Name:_____Date:_____Class:_____

Student Worksheet

Part 2: Characterizing CdSe Quantum Dots
(with Answers in Red)

Materials
- 9 in. Pasteur pipette
- previously synthesized QD of various sizes
- hexane or other solvent
- UV/VIS spectrophotometer (here we use a Ocean Optics Red Tide USB650 UV with a USB-ISS-UV/VIS)

Introduction

In this section, we are going to measure the absorbance of the samples using a UV/VIS spectrophotometer. This device measures how many photons of varying wavelength across the ultra violet and visible light spectrum are absorbed by the sample, and makes a graph of the absorbance of the light at each wavelength versus the wavelength in nanometers.

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 equation (1) below:

Figure 1: Red Tide USB650 optical bench attached to a USB-ISS-UV-VIS light source and cuvette holder from OceanOptics.

$$\Delta E_{fi} = E_{gap} + \frac{h^2}{8m_0R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon R} = h\upsilon \tag{1}$$

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) $\upsilon = c/\lambda$ (where c is the speed of light and λ the onset wavelength of the light) required to excite the QD is given by equation (2):

$$\upsilon = \frac{c}{\lambda} = \frac{E_{gap}}{h} + \frac{h}{8m_0R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon hR} \tag{2}$$

So if we measure either the onset wavelength or onset frequency of this light we can determine the dot's radius R.

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.

Before we can start recording the spectra, we first have to calibrate the spectrophotometer. To do this,

- first, fix the integration time—the time the spectrophotometer takes to record the spectrum so that the absorbance maximum scales nicely on the graph.
- second, record the spectrum of the sample holder with the solvent (the cuvette and the hexane). We do this so that we can subtract the absorption characteristics of the solvent and the holder from the overall spectrum to ensure that we are looking at the absorption characteristics of the QDs, not the glass of the cuvette or the hexane solvent.
- third, record a spectrum for no light entering the detector by placing a black rod, 1cm × 1 cm, in cross-section in the cuvette holder. This helps to set 0% transmission, again, to help scale our absorbance.

Instructions

- If the spectrometer is not already up and running, turn the computer off and make sure that the USB cable between the USB650 module and the computer is attached.
- Make sure that the power cable to the USB-ISS-UV/VIS module is plugged in.
- Turn on the computer and wait to make sure the USB650 module is recognized by XP. You should hear the fan in the USB-ISS-UV/VIS module fire up (it's noisy and the spectrophotometer will not work unless it is up and running).
- If it doesn't start up, check that it is plugged into the wall and the power cord is plugged in to the USB-ISS-UV/VIS module. It takes about 5 minutes on XP to get to this point!
- It may need to install the drivers! Let it. When it acknowledges it is there and knows what the device is, start the *SpectraSuite* application on the Desktop.

Setting Up For An Absorption Measurement:

- Place an empty cuvette in the cuvette holder for this experiment, I recommend using one of the small KIMAX test tubes.
- Take 2 ml of the translucent solution and put it in a labeled cuvette and stopper the cuvette. Take another cuvette and insert 2 ml of your solvent (should be hexane) for a reference and also label that cuvette.
- Go to the computer display and to the SpectraSuite window, go to File > New > Absorbance Measurement > New. This will take you to the Set Acquisition Parameters Wizard.

Set Acquisition Parameters Wizard:

In this wizard, we set the acquisition time for the spectrum (the time it takes to record the spectrum) so that our spectrum's absorbance scales appropriately for the graph.

Setting the Integration Time and Turning on the Lamp

- First insert, in the cuvette holder, a cuvette with 2 ml of one of your samples.

- Check the Strobe/Lamp Enable and the Set Automatically—this will choose an integration time that ensures that the absorbance value fits nicely on the scale of the graph. Wait; it will take time to do this. You will see a progress bar at the bottom right of the main graphing window that shows you the progress. Wait until it says that it has chosen the integration time. If it fails, either you have forgotten to turn on the lamp, or the sample has a lot of particles scattering light (this can be checked by removing your sample and looking to see if you can see all the way through it).
- Once it states that the "*Recommended integration time is acquired*," and before selecting Next, go to the smoothing window in the wizard and do the following:

Smoothing the Spectrum
- Change the Scan to Average to 10 to improve the signal-to-noise ratio.
- Choose a boxcar width of 10 to further smooth the spectrum.
- Now click Next > at the bottom of the window and this will take you to the Store Reference Spectrum Wizard.

