



Teacher's Preparatory Guide

Synthesis and Characterization of CdSe Quantum Dots

Overview: In this laboratory, students will receive an introduction to semiconductor quantum dots, namely CdSe. Students will study how surfactant-based chemistry can be used to synthesize CdSe quantum dots and study how the size of the quantum dots can be controlled by varying reaction time. The laboratory will then demonstrate how the color of these quantum dots can be connected to the size of the nanoparticle by considering the electrons as freely moving particles in a box with the dimensions of the nanoparticle. The model of the free particle will be compared with more exact results, where the particle sizes were measured from scanning electron microscopy, and use this to create a calibration curve. Students will be able to estimate the size of quantum dots by using UV-VIS absorption spectroscopy.

Purpose: This lab is designed to help students understand that nanosize particles of a given substance often exhibit different properties and behavior than macro- or micro- size particles of the same material.

Time Required: One 50-minute time period to introduce the subject; two 3-hour labs, one for quantum dot synthesis and one for optical analysis and size characterization; and, one additional 50-minute period for review of the lab

Level: High school AP level Physics or Chemistry; or University 1st or 2nd year Undergraduate chemistry and physics

Big Idea: Size Dependent Properties

Teacher Background:

Chemistry of Tomorrow Today: Nanotechnology *An Introduction to Nanotechnology through Chemistry*

Everywhere in the manifest universe, (except at the heart of stars and black holes), atoms and molecules are the smallest stable units of matter. So what if we could manipulate matter on the atomic scale using atoms and molecules like Lego bricks? This was essentially the musings of Nobel Prize winning physicist Richard Feynman in 1959 when he gave a talk entitled “*There’s Plenty of Room at the Bottom*”¹. In that talk, he speculated about writing the entire Encyclopaedia Britannica (pre Wikipedia) on the head of a pin. He demonstrated that each letter would have to be written in an area of 32 x 32 atoms across. He mused over being able to individually move atoms; he

Image at: http://www-03.ibm.com/ibm/history/exhibits/vintage/vintage_4506VV1003.html

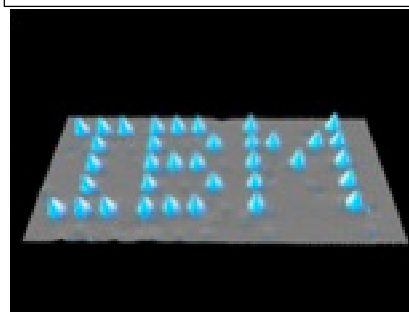


Figure 1: The letters IBM here are written on a nickel surface and the blue pixels are individual xenon atoms. This astonishing feat was accomplished back in 1981 using a Scanning Tunneling Microscope (STM).

speculated about miniaturizing electronic circuits so that there were wires only 10 atoms wide and electronic circuits a few thousand atoms across. If we could do that—he speculated—computers would not only be smaller (in those days a computer filled a room), but they could also be thousands of times more complicated and potentially could be much more capable of handling complex tasks like, say, face recognition! In 1959, it would have taken a computer the size of the pentagon to recognize your face and we can do that today with a device as small as a smart phone (see Table 1 below)!

In that talk, he laid out the field that today we call Nanotechnology, and nanotechnology is the frontier of technology today. Nanotechnology lies at the frontiers of Physics, Chemistry, Biology, Engineering, and Materials Science.

Nanotechnology — What is it?

Nanotechnology is the manipulation of matter on the scale of nanometers from 1 to 100s of nanometers (nm). A nanometer is 10 Angstroms, or one billionth of a meter (10^{-9} m). For a scale comparison on the molecular scale, a C-C bond is 0.12 nm long while DNA has a diameter of 2 nm. The bacterium [Mycoplasma](#), is around 200 nm in length. The essential functions of the cell therefore can only really be truly understood in the nanometer regime, where behavior is dominated by chemistry, molecular geometry, and quantum mechanics. In fact, in this regime, quantum mechanical effects (where particles must also be considered as waves of probability) make materials behave differently from their bulk behavior, and this can be manipulated to the advantage of technology.

Succinctly, we could say that nanotechnology is the engineering of functional systems at the molecular scale. In its original sense, nanotechnology refers to the projected ability to construct items from the bottom up, using techniques and tools being developed today to make complete, high performance products. In a sense, we could say that biology utilizes nanotechnology since it uses specialized molecules and environments to construct the essential elements inside the cell. So we can use nature as seen from molecular biology's perspective as an inspiration for this field of endeavor.

