy levels.

As a result of quantum confinement, QDs have bandgap energies that are size dependent. [9] The general rule is, the smaller the size of the quantum dot, the larger the band gap is (Fig 5).[9] The bandgap energy (E_g) corresponds to the minimum energy that must be provided to move an electron from the valence to the conduction band.[9] During photoexcitation the absorption of a photon of energy greater than E_g, induces excitation of an electron causing it to leave a hole in the valence band. The hole is a positively charged, vacant orbital that in its lowest energy state is electrostatically attracted to the electron because of quantum confinement.[9] This electron-hole pair, is known as an exciton and can move anywhere within the confined three dimensional space of a quantum dot. Relaxation of the excited electron back to the valence band annihilates the exciton and may be accompanied by the emission of a photon, a process known as radiative recombination.[10] The confinement of this process is what leads to high efficiency in fluorescence. However, more likely than not trap states within the material trap either the hole or electron and prevent it from annihilating. Trap

states can be caused by structural defects, atomic vacancies, local lattice mismatches, or dangling bonds.[9] Trap states decrease the efficiency in fluorescence because it makes radiative recombination less likely to occur. In order to create high crystalline Quantum Dots with efficient fluorescence, it is then necessary to eliminate these trap states.
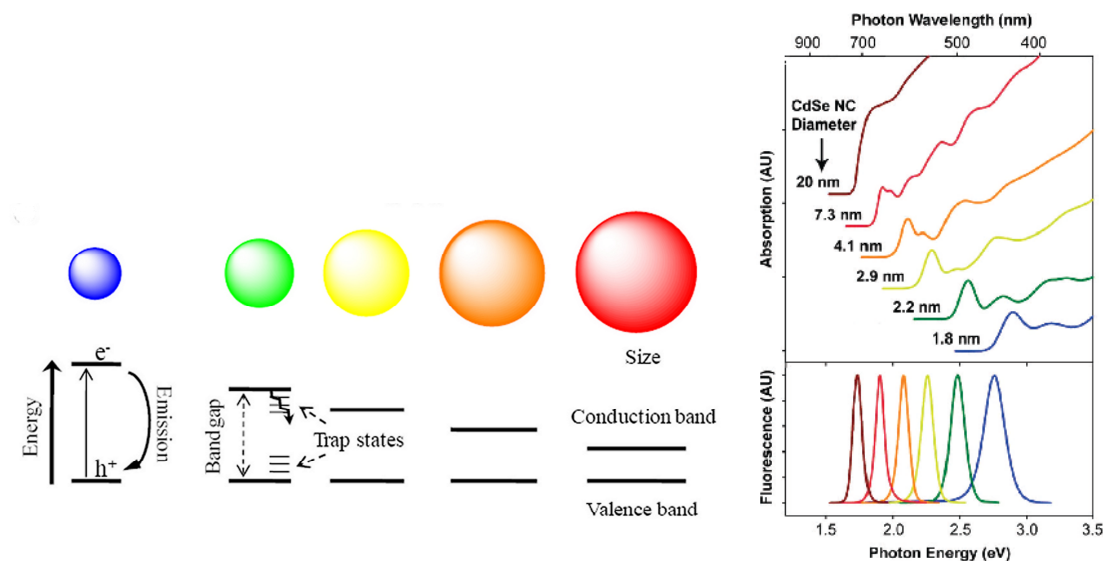

Figure 5: Relation between size, color and spectral properties of Quantum Dots. Image modified from Reference 9 and 10.

Because the bandgap of Quantum Dots is size dependent, tuning of its optical gap by particle size is a possibility. [12] The tunability from the visible to near-infrared region is possible by varying the size, or composition, of QDs. This can be achieved multiple ways including using different types of semiconductors, changing reaction conditions such as composition, temperature, and time, varying type of ligand, adding shells, etc.[10,11] However, relatively little is known about the precise manipulation of the reaction conditions and constituents and its impact on the controllability of the size, composition and interfacial reactivity of nanomaterials.[13] Knowledge of the surface chemistry of QDs is needed to

understand their optical properties and to manipulate them to achieve a desired application.[9]

The optical and spectroscopic properties of QDs are also a function of size and therefore, the variation of size is observed by the shift in wavelength of maximum absorption and fluorescence emission with a change in diameter (Fig 5). The higher in energy of the maximum wavelength, the larger the bandgap is and therefore the smaller the particle is. The lower in energy of the wavelength of maximum absorption and fluorescence emission, the larger the particle is and the smaller the bandgap energy.

QDs exhibit a wide range of unique size-dependent optical and electronic properties including broad excitation and narrow size-tunable emission spectra, negligible photobleaching and high photochemical stability.[9] Therefore, it is thought that QDs can be used in a wide range of applications. Because of their fluorescent properties and size-dependent emission, the most common possible application for QDs is the use as chemical and bio-sensors.[14] In regards to bioimaging, some of the important applications of quantum dots are: labeling of microoganisms, detection of biofilms, drug delivery, and tumor targeting and imaging among others.[9,8] QDs have the advantage over traditional methods of cellular imaging because they are not hindered by photo-bleaching and their emission colors are tunable from the visible to the near-infrared region. The application of Quantum Dots is not limited to bioimaging and biosensors, but they can be used in light emitting diodes and lasers and have the potential to be used for single electron devices and for quantum computing and information.[8] QDs

can also be used in PVs and could be a potential solution the limitations of cost and inefficiency mentioned earlier.[15]
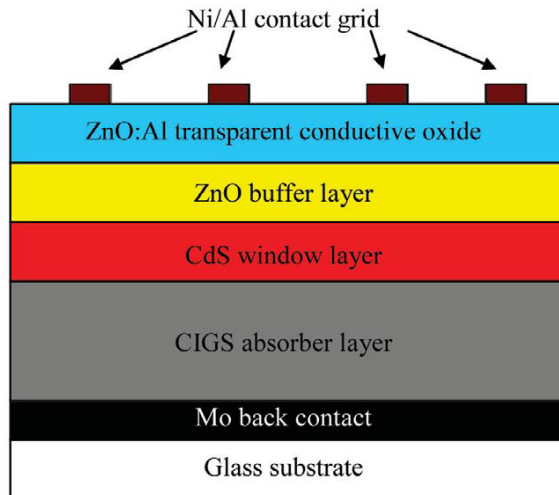

