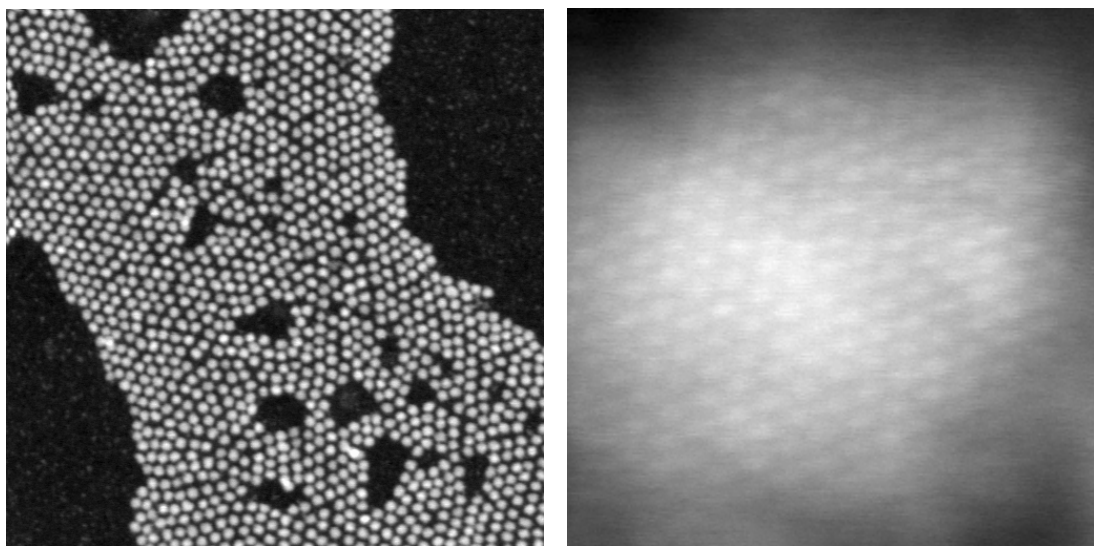


Quantum Dots

Jeff Harbold, Monica Plisch

I. Introduction

Quantum dots are semiconductor nanoparticles that emit light at a characteristic wavelength when excited. The wavelength of the light emitted depends on the size of the nanoparticle; this behavior is quite useful since it is relatively easy to control size. Quantum dots are a subject of intense research at Cornell and other institutions. The figure below shows STEM images of quantum dots taken in the Silcox lab at Cornell.



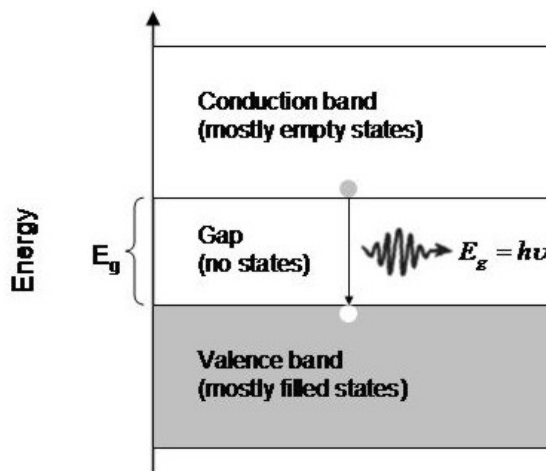
Left: low resolution STEM image of quantum dots; small spheres of semiconducting material that appear as white dots. Right: high resolution STEM image of a single quantum dot; the brighter spots showing the location of individual columns of atoms.

Quantum dots have a variety of potential applications. A collaboration between the Wise and Webb labs at Cornell demonstrated the use of quantum dots for imaging blood flow in mice. Quantum dots may also prove useful as fluorescent tags for biological molecules so that the motion of individual biomolecules can be tracked in a microscope. Another possible application involves fiber amplifiers that boost signals after they have traveled long distances in optical fibers. Current fiber amplifiers work over a narrow range of wavelengths, limiting the bandwidth. Quantum dots of varying sizes could be embedded in a fiber and used to make a broad-band amplifier that would expand the capacity of a fiber several fold.

Quantum dots can be synthesized with a variety of nanofabrication techniques. The CdSe quantum dots we will study in lab were fabricated by injecting Cd and Se precursors into a solution in a reaction vessel. They reacted and precipitated tiny CdSe crystals that grew atomic layer by atomic layer. The final size of the quantum dots was determined by the time of the reaction and the temperature. After fabrication, the quantum dots were embedded in a PLMA polymer matrix to make them stable and easy to handle.