Nanotechnology is very diverse. It fails to fit within the auspices of a single scientific discipline. The appreciation of the subject in all of its diversity requires an appreciation of physics, chemistry, biology, as well as some of the more specialized disciplines including [surface science](#), [organic chemistry](#), [molecular biology](#), [semiconductor physics](#), and [microfabrication](#). The study and exploitation of this field requires very expensive, state-of-the-art equipment, ultra high vacuum systems, as well as ultra clean environments. The field utilizes methods ranging from extensions of conventional [device physics](#) to completely new approaches based upon [molecular self-assembly](#), from developing [new materials](#) with dimensions on the nanoscale to [direct control of matter on the atomic scale](#).

The Birth of Nanotechnology

To be able to work in this regime, we have to have tools that allow us to characterize matter on the nanometer scale. Essentially nanotechnology emerged with the advent of the Scanning Tunneling Microscope (STM), an instrument that can image surfaces on the atomic scale. This was developed at IBM in Zurich in 1981 and for the first time scientists could see the atoms that had been theorized since the time of Democritus.

With the emergence of the STM, we now had a visible window into physics, chemistry, and

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biology on the atomic scale, and the discoveries have led to the new field of nanotechnology.

Why Nanotechnology?

Why is it that today humanity is becoming so interested in nanotechnology? What are the advantages to us? First, let us consider the advantages to the electronics industry. In electronics, we use electrons to do work. We pass the electrons through various devices, resistors, capacitors, transistors, inductors, and all of these devices allow us to control the electrons to do useful work. For example, in a microprocessor (computer chip), by passing electrons through an array of transistors, we can create logic circuits that allow the electrons to perform logical tasks. The smaller each transistor is, the quicker the electrons can perform the task of interest; often, the smaller the device is, the more efficient the device is. So in the electronics industry, the advantage is clear—the smaller the device, the faster and more efficient the device is—and this leads to ultrafast and ultra small computing devices today. For example, an iPhone today has more computing power than the Apollo spacecraft that went to the moon in the late 60s and early 70s (see Table 1 below).

Table 1: The Relentless Advance of Nanotechnology A comparison of the on-board Apollo flight computer that put man on the moon in 1969 (very little nanotechnology) and a modern smart phone (a lot of nanotechnology) in 2011.

	Apollo Guidance Computer circa 1969	iPhone 4S circa 2011	Nano Advantage iPhone / Apollo
Processor Speed	0.004077 GHz	0.8 GHz x 2 cores	392× faster
Memory Size	2 kB	1,000,000 kB	50,000× more memory
Mass	40,000 g	140 g	286× less mass
Storage	32 kB	512,000 kB	1,600× more storage
Functions	Adds, subtracts, multiplies, divides	Plays music in stereo, HD video, portable color TV, makes wireless phone calls, connects to the internet, records video and audio, sound recognition (in multiple languages), wireless router, detects orientation in space and position on Earth's surface	Access to most of human knowledge!

In a battery, ions travel between two electrodes where certain redox reactions occur. The current generated by the battery depends on the number of these reactions occurring at the electrode, and this is often limited by the time it takes ions to travel from one electrode to the other. This is what limits the rate of charging of a typical Li-ion battery in your phone or laptop. In nature, however, the essential distance between the ‘electrodes’ in a biological battery may be of the order of billionths of a meter, so the current can be much higher. So if we can create batteries with nanotechnology, these batteries will be far more efficient and will charge faster.

In nature, chemical reactions can often be conducted at temperatures and pressures that are much lower than we can conduct them in the lab. This happens because reactions in nature are conducted in specialized nanoscale environments with catalyzing atoms that significantly increase the rate of reaction. Again nature—by designing systems that work on the nanoscale—is able to create much more efficient reaction pathways.

Quantum Dots: What are they and why are we interested in them?

Quantum Dots (QDs) are small particles that are 10–40 times the diameter of an atom. These dots are made of elements that, when combined, make semiconductors. For dots with dimensions in the range (1-100 nm) it is found that the optical properties vary with their size. This is illustrated in Figure 2, where we see fluorescence of five colloidal quantum dots solutions irradiated with UV light.

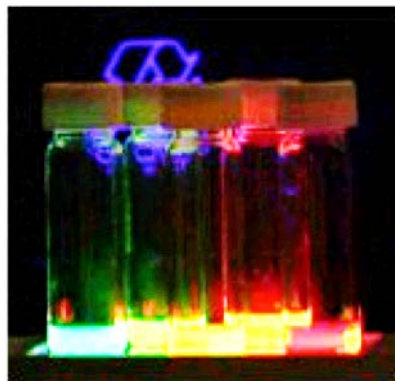


Figure 2: Colloidal Quantum Dots irradiated with UV light. The different emission colors are generated by quantum dots of different sizes.