Store Reference Spectrum Wizard:
Here we want to subtract any effects in the spectrum attributable to the cuvette glass and the solvent (decane or hexane). To do this,
- insert the cuvette containing the transparent solvent into the cuvette holder.
- click on the light bulb icon/button for it to record the spectrum of the empty cuvette and wait for the spectrum to change in the sample graph window (this may take some time).
- then click Next >. This will take you to the Store Dark Spectrum Wizard.

Store Dark Spectrum Wizard:
- Place the black sample into the cuvette holder.
- Hit the darkened light bulb button.
- Wait for the Dark Spectrum Preview window to show its spectrum and for it to say it has recorded the spectrum.
- Hit Finish > at the bottom of the wizard window. You have finished calibrating the machine for your absorbance measurement. Once you hit Finish, the wizard window disappears to reveal the Ocean Optics SpectraSuite Window.

Ocean Optics SpectraSuite Window
- First remove the black sample from the cuvette window and replace it with one of your cuvettes that contains a sample.
- On the left top panel is the *Data Sources*, which shows the USB650 or USB4000 spectrometer. On the left of the icon is a + sign; click it to reveal three additional selections; namely, acquisition, plug-ins, and properties.
- Click the + sign next to acquisition; this will list a series of spectra that are being displayed. Your latest is at the bottom of the list. Select it, and the grayed out buttons and icons in the header area of the window will become active. Make sure that the Strobe/Lamp is checked.
- If asked, choose the Target to either be in the Active Graph (default) or a New Graph, and hit accept.
- Give the spectrum time to converge to a smooth continuous spectrum that is consistent between averages.
- If no spectrum appears, either (a) the Strobe/Lamp is off, or (b) the Store Reference Spectrum contains your sample not the solvent. If so, right click the acquisition in the *Data*

Sources Window. Delete that entry by selecting Terminate Acquisition, and return to File > New > Absorbance Measurement > New.

- To stop the acquisition, click on the current acquisition in the *Data Sources* window and then you can select the pause || button in the header section above the graph window.
- If you right click the Acquisition in the Data Sources window (left side), you can choose to resume or terminate (delete) the acquisition.
- To add a second graph from a different sample, go to File > New > Absorption Measurement New and repeat the above steps. You should ideally end up with a graph not unlike the one below.
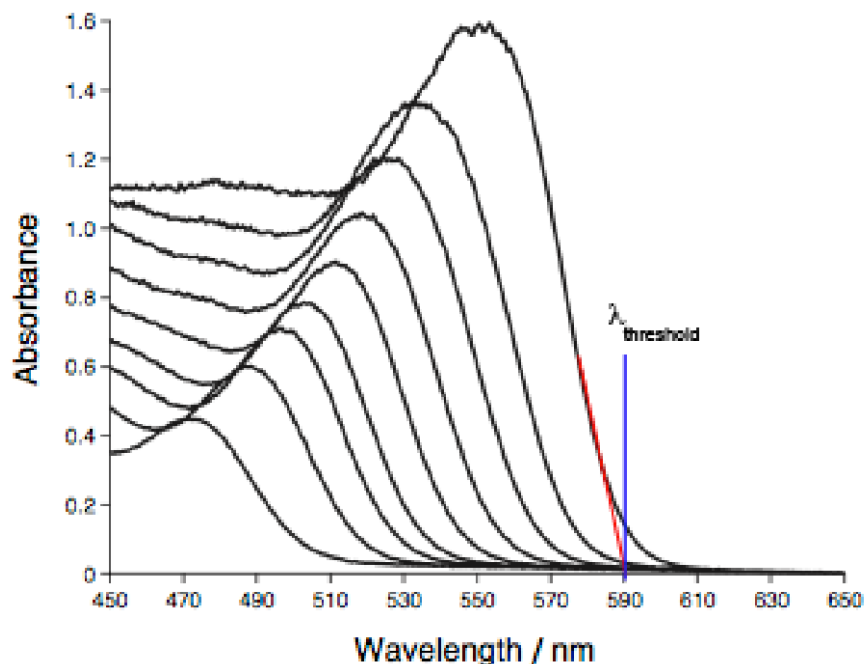

Figure 2: Visible absorption spectra of the CdSe samples. The samples were withdrawn from the reaction mixture in order from left to right. Longer wavelength smaller energy emission corresponds with larger particle sizes. The red and blue lines illustrate how to estimate the threshold wavelength2.

Data Analysis—The Determination of the Size of the QDs
Since the frequency or wavelength for the onset of absorption is dependent on the size of the QDs, we should be able to determine the size of the dots for each absorption spectrum recorded. In this section, we will be using existing data to come up with an equation that relates the size of the dot to the threshold wavelength or frequency of absorption.