Some bulk semiconductors emit light when excited. In general, the composition of semiconductor material determines the wavelength of light emitted. For example, a light emitting diode (LED) that emits red light is made from Gallium Arsenic Phosphide (GaAsP) while an LED that emits green light is made from Gallium Phosphide (GaP). Certain colors are notoriously difficult to generate, due to material growth issues. However, when a semiconductor is made very small (~1 to 10 nm), something new happens—the frequency of emitted light changes with the size of the quantum dot!

In a bulk semiconductor, the frequency (color) of the emitted light is the determined by the energy of the band gap. The energy diagram to the right shows two energy bands separated by a gap in which no states exist. In a semiconductor, the lower energy valence band is nearly filled with electrons and the higher energy conduction band is nearly empty. When an electron in the conduction band transitions to the valence band, it emits a photon of light with energy approximately equal to the energy of the band gap, E_g .






As the dimensions of a semiconductor material are reduced to the nanoscale and begin to approach the wavelength of the conduction electrons, a phenomenon called “quantum confinement” occurs. Energy levels shift and the band gap becomes larger. Appendix M introduces the “particle-in-a-box” model, which can be used to describe the change in the energy diagram for quantum dots. The larger band gaps of the quantum dots result in the emission of higher energy or bluer photons.

To investigate the optical properties of quantum dots, you will use a spectrometer and various light sources to make emission and absorption measurements. An emission spectrum can be used to determine the energy of the band gap. It characterizes the intensity of light emitted by quantum dots as a function of wavelength when they are excited by an ultraviolet source. The ultraviolet light excites electrons from the valence band to empty states in the conduction band. An excited electron loses energy by first giving off heat to the lattice until it reaches the bottom of the conduction band; then the electron emits a photon to fall to the valence band. The wavelength of the emitted photon is measured by the spectrometer.

An absorption spectrum can be used to determine the density of empty states as a function of energy in the conduction band. First the spectrometer is used to collect a spectrum $I_0(\lambda)$ from a white light source that produces a broad range of wavelengths. Then a quantum dot sample is placed between the source and the spectrometer and another spectrum $I(\lambda)$ is collected. The absorbance $-\log(I(\lambda)/I_0(\lambda))$ is plotted as a function of wavelength. Peaks show energies at which photons are most strongly absorbed, indicating energies that contain a high density of unoccupied states.

II. Procedure

1. Observe the CdSe quantum dot samples with your unaided eye:
 - a. Observe the quantum dot samples in the room light.
 - b. Please note--do not stare directly at the UV source!
 - c. Turn on the UV source and illuminate the quantum dot samples. What differences do you notice compared to room light illumination?
2. Measure the spectrum of the UV source:
 - a. Click on the desktop icon *OOIBase32* to open the program.
 - b. Make sure *Correct for Elect. Dark* is selected. With a cap over the end of the fiber optic cable, the intensity should be 0 (within noise) at all wavelengths.
 - c. Turn on the UV source and orient the fiber so that it collects some UV light.
 - d. When you get a reasonably smooth spectrum, click on the *Save* icon to save it.
3. Measure the emission spectrum of each quantum dot sample:
 - a. Place a quantum dot sample under a UV light source. Orient the end of the fiber so that it collects light emitted by the quantum dot.
 - b. Adjust *Integ. time*, the acquisition time for a single spectrum, and *Average*, the number of spectra to average, to minimize noise in your spectrum.
 - c. When you see a well-defined peak, click on the *Save* icon.
 - d. Repeat steps e-g for the other quantum dot samples.
4. Display all five spectra on screen and print:
 - a. Open the UV spectrum by clicking on the *Open* icon.
 - b. In the *Overlay* menu, click on one of the --*Select to add overlay...* menu items and open one of the quantum dot spectra. Repeat for remaining saved spectra.
 - c. In the *View* menu select *Display Properties...* to adjust line color and other properties if needed.
 - d. Print one copy of the data for each person.
5. Measure the peak of each spectrum:
 - a. Point and click with the mouse on the maximum of the UV peak. The green vertical cursor should pass through the maximum.
 - b. In the legend at the top right corner, the three numbers following "Master" are wavelength, pixel number, and intensity for the "Master" (UV) spectrum at the location of the green cursor.
 - c. Record the wavelength and intensity at the UV peak. Label the UV peak on your hard copy with this information.
 - d. Also measure the wavelength and intensity at the emission peak of the four quantum dot samples and label on your hard copy. Note that in the legend, the two numbers following each overlay file are the pixel number and the intensity. The wavelength appears only after the "Master" label.
6. Measure the extent of each spectrum:
 - a. Divide the maximum intensity of each spectrum by two. Measure the wavelength on both sides of each peak at which the intensity equals half the maximum.
 - b. Record the wavelength at the left side and at the right side of each peak on your hard copy.