Generally speaking, the smaller the QD, the bluer the fluorescence spectrum. By controlling the size of QD made, it is possible to make dots with very specific colors, as well as conductivities. As such, QDs are finding applications in transistors, solar cells, LEDs (see Figure 3), and diode lasers. They have also investigated quantum dots as agents for medical imaging and hope to use them as qubits in quantum computing.

Understanding Quantum Dots

For those of you that consider yourselves chemists and have little understanding of physics, there are going to be some ideas from physics with which we are going to have to become familiar. In this section, a brief introduction to the essential ideas from physics is introduced.



Figure 3: Quantum Dot based Light Emitting Diodes (QLEDs) are currently being developed for displays and lighting applications. In the photo above, we are seeing QLEDs manufactured by QDVision. Image at: <http://www.qdvision.com/qleds-the-future>.

Semiconductors

Semiconductors (materials that possess a conductivity that is less than a metal but more than an insulator), along with insulators, are essentially molecular solids where the atoms are covalently bonded in extended crystalline structures.

Since, in crystalline materials, there are many molecular orbitals with the same energy, they hybridize to make orbitals that extend throughout the entire crystal. These hybridized orbitals split in energy to form a continuum of energies in a small range that are called bands. The band created from the Highest Occupied Molecular Orbitals (HOMO) is called the **valence band**, and the band created from the Lowest Unoccupied Molecular Orbitals (LUMO) is called the

conduction band. In Figure 4, this concept is illustrated for ethane (ethylene) which, when stacked in a cofacial configuration, forms a conducting polymer.

The gap in energy between the valence and conduction bands is called the **band gap**. A semiconductor is a solid whose valence bands do not overlap with the conduction bands, and the band gap lies in the range $3 \text{ eV} > E_{\text{gap}} > 0.1 \text{ eV}$ (conductors have no band gap, while insulators have band gaps in excess of 3 eV). So in a semiconductor at low temperature, the valence band is filled and the conduction band is empty.

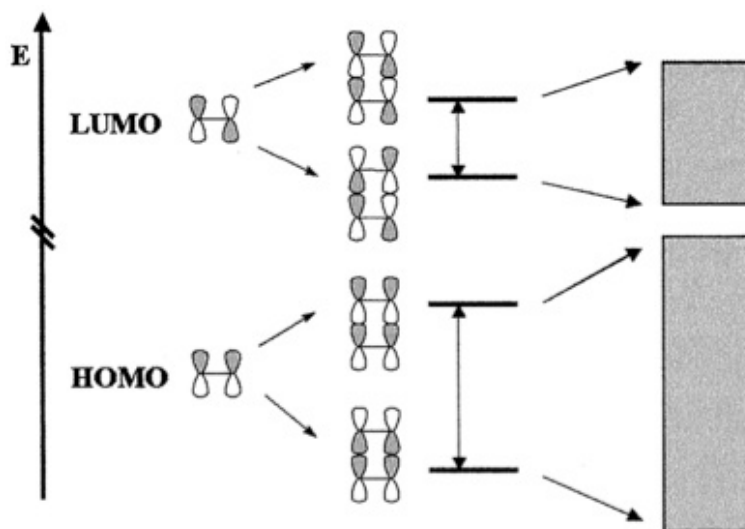


Figure 4: Illustration of the bonding–antibonding interactions between the HOMO/LUMO levels of two ethane molecules in a cofacial configuration. Stacking two ethane HOMO orbitals makes two linearly independent orbitals—a bonding and an antibonding—the lowest two energy levels in the middle of the figure. The next two in energy correspond to linear combinations of the LUMO orbitals in bonding and antibonding configurations. On the right we see how bands are formed when a large number of stacked molecules interact. Essentially one makes a continuum of energy levels, but in a semiconductor and in an insulator, the LUMO-related band never overlaps with the HOMO-related band. The gap in energy between the highest point in energy of the HOMO band and the lowest part of the LUMO band is called the band gap.

Excitons

If a photon, of sufficient energy, is absorbed by an electron in the valence band, it can be excited into the conduction band, leaving a hole³¹ where it once was. The hole and the electron are called an **exciton**. The exciton consists of the excited electron in the conduction band and the hole left in the valence band.

