



Name: _____ Date: _____ Class: _____

Student Worksheet

Part 1: Synthesizing CdSe Quantum Dots (with Answers in Red)

The following synthesis must be performed in a fume hood, and the students engaged in the synthesis must wear nitrile gloves and eye protection. **DO NOT let the mixture come into contact with your skin, and if it does, immediately wash it off.** Left over solutions are to be disposed of in the proper disposal bottles set aside in the fume hoods.

Materials per pair of students

- 0.13g Cadmium Oxide
- 7 mL Octadecene (ODE)
- 0.50g Myristic Acid
- 0.12 g SeO₂
- 25 ml or 50 ml round bottom flask
- 40mL Hexane or Decane
- heating mantle
- 400°C Hg Thermometer
- 9 in Glass Pasteur pipette
- UV/VIS spectrophotometer (here we use a Ocean Optics Red Tide USB650 UV with a USB-ISS-UV/VIS)
- 12 small test tubes or vials
- stop watch (optional) students can use a smart phone or a clock in the laboratory that has a second hand
- scales capable of measuring milligrams
- access to a UV light source

Introduction

In this experiment, we are going to make quantum dots (QDs) with a distribution of sizes as seen in Figure 4 at the end of the procedure. QDs are semiconductor nanoparticles. Notice that the color of the QDs varies with their radii when the dots are smaller than say 10 nm. In the case of CdSe, we see that the Bohr radius of the exciton in bulk CdSe is around 5Å. Given that this is the average distance of the electron from the hole we can expect that for dots of $L < 50\text{Å}$ will like act as QDs. In a quantum dot, the excited state of the electron is delocalized throughout the particle, but it is confined to the particle itself.

Quantum Dots—Particles in a Box

The energy of the excited state is quantized and the energy required to excite an electron from the valence band to the lowest conduction state is given by the following equation:

$$\Delta E_{fi} = E_{gap} + \frac{h^2}{8m_0R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi\epsilon_0\epsilon R} = h\nu$$

where R is the radius of the QD, E_{gap} is the gap in energy between the top of the valence band and the bottom of the conduction band in bulk CdSe, m_0 is the mass of the electron, m_e and m_h are the reduced masses of the electron and the hole, e is the charge on a proton, h is Planck's constant, and ϵ and ϵ_0 are the dielectric constant and permittivity of free space. The energy needed to excite the QD is absorbed from a photon of light. The lowest frequency (the onset frequency) $\nu = c/\lambda$ (where c is the speed of light and λ is the onset wavelength of the light) required to excite the QD is given by

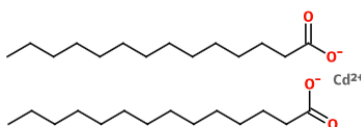
$$\nu = \frac{c}{\lambda} = \frac{E_{gap}}{h} + \frac{h}{8m_0R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi\epsilon_0\epsilon hR}$$

So if we measure either the onset wavelength or onset frequency of this light, we can determine the dot's radius R . In this experiment, we will make dots with different radii, measure the onset wavelength, and use the above formula to calculate the size of the QDs we make.

Making Quantum Dots in Micelles

So how do we make such dots, and how can we make dots that are so small? We will be synthesizing CdSe nanocrystals from CdO and SeO₂ using a kinetic growth method. In such a method, the particle size depends on the reaction time—the longer the reaction time, the larger the average particle size.

In order to be able to make nanoparticles, we are going to need to grow these particles slowly enough that we can stop the reaction when they are the size we desire. To do this we are going to use a special organometallic compound, called cadmium myristate.



As you can see above, the myristate is a C₁₃H₂₇ carbon chain attached to a carboxylate group. This type of compound is called a *surfactant*. Surfactants are *amphiphilic*, meaning that they contain both hydrophobic groups (their tails, here the carbon chain) and hydrophilic groups (their heads, the carboxylic group and the cadmium ion). Surfactants lower the interfacial tension between two liquids. Hydrophobic parts of the surfactant prefer the environment of other non-polar molecules (organics, oils, ethers, alkanes, etc.), while the hydrophilic parts of the molecule prefer the environment of polar molecules, ions, water, etc. When cadmium myristate is dissolved in an organic non-polar solvent, the molecules arrange themselves to form inverse micelles. In this way, the tails are in contact with one another and the solvent, while the solvent repelling hydrophilic head groups aggregate at the center of the micelle.

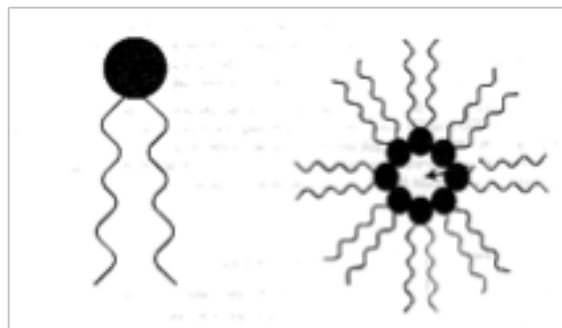


Figure 1: Schematic of cadmium myristate and a cadmium myristate inverse micelle. The head group comprises the cadmium ion and the carboxylic groups, while the tails are the C₁₃H₂₇ alkyl chains.