7. Acquire absorption spectra:
 - a. Place the cap over the spectrometer probe. Adjust the settings to minimize the noise of the dark spectrum. Then save the spectrum using *Store Dark* .
 - b. Orient the spectrometer probe so that it is detecting the spectrum of a broad band white light source. Do not move the probe or the light for the remainder of the measurement.
 - c. Adjust the settings to minimize the noise on the white light spectrum, then store it using *Store Reference* .
 - d. Click on the *Absorbance Mode* icon .
 - e. Place the sample with red quantum dots in front of the probe. Adjust the settings to minimize the noise, then save the spectrum.
 - f. Acquire an absorption spectrum from the orange quantum dot sample. You may need to adjust the position and orientation of the sample to get a good spectrum.
 - g. Overlay your absorption spectra in one window (see step 4) and print one copy for each person.
8. Measure the first absorption peak:
 - a. Point and click with the mouse on the maximum of the lowest energy absorption peak for each spectrum and determine the wavelength.
 - b. On your hard copy, label the wavelength of the lowest energy absorption peak for each spectrum.

III. Analysis

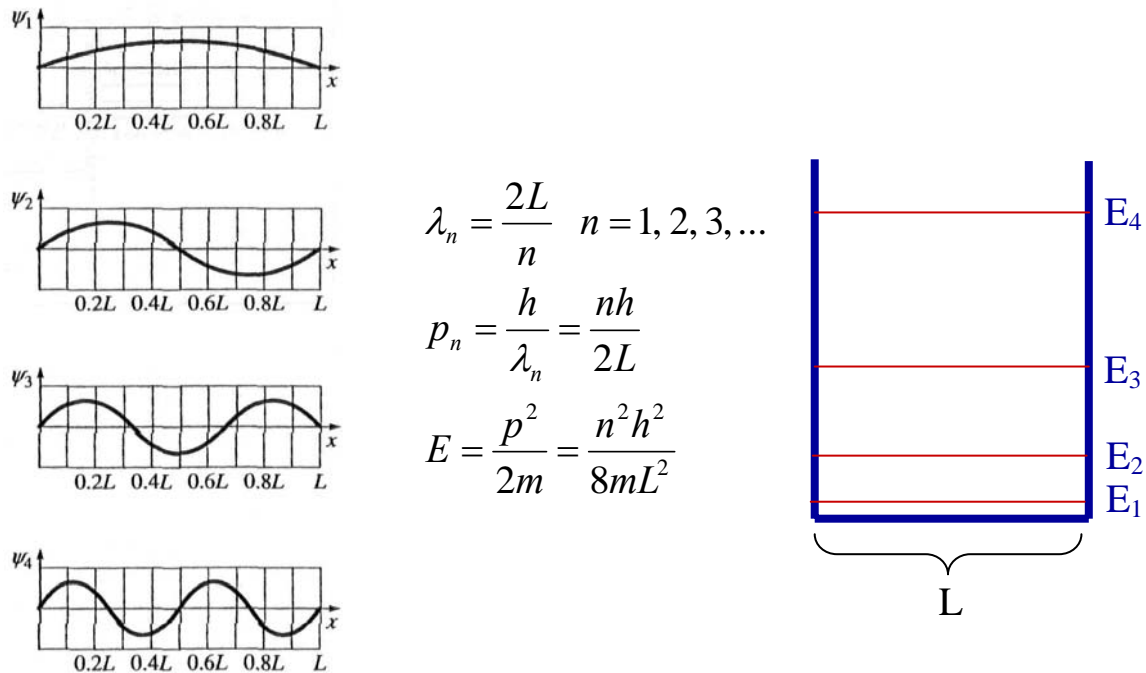
1. Why do the quantum dot samples look different when illuminated with ultraviolet light compared to the room lights?
2. Attach a plot of the emission spectra from the UV lamp and the quantum dot samples with peak wavelengths and left and right side wavelengths marked as described in the Procedure section. Organize your data for each spectrum in a chart with the following columns: peak emission wavelength (nm), peak emission energy (eV), left and right side emission wavelengths (nm), left and right side emission energies (eV).
3. A quantum dot absorbs a UV photon of higher energy and emits a visible photon of lower energy. Assuming energy is conserved, what happens to the “missing” energy?
4. Construct a quantitative energy level diagram showing the electronic transitions that occurred in your quantum dot samples when excited by UV light. Put energy on the vertical axis and label the QD samples on the horizontal axis. Assign the ground state an energy of 0 eV. Electron transitions involving photons should be represented with solid arrows from one energy level to the other. All absorption arrows should start at the ground state and all emission arrows should end there. Represent any unobserved transitions with dotted arrows.
5. Plot peak emission energy vs. radius for the four quantum dot samples and attach your plot. The average radius for each dot as measured using TEM is: (red) 3.44 nm, (orange) 3.18 nm, (yellow) 2.60 nm, (green) 2.15 nm. Does emission energy increase or decrease with dot radius? Explain the trend.
6. Subtract the band gap energy for bulk CdSe from the peak emission energy for each quantum dot sample; the result is the confinement energy. Plot confinement energy vs. radius, using the radius data given in question 6. Using a spreadsheet or graphing program, fit a power law of the form $y = Ax^n$ where A and n are constants determined by the fit. Attach the plot to your report and include the equation. Does the power law exhibit the size dependence predicted by the particle-in-a-box model?
7. The width of an emission spectrum is primarily determined by size variation of the individual quantum dots within a sample. Using your power law fit from question 6 and the left and right side emission energies determined in question 2, estimate the variation in radius for each quantum dot sample. Report your data both in nm and atomic layers noting that the average CdSe atomic layer thickness is 0.36 nm. How well controlled is the growth process?
8. Attach your plot of absorption spectra, labeled as described in the Procedure section. Why does an absorption spectrum have a different shape than an emission spectrum for a particular quantum dot sample? What information does an absorption spectrum provide that an emission spectrum does not?
9. Calculate the energy of the lowest peak of the absorption spectrum and compare it to the energy at the peak of the emission spectrum for each quantum dot sample. Do the absorption and emission spectra for the same sample peak at the same energy? Do you expect them to? Why or why not?