The hole is generally much less able to move around than the electron, so the two form a kind of pseudo hydrogen atom, and as such, the exciton has H-like electron orbitals a_0 (average distance of the electron from the center of positive charge—see Figure 5). However, whereas there is only vacuum ($\epsilon = 1$) within the H atom, in an exciton, the other electrons and nuclei respond to the presence of the excited electron and the hole. Electrons are polarized, moving toward the hole and away from the excited electron. This effectively reduces the strength of the interaction between the electron and the hole. We account for this using the dielectric constant ($\epsilon > 1$) of the material, which effectively reduces the strength of the Coulombic attraction of the electron for

³¹ Even though holes are in fact the absence of a negatively charged particle (an electron), they can be treated theoretically as positively charged particles, whose motion gives rise to electric current.

the hole making the exciton's Bohr radius much larger than that of H (which is a little over half an Angstrom).

$$\alpha_0 = \frac{4! \epsilon_0^2 \hbar^2}{mq^2} = \alpha_0^H \quad (1)$$

where ϵ_0 is the permittivity of free space, m is the mass of the electron, and q is the charge of a proton. Notice that the Bohr radius of an exciton is ϵ times the Bohr radius of Hydrogen α_0^H . So in the case of CdSe quantum dots, the Bohr radius of the exciton is $10.2\alpha_0^H$ or about 5\AA . Since in an H atom, electron density extends out beyond $5a_0$, it is prudent to assume that in bulk CdSe, electron density from the exciton would extend to a radius of 25\AA .

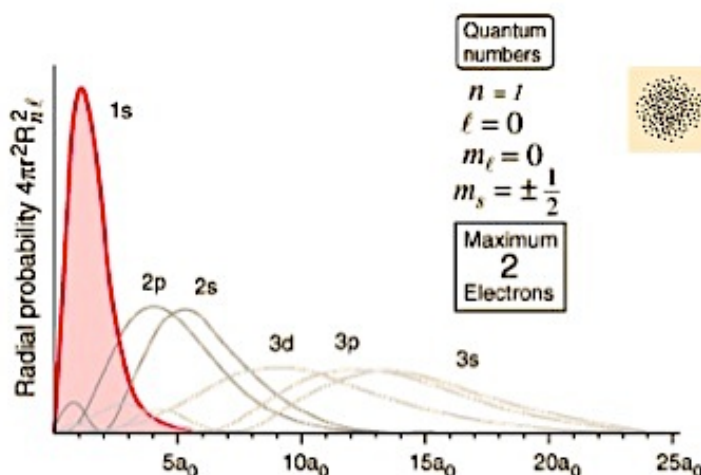


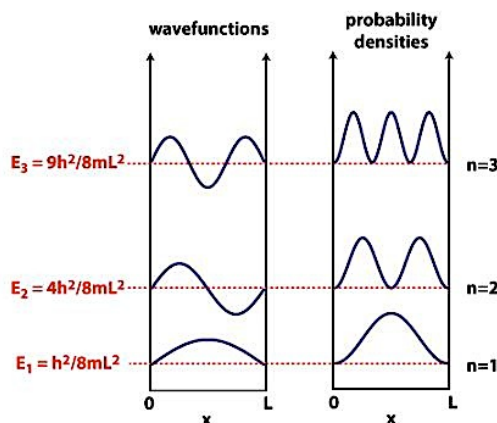
Figure 5: Plots of the Radial distribution functions for different Hydrogen orbitals in units of the Bohr radius a_0 . The shaded curve is for the 1s orbital. Notice that it peaks at a_0 but extends out over $5a_0$ from the nucleus.

Excitons in Quantum Dots

So what happens if the radius of the quantum dot is smaller than the Bohr radius for the exciton? Basically the electron, which is significantly more stable inside the dot than outside, is confined within the dot, Fig. 6 and the situation is analogous to a particle in a box.

Particle in a 1-Dimensional Box

In the normal treatment of a particle in a box, we solve the Schrödinger equation for a particle confined to an infinitely deep well of width L . Inside the well the potential $V(x) = 0$ for $0 < x < L$, and outside the well the potential is infinite $V(x) = \infty$ for $0 > x$ or $x > L$.



Solving the 1D Schrodinger equation is equivalent to solving for a free particle

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = E_x \psi(x) \quad (2)$$

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subject to the boundary conditions $\psi(0) = \psi(L) = 0$. The solutions are

$$\psi_n(x) = N \sin\left(\frac{n_x \pi x}{L}\right) \quad (3)$$

$$E_n = \frac{h^2}{8mL^2} n_x^2$$

The eigenenergies E_n ($n_x=1,2,3 \dots$) are the possible energies of the particle. Since the particle exists within the box where it has no potential energy, this energy is purely

kinetic. The larger the n_x is, the larger the particle's momentum. If we consider a cube, the results become

$$\psi_n(x,y,z) = N \sin\left(\frac{n_x \pi x}{L}\right) \cdot \sin\left(\frac{n_y \pi y}{L}\right) \cdot \sin\left(\frac{n_z \pi z}{L}\right)$$

$$E_n = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

(4)