Figure 6: Typical copper indium gallium (di) selenide solar cell.
Image modified from Reference 7.

Though Si is the most widely used material in PVs, the use of QDs has recently become popular because it is less expensive and could potentially be more efficient. Numerous ventures are currently engaged worldwide in the development of CIGS-based photovoltaic products. CIGS, short for copper indium gallium (di) selenide, are part of a complicated solar cell (Fig 6).[16] CIGS photovoltaic products has the advantage over Si PVs in that the use of direct energy gap materials result in a large optical absorption coefficient which permits the use of thin layers (1-2 μm) of active material and so it is more cost efficient.[16] A more interesting property, however, is the unique ability of quantum dots to create multiple electron – hole pairs, also known as impact ionization.[15] Electrons excited to energies greater than the band gap release energy through lattice vibration. However, the excited electron can transfer its energy to a second

electron promoting the formation of a second exciton in what is known as impact ionzation.[15] Impact ionization has the ability to enhance the photocurrent in solar photon conversion devices and thus increases the efficiency.

In light of this information, the hypothesis is to change the size of quantum dots and therefore the optical properties in order to tune the emission from the visible to near-infrared and to make them more uniform with less trap states for use in a wide variety of applications. The aim is to vary reaction conditions, particularly temperature and concentration, to tune the size of the nanoparticles. Temperature can also be used as a method for thermal annealing and the creation of uniform particles with limited trap states. The specific goal was to create cadmium selenide (CdSe) and cadmium sulfide (CdS) with tunable size, uniformity of size, and restricted trap states. Due to the fact that absorption and fluorescence emission is a function of size, characterization of the QDs was carried out using electronic absorption and photoluminescence.

Experimental

Materials

Cadmium Perchlorate was used in conjunction with selenourea or thioacetamide to make cadmium selenide (CdSe) and cadmium sulfide (CdS) quantum dots respectively. Citrate was used as a capping ligand for all of the experiments detailed below. Zinc chloride was used to make a CdSe core quantum dot with a zinc shell. All syntheses were performed hydrothermally using Microwave Assisted Processing Synthesis or MAPS (Fig 7). Using water as

a solvent is important because particles need to be water soluble for biological applications and it can be used for biofunctionality.[8]

Methods

Method 1: Synthesis of CdSe: Temperature Dependence

      Colloidal CdSe quantum dots were produced by the following procedure: mixed 0.5 mL of Cadmium Perchlorate (0.249 g, 40 mM) with 250 µL of selenourea (11.90 mg, 20 mM), 2.5 mL of sodium citrate (58.82 mg, 10mM), 0.5 mL of dionized water and 20 µL of sodium hydroxide for a 8:2:6 ration of [Cd]: [Se]: [Cit]. The mixture was heated mixture 5 min at 100°C with the microwave. The resulting product was a deep red color. This procedure produces a colloidal solution of CdSe QDs that are capped with citrate. The procedure was repeated with solutions of the same concentration, but synthesized at 110°C, 120°C, 135°C, and 150°C.

Method 2: Synthesis of CdS: Temperature Dependence

      Colloidal CdS nanoparticles were synthesized by the following procedure: mixed 0.5 mL of cadmium perchlorate solution(0.249 g, 40 mM) with 200 µL of thioacetamide soultion (37.56 mg, 25 mM), 2 mL of sodium citrate solution (58.82 mg, 10mM), 0.5 mL of dionized water, and 20 µL of sodium hydroxide for a 4:1:4 ratio of [Cd]: [S]: [Cit]. The resulting mixture was heated for 5 min at 120°C with the microwave. The resulting product was a bright yellow in what is assumed to be CdS nanoparticles capped with citrate. The process was repeated with solutions of the same concentration, but temperatures at 150°C and 180°C.

Method 3: Synthesis of CdS: Composition Study

Nanoparticles with a ratio of [Cd]: [S]: [Cit] of 4:1:4 mM were made using the above procedure. Composition was varied by changing the concentration of thioacetamide solution. For an 8:1:8 ratio, 100 µL of sulfur solution (37.56 mg, 25 mM) was used and for an 8: 2.5: 8 ratio, 250 µL of thioacetamide solution (37.56 mg, 25 mM) was used. Each mixture was heated for 5 minutes using the microwave at 180°C.

Method 4: Synthesis of CdS/CdSe core-shell dot; temperature study

CdS quantum dots with a CdSe shell were created by the following procedure: a solution [Cd]: [S]: [Cit] with a ratio of 4: 1: 4 was created using the procedure for *Method 2* at 180°C. For CdSe shell growth, 20 µL of selenourea (11.90 mg, 20mM) was added. Three separate mixtures were heated at 100°C, 130°C, and 160° for 3 minutes respectively.

