SYNTHESIS AND CHARACTERIZATION OF CADMIUM SELENIDE QUANTUM DOTS

PURPOSE

To understand how increasing synthesis time impacts the size of quantum dots and to characterize quantum dots using various spectroscopic techniques.

INTRODUCTION TO QUANTUM DOTS

Nanotechnology is an emerging field that has greatly contributed to a wide range of applications. One such nanotechnology that holds promise is called quantum dots (QDs), which are colloidal semiconductor nanocrystals. An intense focus has been concentrated on QDs due to their unique photophysical properties. One advantageous property of QDs is less photobleaching than that with conjugated dye systems. However, there are also disadvantages that plague QD systems. Specifically, the stochastic phenomenon of QD "blinking" and acute toxicity of lead and cadmium QDs are both limiting factors to the commercial accessibility of QDs. QD blinking occurs at the single-nanocrystal level and involves fluctuations in the QDs photoluminescence between bright (on) and dark (off) states.

In addition to their interesting photophysical properties, QDs are ideal materials to justify the quantum effect. One such quantum model is the "Particle in a Box" model. The "particle in a box" problem is a common application of a quantum mechanical model to a simplified system consisting of a particle moving horizontally in an infinitely deep well from which it cannot escape. The solutions to the problem give possible values of energy and the wavefunction that the particle can possess. The energy of a particle is related to wavelength and frequency by the following equation, $E = h\upsilon = {hc}/{\lambda}$, where h = Planck's constant, c = speed of light and λ = wavelength.

From the equation above, there is a direct relationship between frequency and energy. As the frequency increases, the energy increases. However due to the inverse relationship between the energy and wavelength, as the wavelength increases the energy for the particle decreases, and vice versa.

In the case of QDs, the "particle" is a delocalized electron in the nanostructure, which would be considered the "box." The wavelength of absorption and emission is affected by the size of the box. The length of the box determines the energy of the various energy levels, as shown by the equation below,

$$E_n = \frac{n^2 h^2}{8mD^2} \quad (\text{n=1,2,3}\ldots)$$

where m= mass of the particle and D = length of the one-dimensional box. A change in the length of the box would greatly affect the energy of the particle, an increase in the length of the box would result in lower energy while a decrease in the length of the box would result in higher energy of the particle. This change in the length of the box corresponds to a change in the radius of the QDs, with decreasing particle size, the energy difference between energy bands increases.

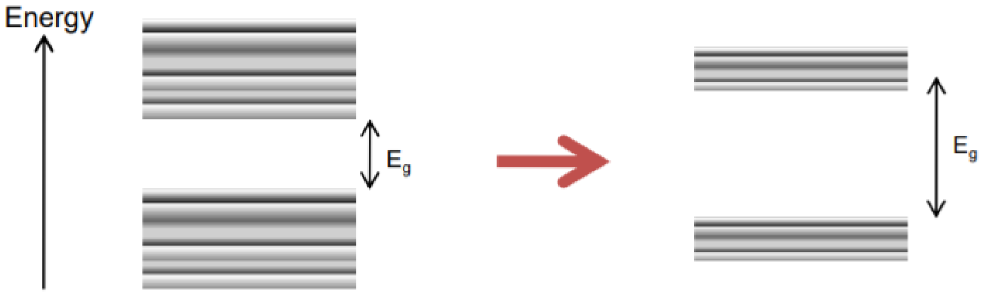


Figure 1: An increase in the bandgap due to a decrease in the QD size. The scheme on the right, represents smaller QDs while the scheme on the left represents larger QDs.

Optical characteristics of QDs

The absorbance spectra of a compound in solution are obtained using ultraviolet-visible (UV-vis) spectroscopy. The absorption of photon energy excites electrons from the ground state to the first singlet excited state of the compound. When it comes to UV-vis spectroscopy, QDs are particularly important since the size of the QDs can be determined by the location of the absorption peak in the UV-vis spectrum. Depending on the size of the particles, QDs absorb various wavelengths.

To excite an electron from its ground state to its excited state, a QD will absorb energy in the form of light over a wide range of wavelengths. The minimum energy needed to excite an electron is determined by the bandgap of the QDs. The bandgap of QDs can be adjusted based on particle size. The energy required to excite an electron from its ground state is equal to the energy required to cross the bandgap. As QDs increase in size, the bandgap energy decreases, and vice versa. This is determined by the first exciton peak at the maximum wavelength (λ max) in an absorption spectrum. The wavelength of the first exciton peak can then be used to estimate the size of QDs.