- You will need to first extract an approximate threshold wavelength from the data. Do this in the manner that is demonstrated with the red and blue lines in Figure 2; namely, we extend a straight line tangential to the curve a third of the way down on the red frequency side of the absorption line. Extrapolate the tangent down to where it intercepts the wavelength axis. The point of intercept is $l_{threshold}$. Obtain a value for $l_{threshold}$ for each sample (there will be 10).

Sample number	$t_{reaction}$ (s)	$l_{threshold}$ (nm)	ΔE_{fi} (J)
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			

Assessing the accuracy of the Particle-in-a-Box Model and Creating a Calibration Curve

To ascertain the size of the quantum dots mono-dispersed in samples 1-10, it is necessary to be able to calculate the size of the QD that is needed for a given $l_{threshold}$. We are going to estimate the size of the QDs by two methods—one that constructs a calibration curve from previously measured size versus wavelength data[*], and one that uses Equation 1 with the parameters that are pertinent to CdSe (these are listed in Table 1 below).

Table 1: Useful physical constants for CdSe along with some useful unit conversions

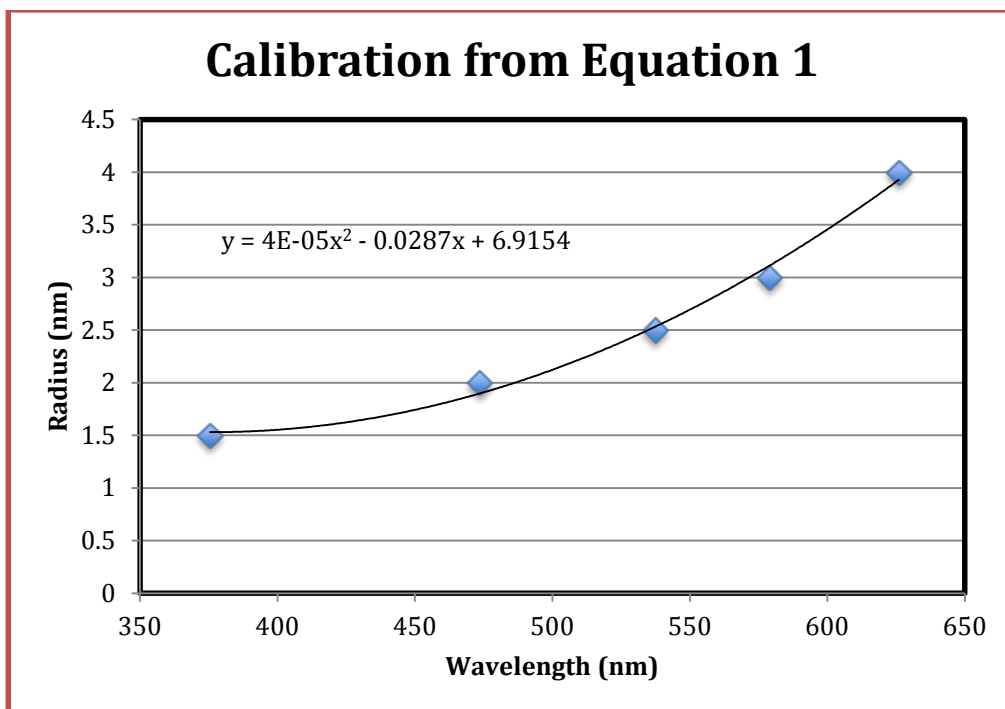| Constant	Value
m_0	9.11E-31kg
m_e	0.13
m_h	0.45
ε	10.72
ε_0	8.85E-12 C^2/Nm
e	1.601E-19 C
h	6.626E-34 Js
c	2.998E8 m/s
E_{gap}	1.8125eV
1 eV	1.601E-19 J

Complete Table 2 (paying special attention to units) and make a plot of ΔE_{fi} vs. $1/R^2$, that compares the experimental ΔE_{fi} to that calculated in equation (1).

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[*] Data for calculating ΔE_{fj} from equation (1) will need the data from Table 2.

