Lab 5: Confinement in Quantum Dots

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April 16, 2015

Abstract

In this lab we explored the properties of quantum dots. Quantum dots are nanometer scale semiconductor crystals which exhibit quantum mechanical properties when interacting with photons (or phonons) due to their small size. This lab consisted of three main parts. In the first part of the lab we characterized the properties of commercial quantum dots. For the second part of the lab we synthesized our own quantum dots. Finally, in the third part of the lab we characterized the properties of our synthesized quantum dots. Using the information obtained, the goal was to determine the emitted photon energy and approximate radius of both the commercial and synthesized quantum dots.

1 Introduction

According to the Pauli exclusion principle an atom cannot have more than two electrons in an orbital. Thus as atoms group together to form particles and their orbitals begin to overlap, their energy sublevels begin to split. When enough atoms come together the splits become too close to distinguish so we can think of the sublevel as a continuous energy band. We define the valence band (the "ground state") as the uppermost band either partially or completely filled with electrons at zero degrees kelvin. The Fermi energy refers to the energy difference between the highest and lowest of these occupied states. The band that is left unfilled above the valence band is called the conduction band. The separation between these two bands where no electron states can exist is called the band gap.

A semiconductor is a material with a band gap that does not overlap like in a metal, but is smaller than that of an insulator. Semiconductors do not normally conduct electricity, but because their band gap is smaller than that of an insulator, electrons in the valence band can be excited into the conduction band. Electrons elevated to the conduction band are free to move through the material and conduct electricity. One way this can happen is for an electron to absorb a photon of sufficient energy. The photon is absorbed by an electron in the valence band which is then elevated to the conduction band. The excited electron leaves a hole in the valence band, and this attraction between the electron-hole pair is called an exciton.

Because the Fermi energy of a particle depends only on the the number of free electrons per unit volume and this electron density is in turn a property of the material, the spread of the sublevels is the same for small particles as it is for bulk material, however, when

the volume of the material is reduced to a very small number of atoms, the continuous energy levels start to become discrete. This is called quantum confinement. In the case of discrete energy levels, adding or removing small amounts of atoms (and consequently adding or removing discrete energy levels) will cause a widening or narrowing of the band gap. So, if the material is sufficiently small (approaching the exciton Bohr radius, 0.053 nm), adding or removing atoms will adjust the size of the band gap and zero point energies. The zero point energies refer to the minimum energy possible for the electron and hole (i.e. the top of the valence band and bottom of the conduction band). Being able to tune the zero point energies is what makes quantum dots so useful. As a consequence of all this, the smaller the quantum dot, the larger the band gap, and the higher in energy a photon needs to be to excite an electron to the conduction band. This is illustrated in Fig. 1
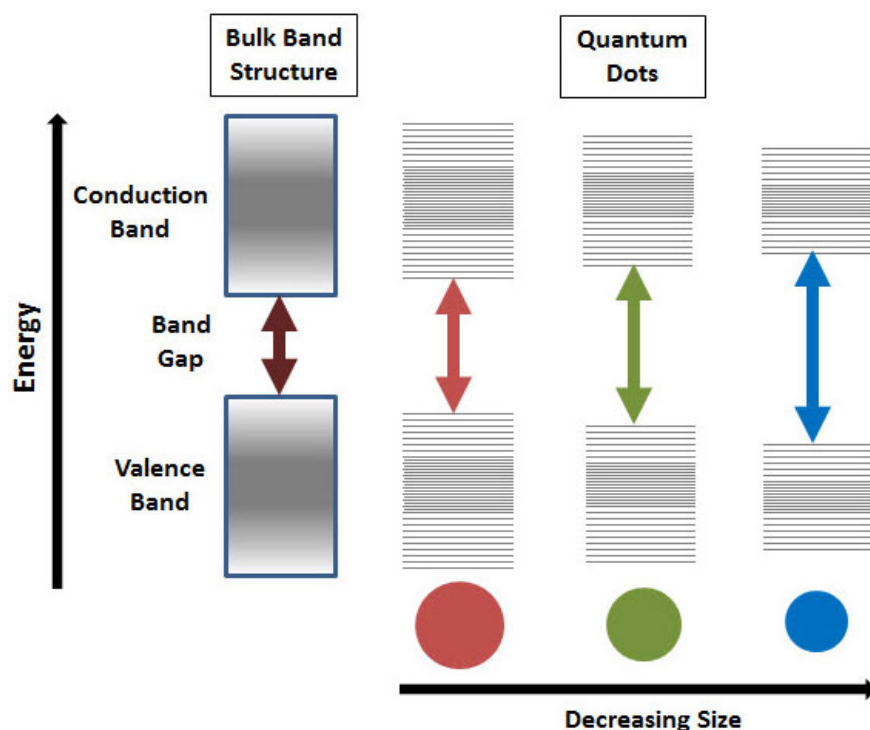