Method 5: Synthesis of CdSe:Zn nanoparticle

CdSe nanoparticles with a possible ZnSe shell were synthesized by mixing 1mL of cadmium perchlorate solution (0.26g, 41.63mM) with 1mL of sodium citrate solution (13.93mg, 10.8mM) , 1mL selenourea (6.9mg, 10 mM), 20µL sodium hydroxide (1.01M), and 1mL of zinc chloride (0.11 g, 40mM) in that order. The solution was heated for 2 min at 120°C. The resulting product was reheated at 100°C, 150°C and 180°C and fluorescence was also monitored over the next two weeks.

Instrumental

Microwave Assisted Processing Synthesis or MAPS (Fig 7) allows for easy control of time, temperature and power during the synthesis of QDs. The

sample is placed in the microwave and the reaction conditions can then be chosen from the machine. Maximum temperature, power, time, and pressure can be specified for each reaction. For example, for the temperature dependence studies, if the designated temperature for synthesis was 110°C, then the settings on the microwave could be set to 110°C for a specific, predetermined time. These settings can be altered for time, pressure and power as well.
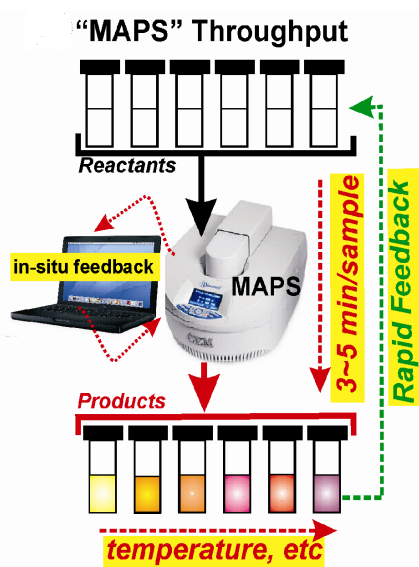

Figure 7: Diagram of a Microwave Assisted Processing Synthesis Throughput.

For all five methods, characterization was done using photoluminescence on a Steady State Fluorescence Spectrometry, Horiba Yvon Jobin, Fluoromax 4. The specifications include excitation at 400 nm, emission from 425 to 755 nm, and an integration of 0.25s. The intensity of fluorescence is the function of radiative recombination,[10] or a photon emission from molecules in an excited electronic state. Photon emission is detected using a spectrofluorometer. In its simplest form a spectrofluorometer is comprised of a light source, slits or grating, an excitation monochromator, a sample cell, a diode array sensor and a detector

and associated electronics. A sample cell intercepts radiation from a light source that excites molecules with a wavelength corresponding to an absorbance band of the molecules to be excited. Excited molecules in the sample fluoresce in random directions. The intensity of the resulting light is measured with the detector and converted with the associated electronics to a spectrum. The spectrum produced charts sample emission as a function of wavelength.

Electronic absorption was also utilized to characterize the quantum dots using a Varian, Cary-100 UV-Visible Spectrometer. For electronic absorption spectroscopy, a spectrometer scans a sample through the electronic region wavelengths (350 - 900nm), and a spectrum is produced, charting sample absorbance as a function of wavelength.

Results and Discussion:

1: CdSe: Temperature Dependence Experiment

One of the very first experiments attempted was the synthesis of CdSe and how changing the reaction conditions would alter the properties of the quantum dots. This was done in an attempt to find the right recipe for CdSe quantum dots that would create 'high quality' nanoparticles. A 'high quality' quantum dot simple means that the nanoparticles were uniform in size, spherical with limited surface defects, and that they had high crystallinity with more defined quantum levels. Whether or not the quantum dots were of 'high quality' can be determined from the fluorescence.
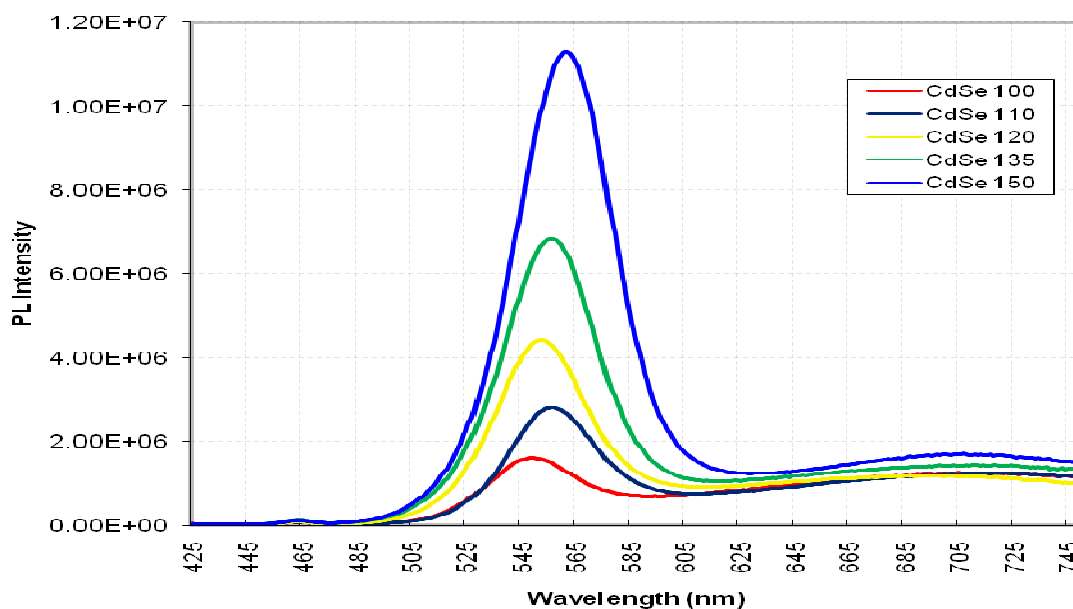
Figure 8: Photoluminescence of cadmium selenide quantum dots synthesized at different reaction temperatures.