The energy E_n can be considered the *confinement energy* which gets smaller and smaller the larger L becomes. Both the electron and the hole are far more stable inside the dot than outside. Because of the fact that the quantum dots dimensions are smaller than the exciton's Bohr radius, we can treat the electron and the hole as fully delocalized throughout the particle. Under these conditions, equation (4) is valid. Notice that there is a lowest energy for the particle that is not zero. The particle in the box has zero point energy just like in a harmonic oscillator. In our case, there are two particles—the electron and the hole. These have effective masses that are different to reflect the fact that the electron is a lot more mobile than the hole. Also, with the hole and the electron, there is an attractive Coulomb interaction to consider, which can be done by averaging the Coulomb potential over the possible positions of the hole and the electron with the result that for a sphere of CdSe of radius R^f

$$E_n = \frac{h^2 (n_x^2 + n_y^2 + n_z^2)}{8m_0 R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi\epsilon_0 \epsilon R} \quad (5)$$

This is the energy of the n^{th} exciton state relative to the *bottom* of the conduction band. The first term is the *confinement energy* and the second term is called the *exciton energy*. Relative to the top of the valence band, one has to add the energy of the band gap. This would be the excitation energy

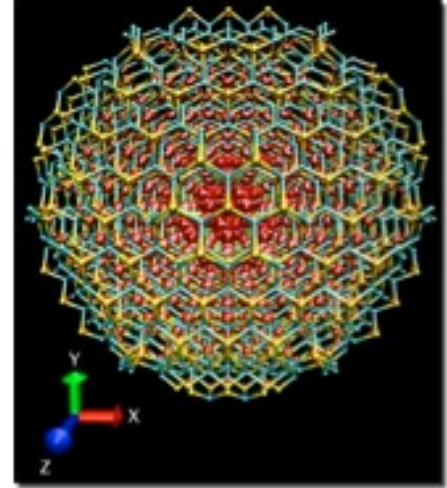


Figure 6: A fluorescing exciton (electron density denoted by the red clouds) in CdSe (Cd in Blue, Se in Yellow). Notice that the electron remains confined to within the quantum nanoparticle (image by Sebastien Hamel, Lawrence Livermore National Labs found at https://newsline.llnl.gov/articles/2008/may/05.09.08_nanomaterials.php).

^f When the equation is solved for a sphere the radial differential equation has solutions that are spherical Bessel functions, and the imposed boundary condition is met by ensuring the energy of the wavefunction is a zero of the Bessel function.

$$\Delta E_n = E_{gap} + \frac{h^2(n_x^2 + n_y^2 + n_z^2)}{8m_0R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi\epsilon_0\epsilon L} \quad (\text{sphere radius } R) \quad (6)$$

When visible and UV light is absorbed by a quantum dot, the excited state of the electron is confined to the spatial dimensions of the dot. Notice that as L gets larger, ΔE_n gets smaller. We call that a *red shift*. As L gets smaller, ΔE_n gets bigger, and we call that a *blue shift*.

Connecting ΔE_n to the Optical Properties of the QD

In the early days of quantum mechanics when Niels Bohr pondered the line spectra exhibited by H atoms, he concluded that emission lines came from transitions between quantum states. The energy of the emitted photon $h\nu$ plus the energy of the final quantum state E_f is equal to the energy of the emitting quantum state E_i line is related to the energy difference of the two quantum states

$$E_i = E_f + h\nu \quad : \text{for emission of a photon} \quad (7)$$

$$E_i = E_f - h\nu \quad : \text{for absorption of a photon}$$

This relation is a mathematical assertion of energy conservation, i.e. the total energy of the system before the transition and the total energy after the transition are the same. We can rearrange the above equation to arrive at expressions for either the frequency or wavelength of the photon

$$\Delta E_{if} = E_i - E_f = h\nu = \frac{hc}{\lambda} \quad : \text{for emission of a photon } (E_f < E_i) \quad (8)$$

$$\Delta E_{fi} = E_f - E_i = h\nu = \frac{hc}{\lambda} \quad : \text{for absorption of a photon } (E_f > E_i)$$

Here h is Planck's constant, c is the speed of light, ν is the frequency of the photon, and λ is the wavelength of the photon.

So let us connect this with the problem of the absorption of light by the QD. If we wish to calculate the lowest frequency of absorption in the QD then

$$\Delta E_{fi} = E_{gap} + \frac{h^2}{8m_0R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi\epsilon_0\epsilon R} = h\nu \quad (9)$$

or

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

The lowest frequency of absorption or emission is inversely related to the size of the dot, so the smaller the dot, the higher this threshold frequency. Referring back to Figure 2, we see a series of test tubes containing dispersed quantum dots of different sizes. As we move from left to right, we

have increasingly large quantum dots. See how emission frequencies are higher as the dots get smaller.