In the experiment, we will first make cadmium myristate and then add 1-octadecene and selenium dioxide to it and reheat. Octadecene is a long chain alkane with an alkene group at the end. It acts as a reducing agent reducing Se^(IV) to Se⁽⁰⁾ and Cd^(II) to Cd⁽⁰⁾, while the alkene bond is oxidized to either a ketone an aldehyde or to a longer chain alkene. The selenium dioxide is polar so it will be attracted to the center of the micelle, and so the reduction of the Se^(IV) and Cd^(II) will occur in the center of the micelle, where the nucleation of the CdSe particle will occur. Over time the CdSe particle will grow as will the micelle as shown left, with the myristate anion “capping” the nanoparticle.

Advantages to Growing CdSe Nanoparticles in a Micelle

So why is it that we choose to grow the CdSe particles in this way? What are the advantages to such an elaborate synthesis? The answer is four-fold:

1. The micelle stabilizes the quantum dot making it more stable, creating a narrower distribution of particle sizes at a given instant, and this makes for better optical properties.
2. The heavy organic tails slow down the rate of diffusion into the center of the micelle, slowing down the rate of formation of the quantum dot, making it easier to control the size.
3. The reaction can only happen at higher temperatures, which ties in with (2) and means that removing sample from the reaction vessel essentially quenches (stops) the reaction as soon as it cools below 200°C.
4. Because the reaction is relatively slow, thermodynamic considerations are important, meaning that the quantum dots are more spherical making for more consistent optical properties. (Spheres are shapes that minimize the ratio of surface area to volume, which is advantageous when you need to reduce the surface tension between two components in a solution.)

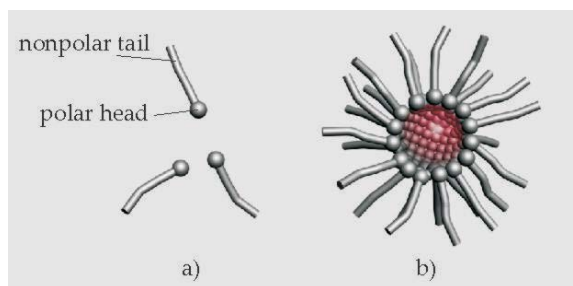


Image from University of Ghent Liquid Crystals and Photonics Group
<http://lcp.elis.ugent.be/research/electrophoresis>

Growing QDs of Different Nanometer Dimensions

The above will be our method, and because the rate of growth is comparatively slow, we will be able to control the size of the dots. Our reactants are colorless so change in color of the reaction mixture is because QDs are forming, and the color of the dots is directly related to the size of the dots. As soon as our mixture develops color, we remove aliquots from the reaction using a Pasteur pipette. As soon as the mixture is drawn into the pipette, its temperature is too low for further reaction to occur and growth of the dots inside the pipette stops. These aliquots are transferred to test tubes for later optical analysis using an absorption spectrophotometer.

By withdrawing aliquots at different moments in the reaction, we will effectively have solutions with dots of different average size and so different optical properties. The later we withdraw the aliquot, the bigger the dots will be.

Procedure

1. A 25 or 50 ml round bottom flask is clamped in place in a heating mantle, (the figure on the right) *in a fume cupboard*.
2. 1 mmole (0.13 g) of cadmium oxide (CdO) and 2.2 mmoles (0.50 g) of myristic acid are added to the flask.
3. Clamp a 400°C thermometer in place inserting it through the neck of the flask.
4. Heat the flask slowly to 190°C as soon as the reaction mixture clears turn off the mantle. (If the temperature gets too high you will cause the myristic acid to reduce to carbon. If this happens the solution will blacken and you will need to stop the reaction, clean the flask, and repeat the preparation.) As the reaction starts, you will see bubbles of both oxygen and hydrogen evolving from the mixture. This starts at around 120°C and is going full force at 140°C, according to the following reaction:



5. When above 180°C, the CdO dissolves and the solution clears. Once it is clear, turn off the mantle. Let it cool to around 60°C; then remove the thermometer and clean it with a paper towel.
6. While the mixture cools, weigh out 1 mmole of selenium dioxide (0.12g SeO₂) in a weighing boat.
7. Measure out 7 ml of 1-octadecene in a measuring cylinder.
8. Prepare and label 12 clean small test tubes in a rack, and make sure you have your Pasteur pipette handy.
9. When the flask has cooled to below 60°C and the thermometer has been removed, carefully add the 1-octadecene followed by the selenium dioxide. The solution will turn a milky white. Reheat the mixture by turning on the mantle. Start timing from this moment.
10. Pay attention. As the temperature rises above 140°C, the color of the mixture may start to change. Note the temperature when you perceive color change.
11. Insert a Pasteur pipette and remove aliquots of the reaction mixture every 10°C, so at 140°C, 150°C, 160°C, 170°C, 180°C, 190°C, 200°C, etc. Each time carefully discharge the pipette



Figure 2: A 25 mL round bottomed reaction flask is clamped into place and inserted into a heating mantle. The CdO and the myristic acid are added to the flask. A 400°C Hg thermometer is inserted into the middle neck. Here we see the reactants before they have melted and reacted.