Fluorescence is the result of radiative recombination.[10] Radiative recombination occurs when relaxation of the excited electron back to the valence band annihilates the exciton and is accompanied by the emission of a photon.[10] Nonradiative relaxation events that do not result in fluorescence are associated with crystalline defects and charge carrier traps on crystal surfaces. Therefore radiative recombination is more likely to occur if there are less trap states.

Figure 8 shows a simple temperature modulation and its effects on a CdSe core nanoparticle through fluorescence. The result was a massive increase in the photoluminescence with an increase in temperature during synthesis at 560 nm (Fig 8). An emission at 560 nm suggests an average particle size between 4 and 20nm. The spectrum obtained showed that as the temperature increased from 100°C to 150°C, the photoluminescence also increased correspondingly (Fig 8). This is most likely the result of the increased

temperature eliminating surface defects. Defects at the surface can trap charge carriers at the surface and reduce the probability of an electron and hole annihilation, thus making nonradiative decay events more likely. The intensity of the photoluminescence and the absence of a red shift indicates that the particles were uniform in size and of 'high quality.' Therefore the experiment was successful in that quantum dots of good caliber were synthesized under different reaction conditions and it satisfied one of the goals of creating uniform quantum dots in water with limited surface defects that are viable for use in various applications. However, despite this success, there was no real shift in the maximum wavelength of emission suggesting that there was no real change in size of the QD with temperature modulation and thus not entirely tunable as desired.

2: CdS: Temperature Dependence

A similar temperature variation study was attempted on CdS nanoparticles in an attempt to make CdS nanoparticles of good quality with tunable properties under hydrothermal conditions. CdS was used because CdS has been previously studied in the literature and it exhibits a different band gap than CdSe. The results were quite different as is shown in Figure 9. Synthesis at 120°C indicated that there was a wide distribution of sizes thus there was non existent fluorescence around 460 nm. However, there was a huge red tail. Traditionally this red shift was thought of as the result of surface defects, but recent models done by Micic et al. suggest that it is actually caused by the core structure of the

QD and not just the surface and that it is a function of size.[17] This 'red tail,' then, suggests that there is a large distribution of sizes and poor quantum confinement.

As the temperature of the synthesis increased to 150°C, the intensity of the red tail decreased and shifted to longer wavelengths and a peak at 440 nm appeared. At 180°C the intensity of the red tail decreased even further and again shifted to longer wavelengths while at the peak shifted from 440 nm to 460 nm and increased in intensity. The shift in maximum wavelength could mean only one thing, the size of the particles was becoming larger and as they become larger there was less of a distribution of sizes which in turn decreased the red shift. Increasing the temperature of the reaction, therefore, increased the size of the nanoparticles synthesized. This may also account for the lack of fluorescence at 120°C. The particles may have been too small and the distribution to large to have photoluminescence, or the fluorescence may have fallen below 420 nm, which is beyond the scope of the spectrum.

Photoluminescence at 440 – 460 nm places the quantum dots at approximately 2 – 4 nm, which is much smaller than the CdSe synthesized in the previous experiment. This means that CdS has a larger bandgap than CdSe. The shift in maximum wavelength, though not enough to cause a change in visible color of the quantum dots, was significant in that it did show that changing the reaction conditions changes the size of the quantum dot. With future work, CdS quantum dots could be tuned by changing the temperature during synthesis. The experiment was then successful in showing that CdS dots could potentially be

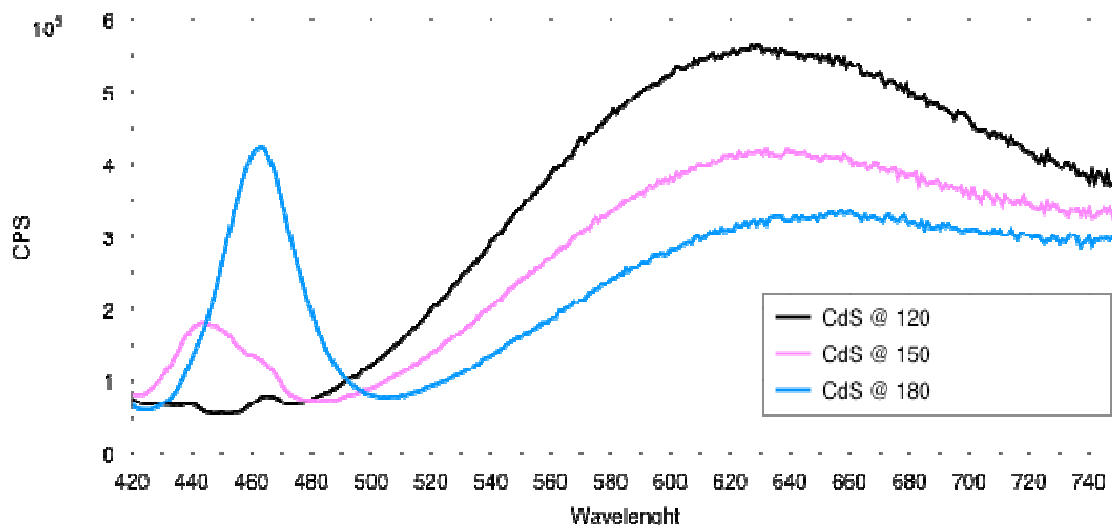synthesized with tunable sizes, but the synthesized nanoparticles were not uniform in size.