Sources

1. Merkle, R., Nanotechnology (hosted by Zyvex). "There's Plenty of Room at the Bottom." (accessed August, 2012) <http://www.zyvex.com/nanotech/feynman.html>
2. Boatman, E.M., Lisensky, G.C. and Nordell, K.J., "A Safer, Easier, Faster Synthesis W for CdSe Quantum Dot Nanocrystals" *Journal of Chemical Education*, 82, (2005): 1697-1699.
3. Li Y., "A Visual Demonstration of "Particle in a Box" theory: Multicolor CdSe Quantum Dots" Department of Chemistry & Biochemistry University of California, Santa Cruz
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5. Norris, D.J. and Bawendi, M.G., "Measurement and Assignment of the Size-Dependent Optical Spectrum in CdSe Quantum Dots", *Physical Review B*, 33, (1996):16338-16346.
6. Chen, O., Chen X., Yang Y., Lynch J., Wu H., Zhuang J., and Cao Y.C. "Synthesis of Metal-Selenide Nanocrystals Using Selenium Dioxide as the Selenium Precursor", *Angew. Chem. Int. Ed.*, 47, (2008): 8638-8641

Materials per pair of students:

- nitrile gloves (per student)
- safety glasses (per student)
- fume hood
- 25 ml or 50 ml round bottom flask (one neck or three necked works; you'll also need 2 Septa if using a 3 necked flask)
- heating mantle
- ring stand
- 2 clamps
- 400°C Hg thermometer
- hold stopper
- 0.13 g cadmium oxide
- 0.50 g myristic acid
- weigh paper or boat
- spatula
- 0.12 g selenium dioxide
- scales capable of measuring milligrams
- paper towel
- 7 ml octadecene (ODE)
- graduated cylinder
- 10-12 small test tubes or vials with stoppers
- test tube rack
- 9 in. Pasteur pipette with bulb
- stopwatch (optional); students can use a smart phone or a clock in the laboratory that has a second hand
- 40 ml of hexane or decane as a solvent
- test tube brush and soapy water
- UV light source (e.g. LED UV Flashlight)

- UV/VIS spectrophotometer (here we use a Ocean Optics Red Tide USB650 UV with a USB-ISS-UV/VIS, but a USB2000 or USB4000 will work)
- SpectraSuite Software installed on a computer that interfaces with the spectrophotometer (from Ocean Optics at www.oceanoptics.com/products/spectrasuite.asp)

Advance Preparation: Purchase materials, which may be found at www.sigmaaldrich.com.

Safety Information: Warning: Octadecene vapor should not be inhaled and contact with the skin and eyes should be avoided. Myristic acid is light and air sensitive and irritates the eyes, skin and respiratory system. Selenium dioxide is toxic by inhalation or absorption through the skin and the effects of ingestion are cumulative. Cadmium myristate is highly toxic through inhalation, ingestion or skin contact. The following synthesis **must be performed** in a fume hood, and the students engaged in the synthesis must wear nitrile gloves and eye protection. Left over solutions are to be disposed of in the proper disposal bottles set aside in the fume hoods.

Suggested Instructional Procedure:

Time	Activity
Day 1	The Day Before the Lab
20 min	<i>Nanotechnology: What Is It?</i> Introduce the students to the idea of nanotechnology (use the information provided in the <i>Teacher's Preparatory Guide</i>).
20 min	<i>Quantum Dots: What Are They and How Do They Work?</i> Introduce students to the topic of quantum dots as well as the concepts of a semiconductor, hole, band gap, and valence and conduction bands.
15 min	Introduce the upcoming experiment. Outline the way the QDs will be made. Provide a diagram showing the experimental set up and some outline of the reaction and how it works.
5 min	Distribute <i>Synthesis Student Worksheets</i> to students. Assign Pre-Lab Homework asking students to read the lab and answer the pre-lab questions.
Day 2	Day 1 of the Student Lab
10 min	Review the synthesis aspect of the experiment. Review what the students will be doing and why students are doing the experiment. Emphasize safety and discuss clean up and disposal procedures.
2.5 hrs	Have students synthesize the QDs.
20 min	Clean up.
Day 3	Day 2 of the Student Lab
25 min	Review the spectroscopy aspect of the experiment. Discuss the connection to the valence-conduction band transition and the particle-in-a-box model of the exciton. Review how to calculate the size of the particle from the absorption data.
5 min	Distribute <i>Characterization Student Worksheets</i> to students. Ask students to follow the procedures.
90 min	Have students measure the absorption spectra and collect data on the QDs.
60 min	Ask students to analyze the data. Students will transfer the data to Excel to make

and analyze graphs to extract the particle size.
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Teaching Strategies I recommend that each synthesis is conducted by two students—one who is conducting the synthesis and a second student who is recording information about the time in seconds, t_{reaction} , and when each 1 ml is withdrawn from the reaction mixture, and is also labeling the 10 samples that this synthesis will create.