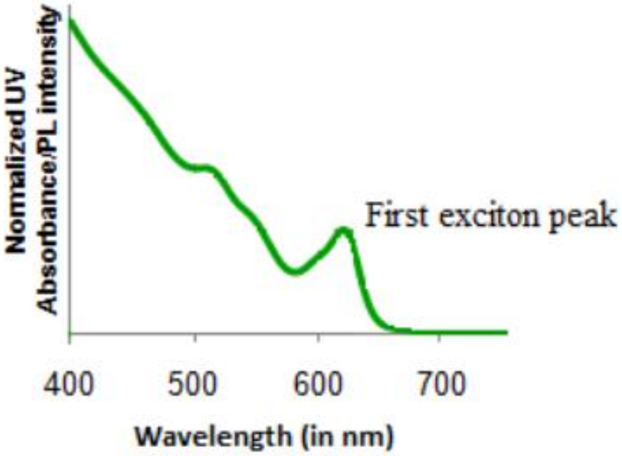
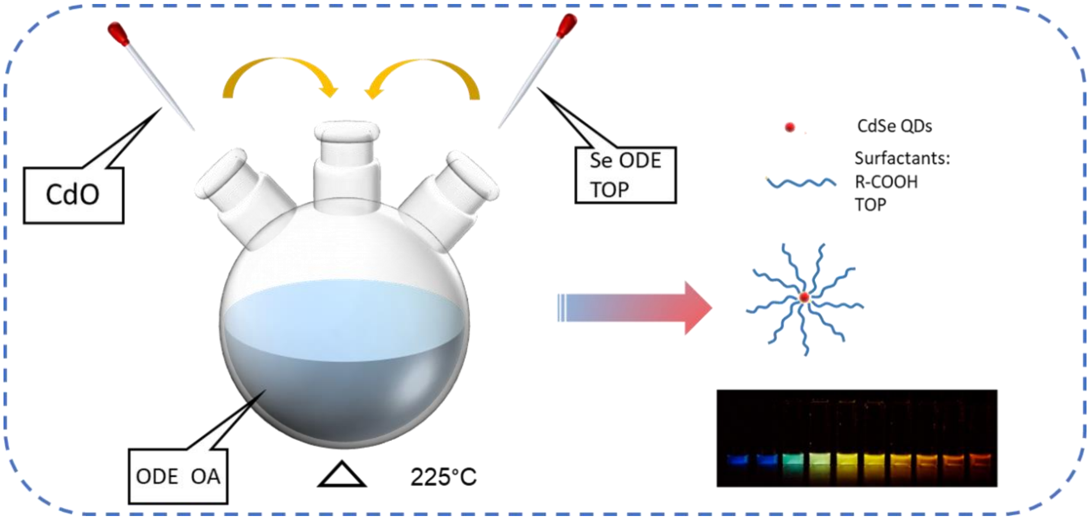


Figure 2: Absorption spectrum of CdTe Tetrapods highlighting the first excitonic peak.

The emission of electromagnetic radiation by a material that has absorbed a photon is known as fluorescence. The electrons in QDs are excited to the conduction state when they absorb a photon/energy equal to or greater than their band distance. However, this excited state is not stable, emitting a photon allows the electron to relax back to its ground state. The color of QD emission is size-dependent due to its dependence on the size of the bandgap. As the size of the QDs increases, the bandgap decreases, and less energy is needed to excite an electron from the valence band to the conduction band, this means that a photon of a lower frequency and higher wavelength would be absorbed resulting in a photon of a lower wavelength being emitted.

Two common elements that are utilized in the synthesis of QDs are cadmium and selenium, which yield cadmium selenide nanoparticles. There are various experimental methods used to synthesis quantum dots. Such methods include metal vapor deposition, sol-gel methods, and organometallic synthesis. In today's experiment, we will be using the widely known technique, pyrolysis, for bulk quantum dot synthesis which involves a high-temperature dual injection of the precursors needed.

SYNTHESIS PROCEDURE



Overview

CdSe quantum dots (QDs) are synthesized by simultaneously injecting cadmium (Cd) with selenium (Se) precursor solutions into the hated mixture of octadecene and surfactants including oleic acid, trioctylphosphine, etc. Before the experiment, the precursor solutions for selenium should be prepared in advance at the beginning period of the laboratory section.

1| Add 7.5 mg of selenium to a vial, along with 1.25 mL octadecene.