Figure 9: Photoluminescence of cadmium sulfide quantum dots synthesized at different reaction temperatures.

However, though water has its advantages as a solvent, in the case of CdS, it was a major limiting factor. The proposed temperature is well above the boiling point of water and it would be dangerous to attempt higher temperatures. Though the red shift is indicative of a large distribution of sizes, it may also be the result of surface defects. Citrate may not be strong enough of a capping ligand for CdS and the presence of surface traps may be attributed to the use of water, or to the use of thioacetamide since this same pattern was not observed for CdSe particles under similar conditions. CdS particles were also not very soluble in water and the resulting nanoparticles tended to crash out of solution fairly quickly, though this may have been due to cadmium oxidizing due to atmospheric oxygen.

3: CdS: Compositional Modulation

Colloidal CdS quantum dots in a water solution were further studied by modulating the concentration of thioacetamide for particles synthesized at 180°C. The results are shown in Figure 10. The modulation of concentration was a double-edge sword. For an 8:2.5 ration of Cd:S, photoluminescence (PL) was very low at 485 nm. For an 8:2 and 8:1 ratio, the PL increased and the wavelength of maximum emission shifted to 465 nm and 455 nm respectively. A shift to higher wavelengths with a decrease in thioacetamide concentrations indicates that the mean particle size decreased with a decrease in thioacetamide. There was also, however, an increase in the red tail which, in this case, is indicative of a larger distribution of sizes and a shift towards smaller sizes, rather than the result of surface defects or enhanced electron-hole exchange. Though these results may be due to the fact that the higher the sulfur concentration, the less soluble the final product was in water. Water, therefore, may not be the best solvent for CdS particles considering the poor solubility and the short lifetime of the particles in solution. The CdS particles also did not have the same fluorescent intensity as the CdSe QDs.
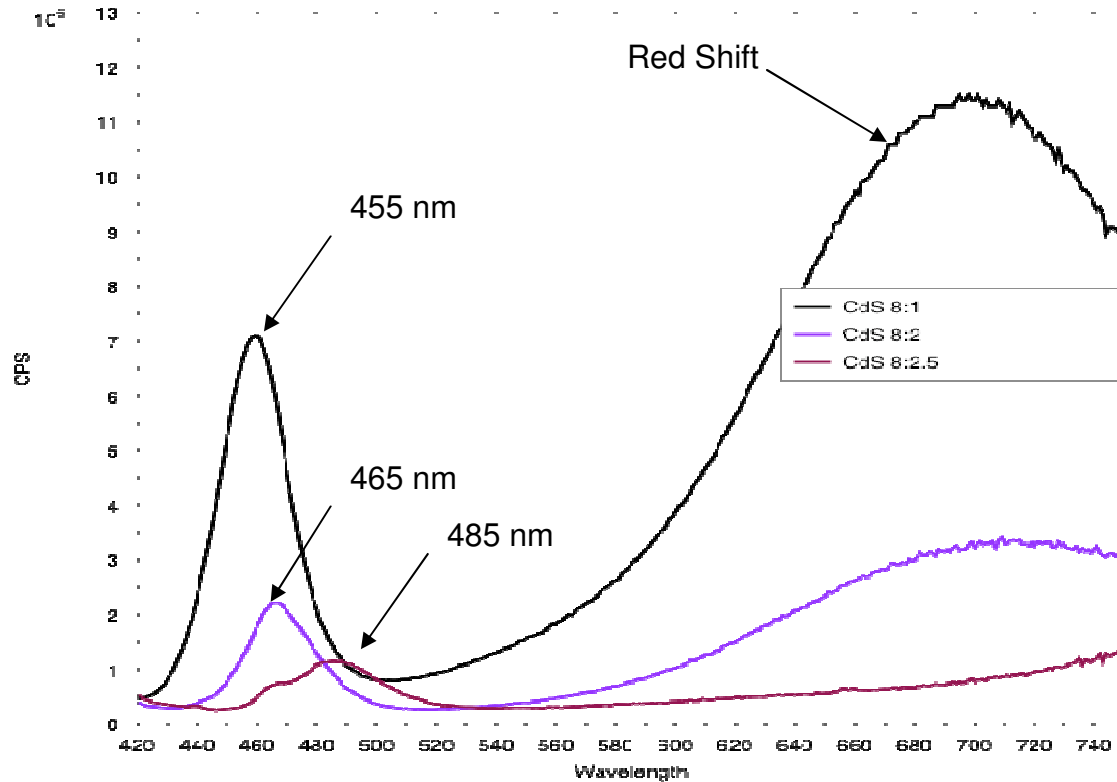
Figure 10: Photoluminescence of cadmium sulfide quantum dots synthesized at varying concentrations of thioacetamide.

The experiment did, however, show that it is possible to change the size of CdS QDs by varying the amount of sulfide introduced into the system during synthesis. Decreasing the average particle size, though, while it does improve the fluorescence of the CdS quantum dots, it also results in a larger distribution of sizes as seen by the increase of the redshift with a decrease of sulfide concentration. The large distribution of sizes means that the particles are not uniform in size, though, and thus are not of high quality enough to be used for any application. With more time, however, and further tweaking of the reaction variables, it is possible to create CdS quantum dots of a better caliber in water.

