Preparation of CdS Nanoparticles by First-Year Undergraduates

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STUDENT LABORATORY HANDOUT

Preparation of Cadmium Sulfide Nanoparticles

Purpose

You will prepare bulk and nano-sized CdS particles, measure their absorbance spectrum, calculate the diameter of the nanoparticles and observe differences between nanoparticles and the analogous bulk material.

Introduction

Nanoparticles are clusters of atoms, ions or molecules with diameters less than 100 nm. The chemical and physical properties of nanometer-sized materials can differ from the bulk material. Background that describes these changes is given below and more information will be provided to you in class. Nanoparticles tend to combine to form larger, bulk particles, so special methods are used to limit their growth.

Review of Quantum Chemistry and MO Theory

Reacquaint yourself with the properties of light, atomic energy levels and molecular orbital theory that are described in your general chemistry textbook. Familiarity with this background information is crucial to understanding the differences between bulk and nanomaterials.

Formation of Bands

Atoms can acquire only specific amounts of energy, equal to the energy difference between two atomic orbitals. Larger collections of atoms or ions, such as a crystal of CdS, have analogous energy levels called "bands." Overlap of two atomic orbitals creates a bonding molecular orbital and antibonding molecular orbital. Remember that the bonding orbital is lower in energy and the antibonding orbital is higher in energy compared to the individual atomic orbitals. Inclusion of more atomic orbitals creates more bonding orbitals of lower energy and more higher-energy antibonding orbitals. As the number of bonding orbitals increases, the individual energy levels become a continuum of energy levels called a band. A band of antibonding orbitals also forms. This transition from atomic orbitals to bands is depicted in Figure 1. Notice that the collection of orbitals "spreads" as more atomic orbitals are added. When two bands spread, the energy difference between the bands decreases. Bands form for all atomic orbitals. Some bands are occupied with electrons, some bands are empty.

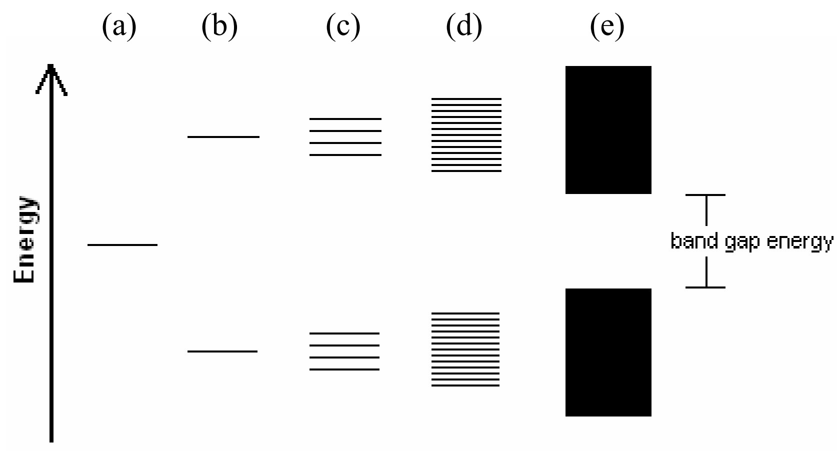


Figure 1. Diagram showing the changes in energy levels as the number of atoms (n) increases. (a) atomic orbital, n = 1; (b) molecular orbitals, n = 2; (c) molecular orbitals, n = 4; (d) molecular orbitals, n = 13; (e) bands, n ~ 6×10^{23}.

The highest energy band that contains electrons (equivalent to an atom's valence orbitals) is the valence band. The next highest band is the conduction band. The difference in energy between these two bands is the band gap (E_g). Band gaps are typically described using units of electron volts, or eV, where one eV is equal to 1.602×10^{-19} J. Energy differences between levels of an atom or molecule are usually greater than the differences between the bands of the analogous bulk solid. When individual formula units assemble together, the band gap of the material decreases until it reaches the band gap of the bulk material. Smaller clusters of formula units, with diameters typically below 100 nm, have band gaps larger than that of the bulk material.