Figure 1: **Band gaps in quantum dots.** This illustrates how the band gaps and required excitation energy get larger as the size of the quantum dots get smaller.

After a very short amount of time, an electron in an excited state in the conduction band loses energy and moves down to the lowest excited state (the electron's zero point energy). The electron then drops back down the the ground state, recombining with the hole and emitting a photon. The emitted photon has lower energy than the photon that was initially absorbed because of the loss in energy moving down to the first excited state. This phenomenon is known as fluorescence, as illustrated in Fig. 2. It is especially noticeable to us when a material absorbs UV light (high energy) that is invisible to us and then emits light within the visible spectrum.
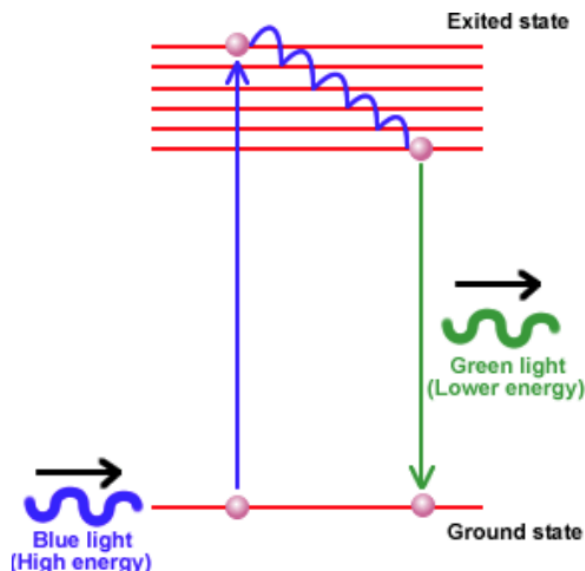
Figure 2: **Fluorescence.** This picture shows an electron being excited to the conduction band with blue light. It loses energy, dropping to the first excited state. It then recombines with the hole (not shown here) in the ground state, releasing green light of less energy.

1.1 Determining the energy states and approximate size of QDs using the Particle in a Box model

The Schrödinger wave equation is an equation used in quantum mechanics that was realized or invented by Erwin Schrödinger. After it was found that particles could also behave like waves and could have diffraction patterns, Schrödinger came up with this equation to model the behavior of particles as waves. It can be stated in several different forms, and it is analogous to F=ma in classical mechanics in that it is central to the field, but cannot be derived. The Time-dependent Schrödinger equation for a single non-relativistic particle is a partial differential equation that takes the form where total energy equals kinetic energy plus potential energy. The solution to the equation is the wave function, which can be interpreted as a probability amplitude for the system.

If we model a particle inside a box (in this case an infinite potential well) where its potential energy is zero, Schrödinger's equation can be simplified and a general solution can be found. This general solution is of the form:

$$\Psi(x) = A sin(kx) + B cos(kx)$$

We then apply boundary conditions so that the probability amplitude is zero at the left and right edges of a box of length L. After doing this we obtain a solution to the above wave function that takes the form:

$$\Psi_n(x) = A \sin(\frac{n\pi x}{L}) \quad \text{where n = any positive integer}$$

Finally, if we do a substitution for the wavenumber and rearrange the equation we get:

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \tag{1}$$

This equation gives us solutions for the energy states of a particle in an infinite potential well, which are discrete because n must be a positive integer. Because the excitons (electrons and holes) in quantum dots are confined due to the size of the particles, we can use the model of the infinite potential well to characterize their zero point energies. In this case we consider the exciton to be hydrogen in the Bohr model where the nucleus is replaced by the hole. Doing this allows us to represent the energy levels of the exciton as the solutions to the particle in a box at the ground state (n = 1).