APPENDIX M

The Particle in a Box Model

Understanding the size-dependent frequency of light emission from quantum dots requires the wave description of matter, specifically, of the electrons inside the quantum dot. The one-dimensional “particle in a box” model is useful for gaining some insight. After this model is introduced, a discussion of how it applies to the quantum dot follows.

Picture a particle such as an electron bouncing around inside a one-dimensional box of length L . However, the “correct” picture in modern physics is that of an electron wave reflecting back and forth from the walls of the box. The wave is a probability wave, and the square of the amplitude at any location gives the probability of finding the electron there. The addition of reflected traveling waves sets up a standing wave. The waves must have a node at the edges of the box (since the electron cannot escape the box and its probability must go to zero at the edge), so only certain wavelengths fit inside. Analogous to a wave on a string that is clamped at both ends, the size of the dot determines the characteristic wavelengths of the electrons that can exist inside of it.



$$\lambda_n = \frac{2L}{n} \quad n = 1, 2, 3, \dots$$

$$p_n = \frac{h}{\lambda_n} = \frac{nh}{2L}$$

$$E = \frac{p^2}{2m} = \frac{n^2 h^2}{8mL^2}$$

The diagram above shows how the wavelength λ of the electron wavefunction depends on the size of a one-dimensional “box” of length L . The allowed wavefunctions have wavelengths that are half-integer multiples of L , and each allowed state can be labeled according to the number of half-wavelengths n that it contains. Using the De Broglie relationship, $p = h/\lambda$, the momentum p of the particle can be calculated from its wavelength. Finally, the kinetic energy $E = p^2/2m$ of each allowed state n for the electron can be computed. Notice that the energy of the electron states varies inversely as L^2 . Therefore, as the box gets smaller, the energy for each state increases.

The one-dimensional model of a particle in a box can easily be extended to a three-dimensional box, which is somewhat more relevant to describing the behavior of quantum dots. In three dimensions the energy of the particle (an electron) becomes

$$E = \frac{h^2}{8m} \left(\frac{n^2}{L_x^2} + \frac{m^2}{L_y^2} + \frac{l^2}{L_z^2} \right),$$

which is a sum of the individual energies along the three orthogonal directions. n , m , and l can all take on integer values greater than or equal to one, and L_x , L_y and L_z are the dimensions of the box in the x , y , and z directions. Notice that the energy of the particle still depends on the inverse square of the box's dimensions.

While the particle-in-a-box model cannot be perfectly applied to quantum dots, it is a good first approximation and can be used to gain some insight into their behavior. One important feature of the particle-in-a-box model is "confinement energy." Notice that the lowest possible energy for the particle is not zero; rather, it is $E_1 = h^2/8mL^2$, which increases with decreasing size. The confinement energy is observed in quantum dots through an increase in the energy of the band gap. The band gap for bulk CdSe at 300 K is $E_g = 1.74$ eV. As you will measure in the lab, the energy of the band gap is greater for CdSe quantum dots. The confinement energy for the quantum dot sample is equal to the band gap energy minus 1.74 eV.

A second important feature of the particle-in-a-box model is that the energy spectrum is discrete rather than continuous. Only certain energies are allowed for the particle. This also begins to happen in quantum dots; the density of states gets peaked at certain energies. This can be observed in the absorption spectrum.