Guided Dialog: *Before beginning the lab, review the meaning of these terms:*

Semiconductor *A material that possesses a conductivity that is less than a metal but more than an insulator.*

Valence band *A continuum of energies created from the hybridization of the highest occupied molecular orbitals in a crystalline material.*

Conduction band *A continuum of energies created from the hybridization of the lowest unoccupied molecular orbitals in a crystalline material.*

Band gap *The gap in energy between the top of the valence band and the bottom of the conduction band.*

Quantum Dot *Small particles that are 10-40 times the diameter of an atom.*

Micelle *A molecular aggregate that constitutes a colloidal particle.*

Amphiphilic *Pertaining to a compound or surfactant that contains both hydrophobic and hydrophilic groups.*

Hydrophilic *Having the affinity for an environment of polar molecules like water or ions.*

Hydrophobic *Having the affinity for an environment of other non-polar molecules such as organics, oils, ethers, alkanes etc....*

Alkane *Saturated hydrocarbons that consist of only H, C and exclusively single bonds.*

Alkene *Unsaturated chemical compound that contains at least one C=C double bond.*

Carboxylic group *A functional group consisting of a C atom double bonded to an O and single bonded to a hydroxyl group (-OH).*

List any last minute details that the students must remember, including reiterating all safety precautions. Now, begin the lab.

Procedure Checkpoints

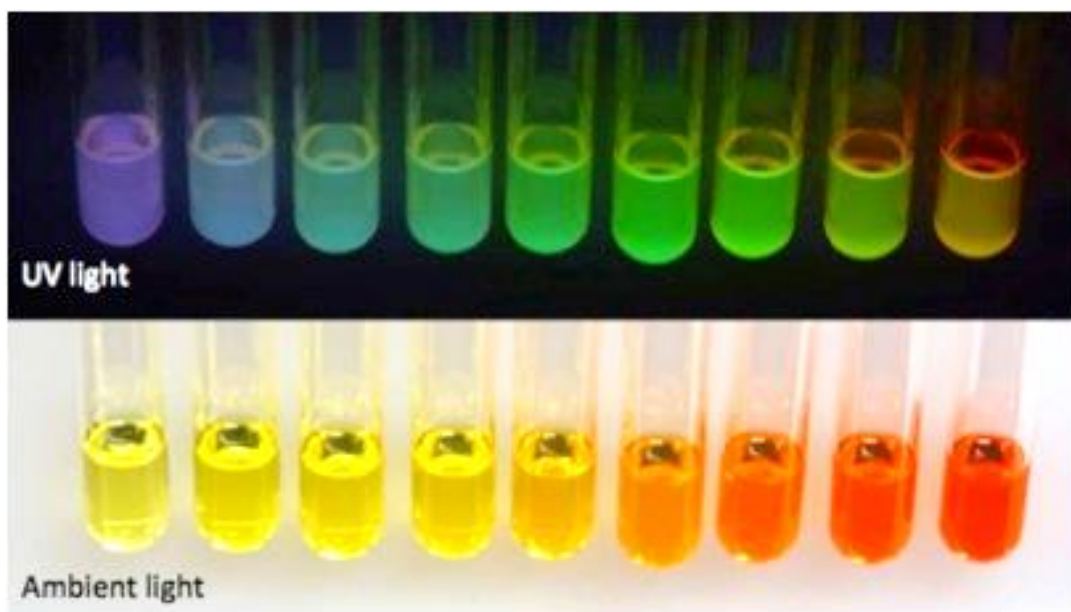


Figure 7: CdSe Quantum Dots. Each test tube contains quantum dots of different average sizes, ranging from smallest on the left to largest on the right. Notice how quantum dots have size dependent optical properties. In this figure, the test tube on the left contains CdSe QDs that are approximately 1.8 nm in diameter, while on the far right the QDs are approximately 4 nm in diameter (image by Yat Li, University of California, Santa Cruz).

Synthesizing CdSe Quantum Dots

In this experiment we are going to make quantum dots (QDs) with a distribution of sizes like seen in Figure 7. In the case of CdSe, we saw that the Bohr radius of the exciton in bulk CdSe is around 5\AA . Given that this is the average distance of the electron from the hole, we can expect that for dots of $R < 50\text{\AA}$ (5 nm) will like act as QDs. So how do we make such dots?

We will be synthesizing CdSe nanocrystals from CdO and elemental Se 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.

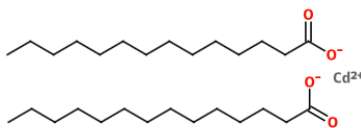


Figure 8: Cadmium Myristate

As you can see in Figure 8, the myristate is a $C_{13}H_{27}$ 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.