4: CdS/CdSe shell and temperature dependence

After determining viable reaction conditions for CdS and CdSe core quantum dots, adding a CdSe shell to a CdS core was attempted. The addition of a shell to a QD core has been known to improve fluorescence and quantum yield by eliminating the significance of surface defects and trap states on the nanoparticles.[10] Shell passivation also buries the core semiconductor in a potential energy well, concentration charge carriers in the core away from the surface and trap states.[10] Therefore a CdSe shell was added to a CdS core in an attempt to increase fluorescence and quantum yield. Figure 11 shows the electronic absorption spectra of CdS/CdSe with an increase of temperatures during synthesis. Increasing absorbance generally means an increase in size, while a blue shift in absorbance means a decrease in size. It therefore makes sense that the absorption would increase by adding a shell to the CdS core. This is not enough proof, but the absorption spectrum is indicative of a successful addition of a CdSe shell to the CdS. The absorption spectrum also suggests that there was an initial increase in size, but at higher temperatures, the size begins to decrease again or the particles became more uniform in size.
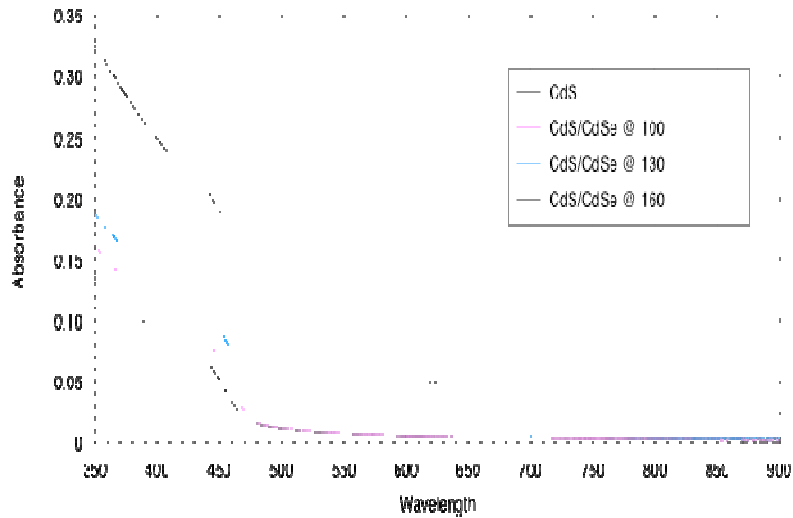
Figure 11: Electronic absorption of cadmium sulfide core quantum dot with a cadmium selenide shell synthesized at varying temperatures.

The data from the fluorescence did not show nearly as nice data as that of the absorption spectrum. Though it is not certain, the fluorescence spectrum (Fig 12) may be trying to say that initially after the addition of CdSe, there is a huge distribution of sizes, hence the giant red tail, but intensity starts to decrease with temperature, not only the red tail, but intensity on a whole of the CdS dot decreased by the addition of the CdSe shell. The shell is supposed to neutralize surface defects and increase PL, but this does not appear to be happening here, in fact the opposite seems to be happening.
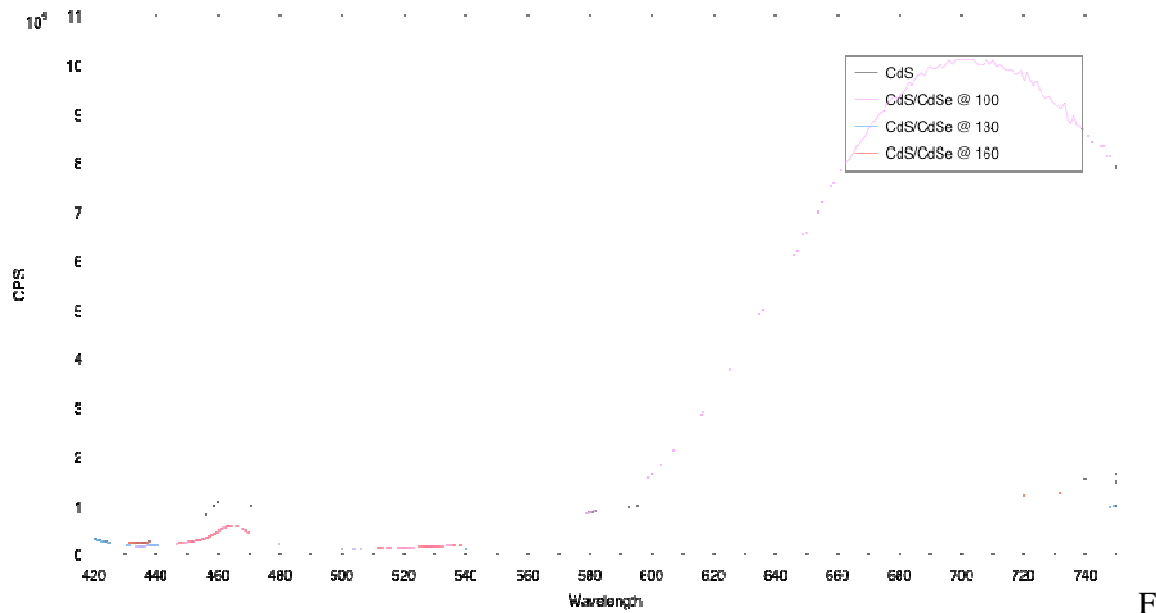
F
igure 12: Photoluminescence of cadmium sulfide core quantum dots with a cadmium selenide shell synthesized at varying temperatures.

Heat treatment may have lengthened the lifetime of the electron-hole pair, leading to eventual recombination that is mainly nonradiative. In general, the successful addition of a shell and subsequent intensity increases result from adding a shell with a bandgap larger than the core. This is not the case here. The bandgap for CdSe is smaller than that of CdS. There is also no shift in maximum wavelength of emission that would suggest a change in size after the addition of a CdSe shell. Therefore the experiment did not appear to be successful, nor did it satisfy any of the goals.