! CAUTION Performed in a fume hood since selenium is an inhalation hazard AND wear nitrile gloves and safety goggles.

2| Measure out 0.10 mL of trioctylphosphine from its Sure-Seal bottle with a syringe and add it to the same vial containing selenium and octadecene. Put on the cap of the vial and tie it.

! CAUTION TOP is extremely air-sensitive and should be handled with care.

3| To dissolve all the selenium, shake or sonicate the solution until all the selenium has been dissolved. **• TIMING 5 min**

4| Add 0.0141 g of cadmium oxide to a 50 mL three-neck round bottom flask.

! CAUTION Cadmium oxide is also an inhalation hazard, so this step should be performed in a fume hood.

5| Add 0.60 mL of oleic acid via a syringe and 10 mL of octadecene to the same 50 mL round bottom flask. Connect the middle neck with a condenser. Use one rubber stopper to cap one side of the neck. Connect the other neck with a glass adaptor for the temperature probe of the heating mantle. Set the target heating temperature to 225°C. Here are the schematics of the QD synthesis setup.

! CAUTION Octadecene and oleic acid vapors should not contact skin or eyes or be inhaled.

6| Heat cadmium oxide solution to a temperature of around 225°C. Once the temperature reaches about 225°C, quickly add 1 mL of the room temperature selenium stock solution via a syringe to the heated cadmium oxide solution. Start timing the reaction with a stopwatch.

7| Remove about 0.50 mL samples at 20-second intervals using a syringe. Place samples into separate vials.

! CAUTION The solution in the flask is hot and should handle with care.

8| To observe a more apparent color change, remove samples at a longer time interval.

Virtual Lab Link:

- How to Make Quantum Dots: https://www.youtube.com/watch?v=s3H0_8TLs-A
- Lead Sulfide Quantum Dots Synthesis: https://www.youtube.com/watch?v=bKLdkjV6Mbc
- Quantum Magic in Nanocrystals Moungi Bawendi: https://www.youtube.com/watch?v=EMdUfMF-8IU

CHARACTERIZATION

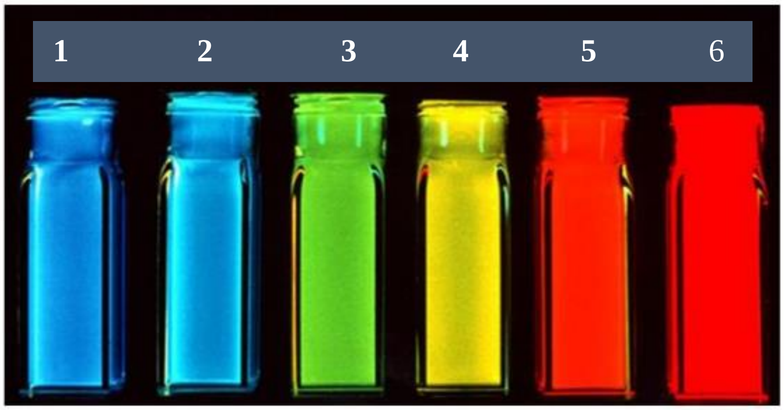


Figure 3: CdSe QDs irradiated with a UV lamp. From left to right, samples were taken as the synthesis progressed.