The total energy of a photon emitted by a quantum dot in fluorescence is equal to the Planck-Einstein relation which is also equal to the band gap energy plus the quantum confinement energy:

$$E_{photon} = \frac{hc}{\lambda_{max}} = E_{bg} + \Delta E_{qc}$$

The value for the band gap energy depends on the type of quantum dots used and must be looked up. For our commercial InP quantum dots E_{bg} = 1.34 eV and for our synthesized CdSe quantum dots E_{bg} = 1.74 eV. The value of the quantum confinement energy ΔE_{qc} obtained in equation (1) can be simplified for both the electron and the hole to the form:

$$\Delta E_{qc} = \frac{h^2}{8mR^2} \tag{2}$$

The total quantum confinement energy equals the sum of ΔE_{qc} for both the electron and the hole, where the mass is replaced by the reduced mass for each. The reduced masses are another quantity that depends on the type of quantum dot used. For the commercial Inp QDs the reduced masses are equal to m_e = 0.08m_o and m_h = 0.6m_o where m_o is the standard mass of an electron which is equal to 9.11×10^{-31} kg. Then, m_e = 7.288×10^{-32} kg and m_h = 5.466×10^{-31} kg. For our synthesized CdSe QDs the reduced masses are equal to m_e = 0.13m_o and m_h = 0.45m_o. This simplifies to m_e = 1.18×10^{-31} kg and m_h = 4.10×10^{-31} kg. We can do a further simplification to ease in the later calculations by adding the reduced masses of each electron/hole pair together to get a total reduced mass for each QD sample:

$$\left(\frac{1}{m_e} + \frac{1}{m_h}\right) = \left(\frac{m_e + m_h}{m_e m_h}\right) = \frac{1}{m_{equiv}} \tag{3}$$

The use of this equivalent mass allows us to use one equation for the quantum confinement value instead of a separate one for the electron and hole:

$$\Delta E_{qc} = \frac{h^2}{8m_{equiv}R^2} \tag{4}$$

Finally, the last step in obtaining the total energy of a photon emitted by a quantum dot in fluorescence is to subtract the binding energy of the electron/hole recombination. This is given by the modified Rydberg:

$$Ry* = -\frac{1}{\varepsilon_r^2}\frac{m_{equiv}}{m_o}13.6 \ eV \tag{5}$$

Where epsilon is the dialectric constant (approximately equal to 1 in air). The modified Rydberg then has to be multiplied by a prefactor of 1.782 due to the strong confinement regime (when R is less than the exciton Bohr radius). The final equation we obtain for the photon emission energy is then:

$$E_{photon} = \frac{hc}{\lambda_{max}} = E_{bg} + \frac{h^2}{8m_{equiv}R^2} - (1.782)\frac{1}{\varepsilon_r^2}\frac{m_{equiv}}{m_o}13.6 \ eV$$

Not only can we solve for the photon emission energy, but due to the Planck?Einstein relation, by measuring the peak wavelength of the emitted light we can also solve for the approximate radius of the quantum dots.

2 Experimental setup and procedure

2.1 Part 1: Emission Spectra of Commercial InP Quantum Dots

The first part of this lab was the characterization of four samples of commercial Indium Phosphide quantum dots. In order to do this, the first thing we had to do was record the spectra for the strip of LEDs that would be shined onto the quantum dot samples so that we knew what the peak wavelength of each one was. The strip consisted of six LEDs including blue, green, orange, red-orange, red, and infrared. We obtained their peak wavelength by pointing each LED directly at the fiber optic cable of the Ocean Optics spectrometer that we used throughout this experiment. Next, we held each of the four commercial QD samples over each of the six LEDs and took a qualitative observation of which LEDs caused which QDs to fluoresce.

The next step in Part 1 was to measure the fluorescence spectra of the commercial QDs. This was done by illuminating each with a high powered UV LED and taking a right-angle measurement with the spectrometer to record the emission spectra of each of the QD samples. This data should enable us to determine the center wavelength and photon energy of each sample. We should also then be able to estimate the size of the QDs using a first order approximation.