Experiment 5: CdSe:Zn

The results from the addition of a CdSe shell to a CdS core are debatable, but the addition of a Zn shell to a CdSe QD showed promising results. A temperature modulation study was again attempted. The original product of Cd, Se and Zn showed a broad fluorescence peak, but as the temperature of synthesis was increased, after an initial decrease in fluorescence, the

photoluminescence eventually increased. The peaks also become narrower as the temperature increased. The nanoparticles experienced thermal annealing, in other words self-organized crystal growth. The data suggests that CdSe/Zn crystals began forming under successive heat treatments. The heat treatment altered the nanostructure of the particle and caused changes in its properties. Thermal annealing is indicated by the enhancement of the integrated photoluminescence emission and narrowing of the full width half-maxima occur together in Figure 13.[18] The dots, on average, are becoming larger in size as crystals form with the annealing process which is also suggested by the shift towards a higher maximum wavelength (Fig 13). The maximum wavelength at approximately 595 nm, is higher than 560 nm for a typical CdSe dot which also suggested growth in average particle size.
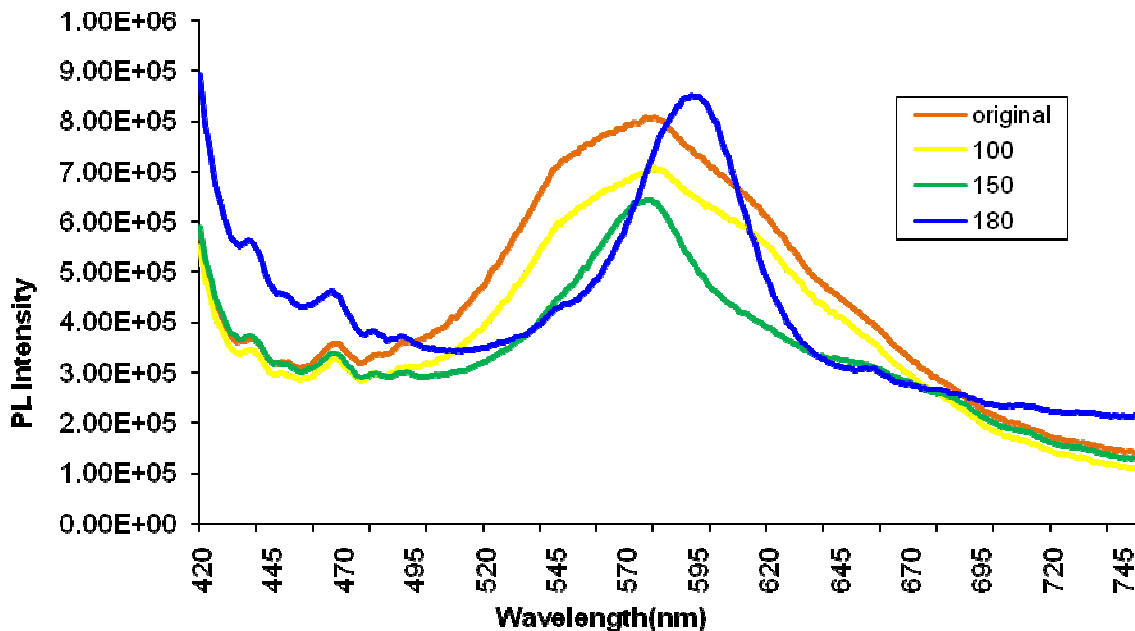

Figure 13: Photoluminescence of cadmium selenide core quantum dots with a Zinc shell undergoing successive heat treatments.

The nanoparticle was monitored over time and it was shown that while the mixture does not continue to anneal, the fluorescence does increase with time (Fig 14). This indicates that crystals get better with time, they become more uniform. Thermal annealing is particularly interesting because they are self assembled dots. However, the problem with annealing is that is it unclear whether or not the nanoparticles are still dots and a ZnSe shell was formed or it if was simply a Zn coated CdSe dot. Despite this, the experiment was a success. Not only was a Zn shell successfully added to a CdSe core, the quantum dots showed good photoluminescence and with successive heat treatment the particles became more uniform in size. For future work, it would be beneficial to possibly monitor crystal growth before and after thermal annealing.
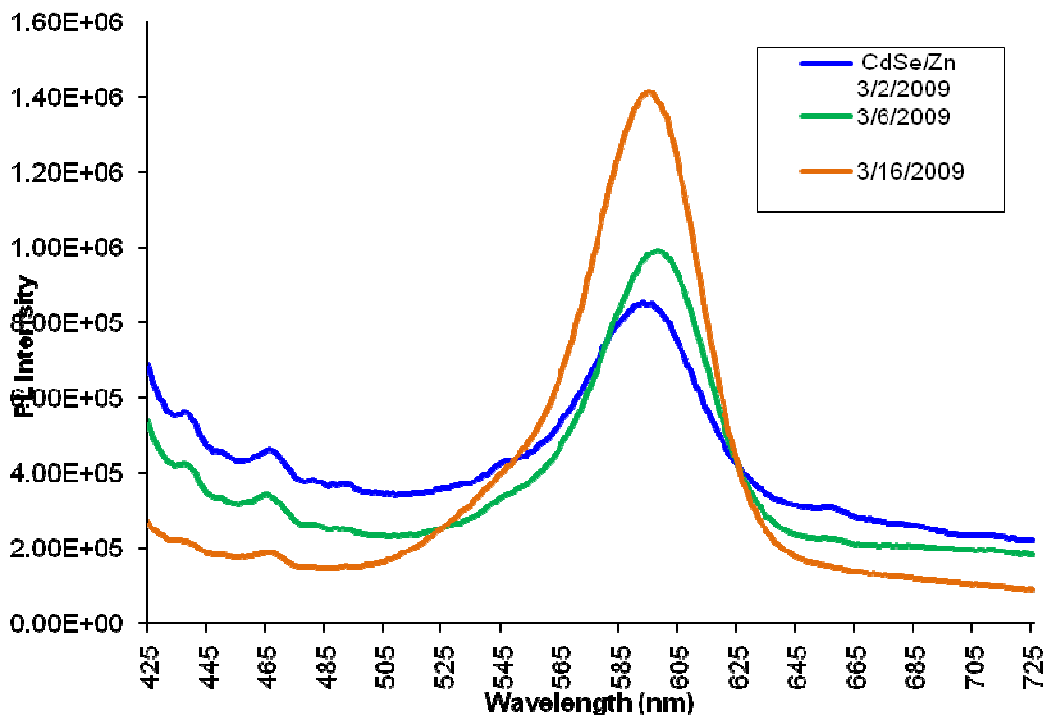