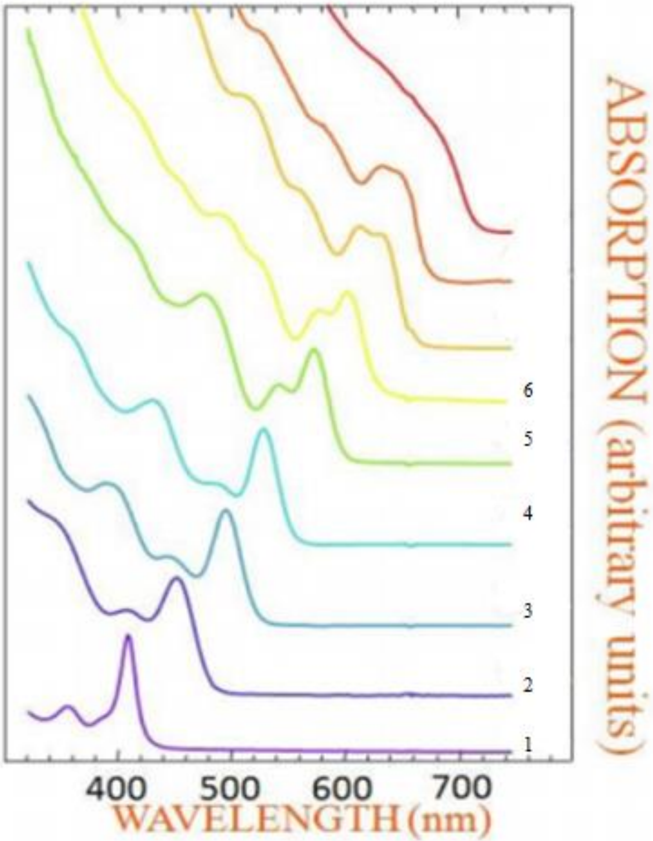


Figure 4: Absorption spectrum of different sizes of CdSe quantum dots

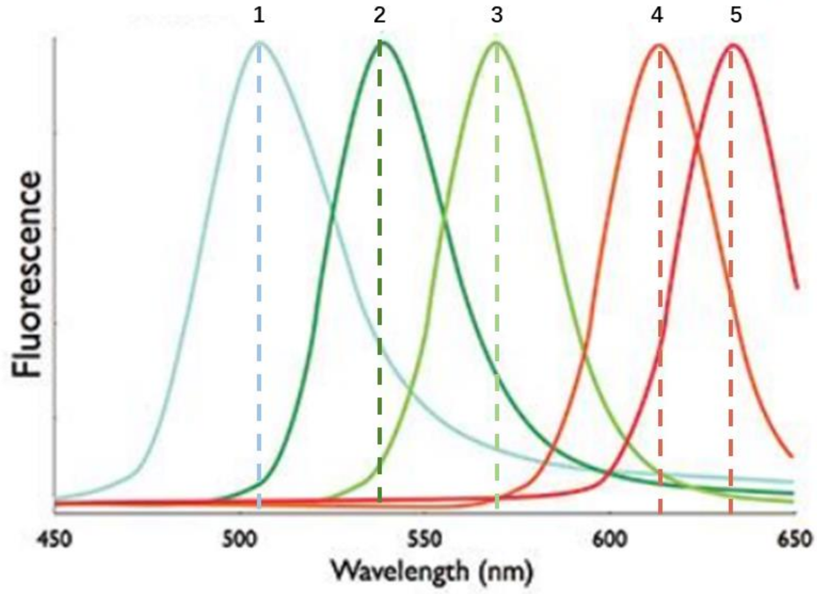


Figure 5: Size-dependent fluorescence emission of CdSe quantum dots

Choose four QD samples that are illustrative of the vast color range. In addition to these four samples, including the first and last samples obtained from the synthesis. Students will characterize a total of six samples.

1. Irradiate samples with a UV lamp to observe the fluorescence of the samples. By referring to Figure 3, fill in the table below. What do you observe?

Sample Collected	Color observed
1	
2	
3	
4	
5	
6	

2. Take the UV-vis spectra of the six samples to determine the wavelength at maximum absorbance. By referring to Figure 4, choose the bottom six spectra and fill in the table below. What significant things do you observe? How does this compare to the samples in Figure 1?

Sample	The wavelength First Exitonic peak (nm)
1	
2	
3	

4	
5	
6	

3. Gather the fluorescence spectra of the samples using an excitation wavelength of 450 nm to obtain the wavelength at maximum emission. The QD solution may need to be diluted with hexane to fill the quartz cell. By Referring to figure 5, fill in the table below.

Sample	The wavelength at Maximum Emission (nm)
1	
2	
3	
4	
5	

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QUESTIONS

1. What absorbance wavelength trends do you expect to observe for increasing QD size?

2. Determine the QD size for each sample using the UV-vis spectra. (It needs some standard reference or equations to calculate or estimate the sizes of QD samples)

QD size can be calculated using the following equation from Peng *et al.* [*Chemistry of Materials,* ***2003****, 15, 2854-2860*]

CdSe: $D = (1.6122 \times 10^{-9})\,\lambda^4 - (2.6575 \times 10^{-6})\,\lambda^3 + (1.6242 \times 10^{-3})\,\lambda^2 - (0.4277)\,\lambda + (41.57)$

In this equation, D equals the size of the QD in nm and λ is the wavelength (nm) for the first absorption peak.

3. Plot QD size as a function of synthesis time, assuming each sample in Figure 4 was collected at a time interval of 30 seconds. Can you elucidate any trend from the plot? If so, what is the trend?