2.2 Part 2: Synthesis of CdSe Quantum Dots

In the second part of this lab we created our own Cadmium selenide (CdSe) QDs. Because Cadmium is extremely toxic several of the initial steps were prepared for us ahead of time. The steps that were pre-prepared were as follows: First, 30mg of Se, 5ml of octadecene and 0.4ml of trioctylphosphine were added to a 10ml round bottom flask along with a magnetic stir bar. This was put on a heater on low temperature until the Se dissolved. Separately, 13mg of CdO, 0.6ml of oleic acid and 10ml of octadecene were added to a 25ml round bottom flask along with a thermometer capable of reaching 225C. This second solution was then heated to a temperature of 225C while the Se solution cooled to room temperature.

The next steps of the synthesis procedure were then completed by my lab partner and I. When the 25ml flask reached 225C we added 1ml of the Se solution to it. Immediately following the reaction we began to pipette out 1ml samples out of the solution into test tubes. Because this reaction begins extremely quickly and then slows down after a period of time, the first few samples were extracted as quickly as possible. The rest of the samples were drawn at progressively longer time intervals until we obtained a total of twelve samples. The time of each sample interval was recorded. We then took a qualitative observation of our synthesized QDs.

2.3   Part 3: Emission Spectra of Synthesized CdSe Quantum Dots

The last part of this lab was the characterization of our synthesized CdSe QDs. First we pipetted each of our samples from test tubes to cuvettes so that they could be placed in the spectrometer. With the spectrometer set to Scope Mode, first we recorded a reference spectrum of plain water, and then we recorded the spectrum for each of our synthesized QDs. Next, we recorded the fluorescence spectra for each synthesized QD using the same UV LED and right-angle technique used in Part 1. From this data we should then be able to estimate the size of our synthesized QDs. The growth rate of our QDs should also be able to be determined based on our sampling times.

3   Results and Discussion

3.1   Results

Fig. 3 shows the spectrum we recorded for each of the six LEDs on the LED strip.

We did a qualitative observation to see how the four commercial InP quantum dots reacted to each LED. The red colored quantum dots fluoresced with the 4 highest wavelength LEDs. The orange colored quantum dots fluoresced with the 3 highest wavelength LEDs. The yellow colored quantum dots fluoresced with the 2 highest wavelength LEDs. The green colored quantum dots only fluoresced with the highest wavelength LED. This behavior led us to believe that the size of the commercial QDs from smallest to largest was: green, yellow, orange, red. This should be the order for their band gap size from largest to smallest.

Fig. 4 matches what our qualitative observations led us to believe. The peak wavelength was smallest for the green colored commercial QDs and then progressively larger from orange to yellow to red.

Fig. 5 shows the expected trends for the quantum dots. As they get smaller their energy
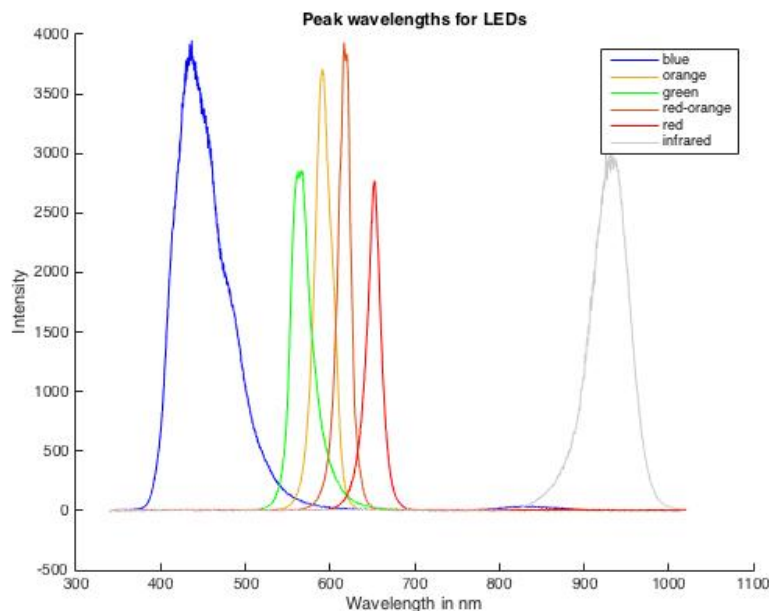
Figure 3: **Peak wavelengths for six LEDs on strip.** This shows that the peak wavelength is lowest for blue and highest for IR light.
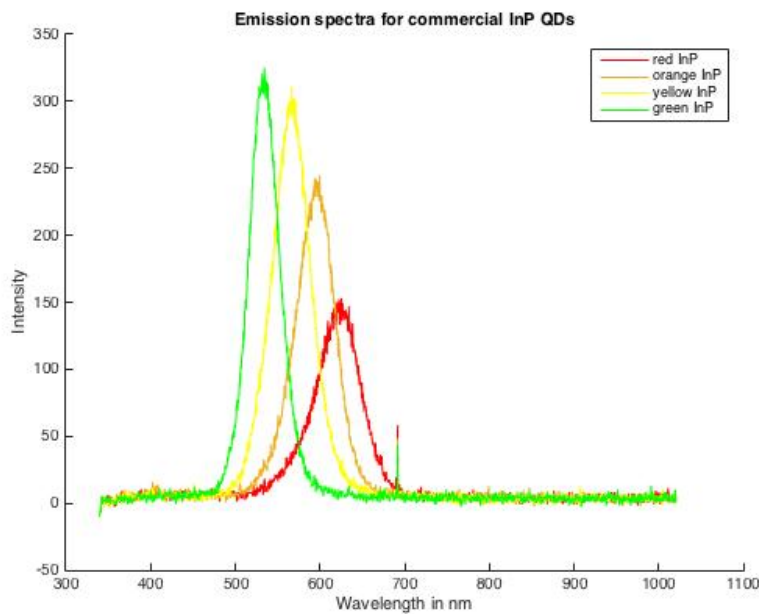