Figure 14: Photoluminescence of cadmium selenide core quantum dots with a Zinc shell monitored over time.

Conclusions

The specific goal was to create CdSe and CdS with tunable size, uniformity of size, and restricted trap states. High quality CdSe nanoparticles were successfully synthesized, but they did not express tunable emissions. CdS quantum dots, on the other hand, showed a shift in sizes under various reaction conditions, but the particles were not 'high quality' in that they were not uniform in size and did show high crystallinity. It was also shown that it is possible to thermally anneal CdSe/Zn nanoparticles using heat treatment, but without further data is it unsure whether or not the resulting product is still a quantum dot.

Future Work:

Future work could include a continuation in trying to find the right 'recipe' for CdS quantum dots in a water solution that would produce high quality dots with tunable emission. In conjunction with that, solubility and stability would need to be monitored overtime, due to the low solubility and stability of the synthesized quantum dots under hydrothermal conditions. A compositional modulation study would be beneficial in the future in regards to varying the capping ligand which may increase solubility and stability. Using varying semiconductors could possibly be done as well, because cadmium is a very toxic chemical and will one day no longer be used for these applications.

During annealing, monitoring the crystal growth, will determine first of all if there is crystal growth and whether or not the resulting product is indeed a quantum dot. Attempting annealing with different types of quantum dots for

reproducible results would be interesting to accomplish as well as energy transfer

studies.

References

[1] Bender, M.A., Knutson, T.R., Tuleya, R.E., Sirutis, J.J., Vecchi, G.A., Garner, S.T., Held, I.M. *Science,* **2010,** *327*, no 5964, pp 454 – 458.

[2] Mousavi, M.E., Irish, J.L., Frey, A.E., Olivera, F., Edge, B.L. *Climate Change,* **2009,** DOI 10.1007/s10584-009-9790-0.

[3] 2008. Floodplain Management Association. *Floods May Worsen as the Climate Changes* and *Annual Global Climate Change Report 2008.* http://floodplain.org/documents.php

[4] van Aalst, M. *Disasters,* **2006,** *30*, no 1, pp 5 – 18.

[5] Trenberth, K.E. *Consequences,* **1999,** *5*, no 1, pg 3 -15.

[6] Frederick, K.C. 2002. Introduction. In *Water Resources and Climate Change,* ed. K. D. Frederick, xi – xxxviii. Edward Elgar Publishing, Inc.

[7] Miles, R.W., Zoppi, G., Forbes, I. *Materials Today,* **2007,** *10*, no. 11, pg 20 – 27.

[8] Mazumder, S., Dey, R., Mitra, M.K., Mukherjee, S., Das, G.C. *Journal of Nanomaterials,* **2009,** *2009,* pp 1-17.

[9] Frasco, M.F.; Chaniotakis, N. *Sensors,* **2009,** *9*, pp 7266-7286

[10] Smith, A.M., Nie, S. *Accounts of Chemical Research*, **2010,** *43*, No. 2, pp 190-200

[11] Carrillo-Carrion, C., Cardenas, S., Simonet, B.M., Valcarcel, M. *Chem. Commun.,***2010,** pp 5214 – 5226.

[12] Kalasad, M.N., Rabinal, M.K., Mulimani, B.G. *Langmir,* **2009,** *25*, no 21, pp 12729 – 12735.

[13] Wang, L., Luo, J., Maye, M., Fan, Q., Rendeng, Q., Engelhard, M.H., Wang, C., Lin, Y., Zhong, C. *J. Mater. Chem.,* **2005,** *15*, pp 1821-1832.

[14] Selvan, S.T., Tan, T.T.Y., Yi, D.K., Jana, N.R. *Langmir,* **2009.**

[15] Nozik, A.J. *Inorganic Chemistry,***2005,** *44*, no 20, pp 6893- 6899.

[16] Miles, R.W., Zoppi, G., Forbes, I. *Materials Today,* **2007,** *10*, no. 11, pg 20 – 27.

[17] Micic, O.I., Cheong, H.M., Fu, H., Zunger, A., Sprague, J.R., Mascarenhas, A., Nozik, A.J. *J. Phys. Chem. B.* **1997,** *101*, pg 4904 – 4912.

[18] Malik, S., Roberts, C., Murraya, R., *Appl. Phys. Lett.,***1997,** *71*, no 14, pp 1987-1989.