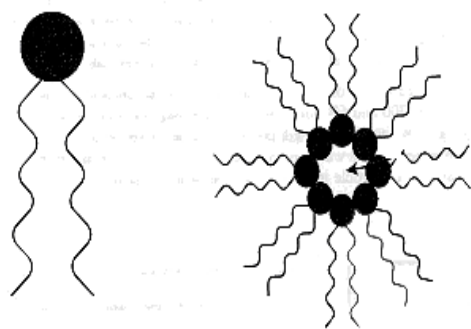


Figure 9: Schematic of cadmium myristate and a cadmium myristate inverse micelle. The head group comprises the cadmium ion and the carboxylic groups, while the tails are the $C_{13}H_{27}$ alkyl chains.

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

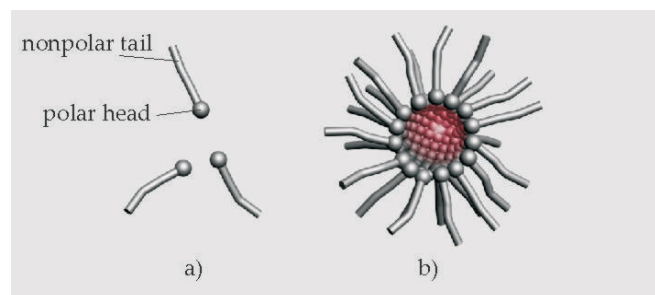


Image from University of Ghent Liquid Crystals and Photonics Group at: <http://lcp.elis.ugent.be/research/electrophoresis>

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 $200^{\circ}C$.
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.)

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.

Characterizing QDs Using Absorption Spectroscopy

Using the equation from the introduction, we have a way to assess the size of the dots from the onset wavelength for absorption. The only problem with this is that the model simplifies the exciton energy by treating it as a particle in a box, and we need to assess the accuracy of this model first. To do this we will take data from a previous experiment that is able to measure the size of the dots using an alternative method whereby the dots are imaged using an electron microscope. Using these data, we will create a calibration curve and we will compare the experimental results with the results predicted from the equation in the introduction. We will use both the calibration curve and our model to predict the sizes of the QDs in our samples.

Cleanup: For Day 1: When the flask is cool enough to handle, dispose of the remaining mixture in the waste container provided. Rinse with hexane to help remove any remaining particles. 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.

Enhancing Understanding: Review the findings with students *after* the activity:

- Different sizes of CdSe nanoparticles can be made in micelles.
- Size distributions can be controlled kinetically.
- The size of the quantum dot can be measured using spectroscopy.
- The particle-in-a-box model can be used to approximately account for the optical behavior of the dots.
- Discuss applications of QDs, including solar cells, LEDs, and LASERS.

Assessment: Students should be able to:

- Have an understanding of why nanotechnology is currently of interest
- Understand the idea of the Bohr radius
- Have a rudimentary comprehension of a semiconductor, valence and conduction bands, and the band gap and how it relates to the concepts of LUMO and HOMO in chemistry
- Understand that when an exciton radius in a bulk semiconductor is larger than the radius of the nanoparticle that the semiconductor behaves as a quantum dot

- Have an idea of why quantum dots are useful technologically
- Understand that the smaller the dot, the larger the gap between the valence and conduction band in the dot
- Have a basic comprehension of the particle-in-a-box model and what it predicts
- Have a grasp of surfactants and why they form micelles
- Have an understanding of why synthesizing a nanoparticle in a micelle is advantageous
- Understand the role of the 1-octadecene in the synthesis
- Use a visible spectrophotometer to record the visible spectrum of the given sample
- Calculate the radius of a quantum dot given the threshold wavelength for absorption in the visible spectrum

National Science Education Standards (Grades 9–12)

Content Standard A: Science as Inquiry

- Abilities necessary to do scientific inquiry

Content Standard B: Physical Science

- Structure and properties of matter
- Chemical reactions

Content Standard E: Science and Technology

- Understandings about science and technology

Next Generation Science Standards

- HS-PS1-1. Use the periodic table as a model to predict the relative properties of elements based on the patterns of electrons in the outermost energy level of atoms
- HS-PS2-6. Communicate scientific and technical information about why the molecular-level structure is important in the functioning of designed materials
- HS-PS4-3. Evaluate the claims, evidence, and reliability behind the idea that electromagnetic radiation can be described either by a wave model or a particle model, and that for some situations one model is more useful than the other.
- HS-PS4-4 Evaluate the validity and reliability of claims in published materials of the effects that different frequencies of electromagnetic radiation have when absorbed by matter.