Figure 4: **Emission spectra of commercial InP QDs.** This shows the peak wavelengths of the emission spectra for the four commercial InP quantum dots that was obtained by doing a right-angle measurement with a UV LED and the spectrometer.

increases and wavelength decreases.

	Red InP	Orange InP	Yellow InP	Green InP
Peak Wavelength (nm)	625.4800	599.7300	566.6800	534.3500
Photon Energy (eV)	1.9838	2.0689	2.1896	2.3221
Approximate Radius (nm)	2.8768	2.7035	2.5041	2.3291

Figure 5: **Commercial InP QD calculated results.** This table shows the photon emission energy, peak wavelength and approximate radius of the commercial InP quantum dots.
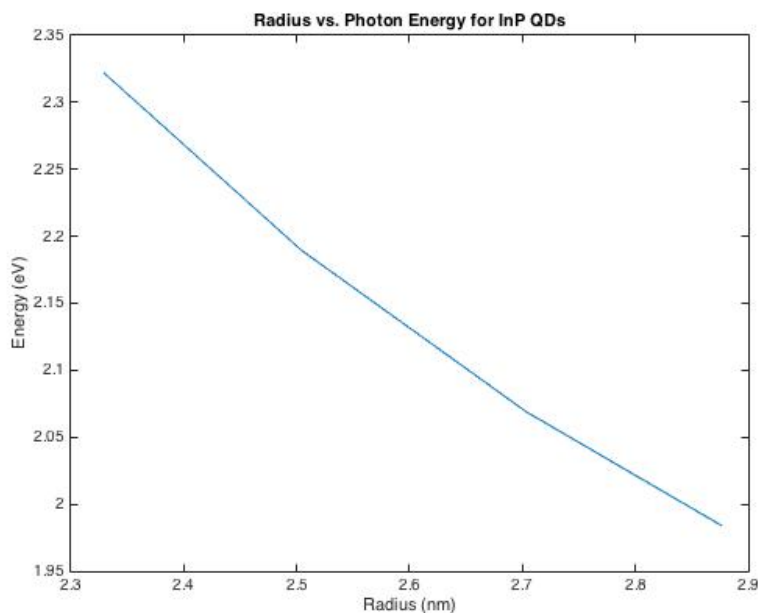

Figure 6: **Plot of radius vs. photon energy.** This shows the relationship between the radius and the emitted photon energy of the commercial InP QDs.