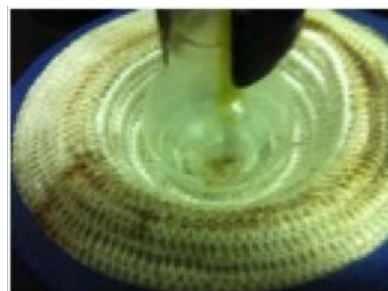


Figure 3: The CdO here has now reacted with the myristic acid. The solution has cleared. The temperature is 190°C.

into the test tubes sequentially having one person noting the temperature and time the reaction mixture is removed. Each sample should appear a different hue from the previous samples.

12. Continue removing aliquots until either each test tube contains a sample or the color has stopped evolving in the flask.
13. Add 3 ml of hexane (or decane) to each test tube, stopper the tube, and shake it to dissolve the quantum dots in the hexane.
14. When the flask is cool enough to handle, dispose of the remaining mixture in the waste container provided. Use hexane to rinse out any remaining mixture. **DO NOT let the mixture come into contact with your skin, and if it does, immediately wash it off.** Clean the glassware in a hot soapy water mixture using a test tube brush to help remove the myristate.

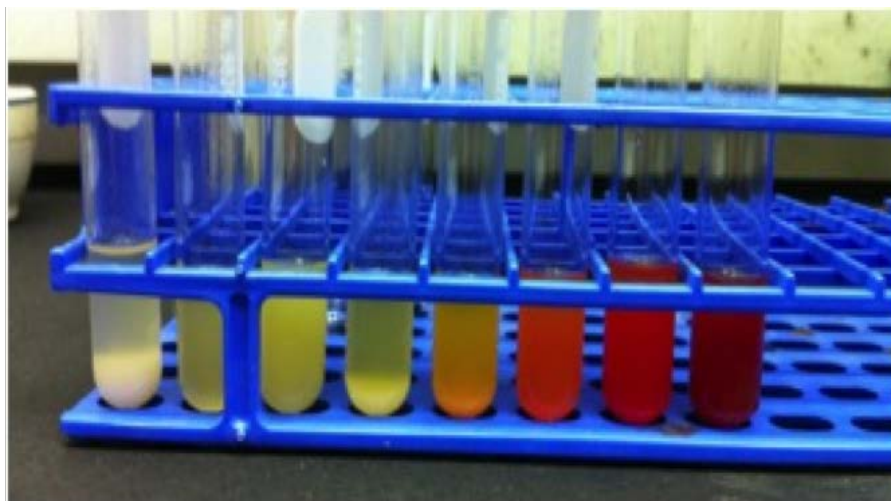


Figure 4: Here from left to right are samples removed at approximately 10°C intervals starting at 140°C. These samples have been diluted with 3 ml of hexane. (The reaction mixture here started with 5 mmoles of CdO and SeO₂. This is responsible for the intensity of the solutions. These are saturated, but yours will appear more dilute.)

Record your Observations

Sample Number	t _{reaction} (s)	T _{reaction} (°C)	Color notes
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			

Pre-Lab Questions – to be completed before the experiment is conducted

1. How small does a particle of CdSe need to be to behave as a quantum dot?

< 40~50 nm

2. What are quantum dots normally made of?

semiconductors

3. Why does cadmium myristate form an inverse micelle in a non-polar solvent?

The non-polar tail needs to be in contact with the non-polar solvent, while the polar tail needs to avoid the non-polar solvent. By forming a sphere with the tail at the center of the micelle and the tail on the outside, these conditions are met, and the solution is most stable.

4. Why would the inverse micelle be spherical in shape?

The inverse micelle is spherical in shape because this minimizes the surface area between the hydrophilic and hydrophobic parts of the system minimizing the surface tension.

5. Give 3 advantages to growing CdSe nanoparticles in an inverse micelle.

(i) slows down rate

(ii) stability

(iii) uniformity of particle size distribution

6. What role does the 1-octadecene play in the synthesis?

It reduces the Cd and the Se.

7. How do we create QDs of different sizes?

By quenching the reaction at different times

8. (a) Calculate the onset wavelength (in nm) for absorption for a CdSe dot that has a radius of

2.1 nm. 507 nm

(b) What is the color of light absorbed? green light

(c) What would the color of the solution appear? brown solution

9. Name 3 technological applications for QDs.

LEDs, lasers, solar cells, transistors, medical imaging, etc.

10. Where does the synthesis need to be conducted?

fume cupboard

11. What special precautions are needed for this synthesis?

nitrile gloves, goggles, fume cupboard, long sleeves