Table 2: Experimental Data for the radius of mono-dispersed Quantum dots versus the threshold transition energy. (Data taken from "Measurement and assignment of the size-dependent optical spectrum in CdSe quantum dots" by D.J. Norris and M.G. Bawendi, Physical Review B 33 (24) 16338-16346 (1996))

R (m)	ΔE_{fi} (eV)	$1/R^2$ (m^{-2})	ΔE_{fi} (J)	ΔE_{fi} (J) From eqn (1)	l$_{fi}$ (nm) From eqn (1)
4E-9	1.91	6.25E16	3.06E-19	3.18E-19	626
3E-9	2.06	1.11E17	3.30E-19	3.44E-19	579
2.5E-9	2.15	1.60E17	3.44E-19	3.70E-19	537
2.0E-9	2.30	2.5E17	3.68E-19	4.20E-19	474
1.5E-9	2.50	4.44E17	4.00E-19	5.30E-19	5376

Use the ΔE_{fi} vs. $1/R^2$ plot as a calibration curve to ascertain the approximate size of the particles in samples 1-10, and complete the following table:

Calibration from Equation 1

$y = 4E\text{-}05x^2 - 0.0287x + 6.9154$

Sample number	$t_{reaction}$ (s)	$l_{threshold}$ (nm)	R (nm)
1			*Answers may vary*
2			
3			
4			
5			
6			
7			
8			
9			
10			

Draw Conclusions:

1. How large is a nanometer?

   1 x 10^{-9} m or 10Å (10 Angstroms)

2. Give the length of a C-C bond and the Bohr radius for H in nanometers.

   0.12 nm for a C-C bond and 0.05 nm for the Bohr radius

3. Define a semiconductor.

   A semiconductor is a solid whose valence bands do not overlap with the conduction bands, and the band gap lies in the range of 3 eV $> E_{gap} > 0.1$ eV.

4. What is a hole?

   A hole is a vacant position in a crystal left by the absence of an electron. A hole is created in the valence band when an electron is excited across the gap into the conduction band. 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.

5. What is an exciton?

   A mobile neutral entity in a crystalline solid created when an electron is excited from the valence to the conduction band. The exciton consists of the excited electron bound to the hole produced by its excitation.

6. What is the definition of the Bohr radius? And what is the Bohr radius for a 1S electron?

   It is the average distance of the electron from the nucleus for a given orbital. In the hydrogen atom, the 1S orbital has a Bohr radius of 0.529Å.

7. What makes the Bohr radius of an exciton in a semiconductor so much larger than the Bohr radius of an H atom?

   In a semiconductor, the presence of the electrons and nuclei readjust themselves in response to the creation of the exciton, with electrons moving toward the hole and away from the electron. This movement screens the size of the charge the hole sees when looking toward the electron, and simultaneously screens the size of the charge the electron sees when looking toward the hole. Instead the magnitude of the charge Q is reduced to Q/e where e(>1) is the dielectric constant of the semiconductor.

8. How large or small does a CdSe dot need to be to behave as a QD?

   In H, the Bohr radius is 0.529Å while the effective radius of the orbital is around 5Å (e=1) in CdSe the dielectric constant e=10. This increases the Bohr radius of the exciton to around 5Å, meaning that its effective radius must be of the order of 50Å. For the nanoparticle to behave as a QD, its size must be less than the size of the Bohr radius of the exciton in the bulk semiconductor, so the QD must be less than 50Å in radius.

9. Why do you think that the particle in a box approximation works at all for a quantum dot?

   Even in the bulk semiconductor, the exciton would be delocalized in the entire space of the dot. However, the electron is much more stable inside the dot than outside of it. Consequently, while the electron can freely move within the dot, it will not venture outside of the dot. This makes the situation similar to that encountered in the particle in a box model.

10. Define (a) the valence band, (b) the conduction band, (c) the band gap.

    *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 of energy that are called bands. The band created from the Highest Occupied Molecular Orbitals is called the **valence band**, and the band created from the Lowest Unoccupied Molecular Orbitals is called the **conduction band**. The **band gap** is the energy gap between the highest energy state in the valence band and the lowest energy state in the conduction band.*

11. Name three applications of Quantum Dots.

    Lasers, LEDs, medical imaging, transistors, solar cells

12. Name two other quantum dot compositions other than CdSe.

    ZnS, PbSe, InAs, GaAs, CdS, to name a few

13. In your calculation of the data for Table 2, which term is dominant—the confinement energy or the exciton energy? (Show calculations.)

    The confinement energy is 2–5 times the magnitude of the exciton energy.

14. If the spectrum blue shifts, does this mean the wavelength increases or decreases? Explain.

    The wavelength of blue light is around 400 nm and the wavelength of red light at the other end of the visible spectrum is around 700 nm. Red is the longest wavelength of visible light and blue light is the shortest wavelength of visible light. So a blue shift is a shift to smaller wavelength.