	1	2	3	4	5	6	7	8	9	10	11	12
seconds	4	10	16	22	27	32	47	1.0500	1.3000	2.0100	4.0600	6.2700

Figure 7: **Sampling times for our synthesized CdSe QDs.** There were twelve samples taken in total over a span of 6 minutes and 27 seconds.
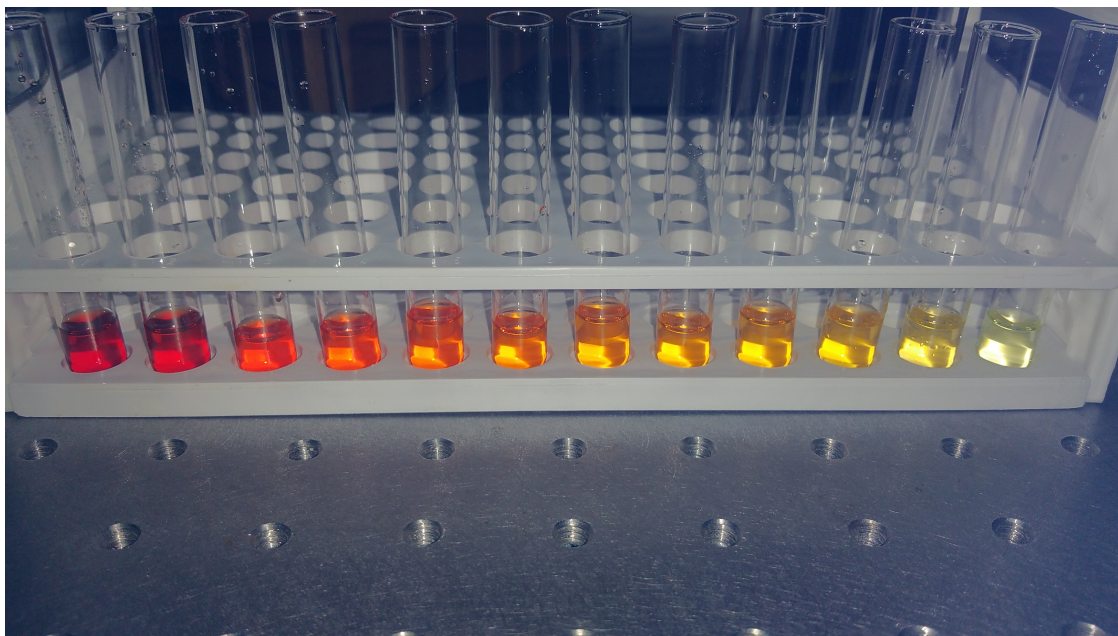
Figure 8:   **Synthesized CdSe QDs.** This is what our twelve CdSe samples looked like. They go in order starting from the first sample taken on the far right.

3.2   Discussion

For the commercial QDs I calculated an energy range of 1.9838 eV to 2.3221 eV and a radius in the range of 2.8768 nm to 2.3291 nm. The values I obtained for these seem to be reasonable and to be in agreement with the qualitative observations of the reaction of each QD sample to the LED strip. There are several quantities that could have led to a potential error in my calculation of R including the measured wavelength, referenced band gap energy, referenced reduced masses and the prefactor to the modified Rydberg constant.

In part two we took a qualitative observation of our synthesized QDs. The relative size of the particles can be observed just by looking at the color change of the QDs. We increased the time in between each progressive sample in order to account for the logarithmic decay in growth rate. For example samples 1 and 2 were taken only 6 seconds apart, but the calculated size difference as well as the visual appearance of the two is significantly larger than the difference between the 11th and 12th samples which had difference in sampling time of over two minutes.

The calculated photon energies and radii for the synthesized CdSe QDs also seem to be reasonable. They follow the established relationship in which smaller particles have smaller wavelengths and higher energies. The smallest particle was the first sample which had a photon energy of 2.5543 eV and an approximate radius of 2.1428 nm. The largest particle was the last sample which had a photon energy of 2.1389 eV and an approximate radius of 3.0615 nm. Using Excel I found the trendline for the growth rate of these particles to be:

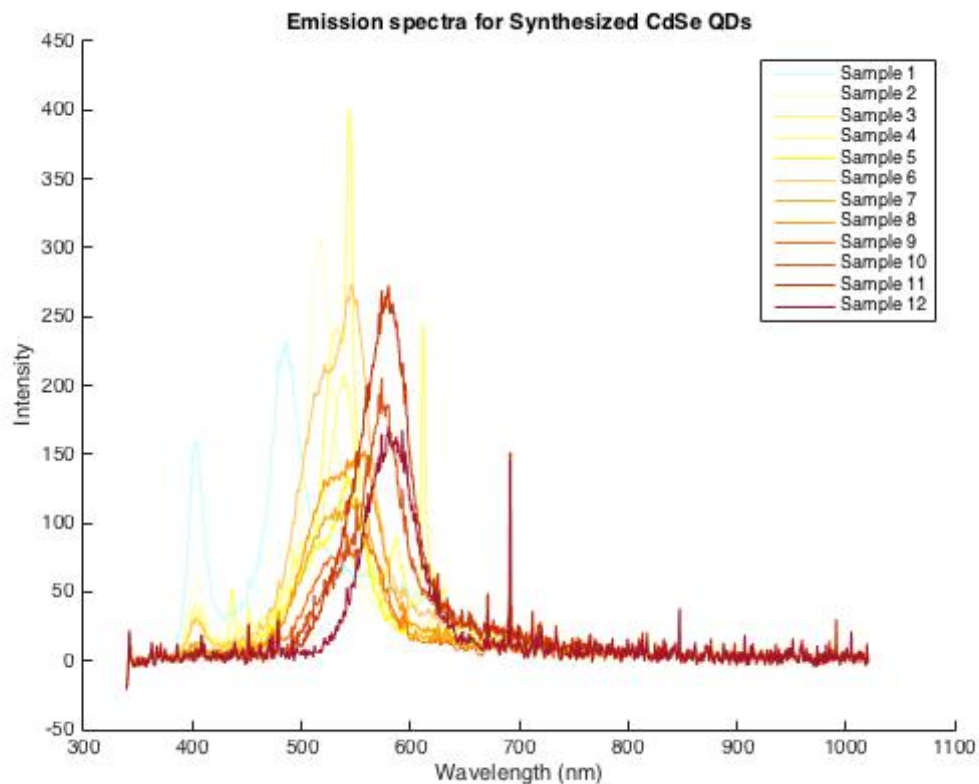$$Size_{nm} = 0.2001 ln(time_s) + 1.9468$$

Figure 9:   **Emission spectra for synthesized CdSe QDs.** This shows the peak wavelengths of the emission spectra for our twelve synthesized CdSe quantum dots. This was obtained by doing a right-angle measurement with a UV LED and the spectrometer.

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10	Sample 11	Sample 12
Peak Wavelength (nm)	485.7700	517.8700	538.9900	541.4800	544.3300	546.1100	550.7300	557.8300	560.3100	574.1000	580.0900	580.1100
Photon Energy (eV)	2.5543	2.3960	2.3021	2.2915	2.2795	2.2721	2.2530	2.2243	2.2145	2.1613	2.1390	2.1389
Approximate Radius (nm)	2.1428	2.3874	2.5791	2.6038	2.6326	2.6509	2.6997	2.7784	2.8071	2.9791	3.0613	3.0615

Figure 10:   **Synthesized CdSe QD calculated results.** This table shows the photon emission energy, peak wavelength and approximate radius of our synthesized CdSe quantum dots.
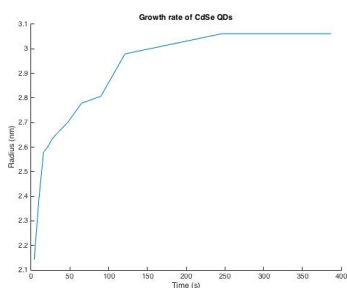

Figure 11:   **Growth rate of CdSe QDs.** This plot shows what we were able to tell experimentally. The quantum dots grow very quickly initially, but then the growth decays exponentially.

4 Conclusion

The first thing I noticed was the difference in calculated radii between the commercial and synthesized QDs. The smallest synthesized QD (sample 1) was visibly blue when it fluoresced and was calculated to have a smaller radius than the smallest of the commercial QDs, the one that was green in color. The largest synthesized QD (sample 12) was darker red than the largest commercial QD which was the one that was red in color. It was calculated to have a larger radius than the commercial QD. The photon energies for the synthesized QDs also span between higher than the largest commercial energy and lower than the lowest. I believe this shows that my results are accurate.