Quantum Confinement

The energy of the nanoparticle's band gap can be calculated using the following equation:

$$E_g^{nano} \cong E_g^{bulk} + \frac{h^2}{8r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_o r}$$

with the following values for variables and physical constants:

E_g^{nano} = band gap energy of the nanoparticle as determined from the UV/visible absorbance spectrum, J (you will measure this at the end of the experiment)

E_g^{bulk} = band gap energy of bulk CdS at room temperature, 3.88×10^{-19} J

h = Planck's constant, 6.626×10^{-34} J s

r = particle radius, m

m_e^* = effective mass of conduction band electron in CdS, 1.73×10^{-31} kg

m_h^* = effective mass of valence band hole in CdS, 7.29×10^{-31} kg

e = elementary charge, 1.602×10^{-19} C

π = pi, 3.1416

ε = relative permittivity of CdS, 5.7

ε_o = permittivity of a vacuum, 8.854×10^{-12} C^2 (N m)$^{-1}$

You may recognize some of the variables, such as *h, e* and π and you will learn about others during this laboratory experiment. Notice the two masses in the equation. You are familiar with electrons but what is a hole? What is an effective mass? When a semiconductor absorbs enough light to excite an electron from its ground state, the electron is allowed to move somewhat freely through the crystal. However, as the electron moves from its parent CdS unit cell, a positive charge is left behind (just like ionization of an atom creates an electron and a positively charged ion). This positive charge is called a "hole" and can move throughout the CdS nanoparticle just like the electron can. To understand how a positive charge can move, consider what happens when an electron moves from a neighboring CdS unit (cell #2) to the CdS^+ unit that "lost" its electron (cell #1). Now cell #2 has a positive charge and cell #1 is neutral. The positive charge has just moved. Due their attraction with each other the cadmium and sulfide ions, the electrons and holes appear to move with an *effective* mass, not the true mass of an electron.

The equation above takes into account the wave nature of the electron. When the electron "wave" is confined within a spherical particle (as is the case for an electron in a CdS nanoparticle), the energy of the electron is quantized. The energy difference between the ground state (valence band) and the excited state (conduction band) varies depending on the size of the sphere. That is why the band gap energy depends on *r*, the particle radius. If the sphere is too small, the movements of the electron and hole are restricted and so they "feel confined," which raises the energy necessary to excite the electron into the conduction band.

Color Change

As a particle becomes smaller, the wavelength of absorbed light decreases and the band gap energy increases. This causes the color to "blue shift" or move towards the blue/purple end of the visible spectrum. For example, in this experiment you will prepare bulk cadmium sulfide crystals and 5 nm CdS particles. Bulk CdS has an orange color but CdS nanoparticles are yellow.

Controlling Particle Growth

Particles grow quickly because many small particles combine to form one larger particle. Nanometer-sized particles combine especially quickly because they are more reactive. It is generally true that chemical reactivity increases as the material changes from bulk to nanosized dimensions. This means that if we want to study nanoparticles, we need to control their growth and prevent them from forming bulk particles. How can this be done?

The answer is as close as the nearest sink. You use soap to remove grease from your hands – water by itself does not work. Oils contain molecules called hydrocarbons which consist of long chain of carbon atoms with hydrogen atoms attached. Hydrocarbons do not mix with water and are considered hydrophobic ("afraid" of water). Soap contains molecules, called surfactants, with a hydrophobic end and an ionic charged group at the other end. The ionic charge makes that portion of the molecule hydrophilic ("likes" water). Water dissolves hydrophilic compounds, so water will dissolve soap. Hydrophobic substances tend to mix well, so the hydrophobic ends of many soap molecules will form a shell around a few hydrocarbon molecules. These shells, called micelles, consist of 50 – 100 soap molecules. The hydrophilic end of the surfactant molecule is located on the outer surface of the micelle and continues to interact with water so that the micelle remains soluble. Soap molecules surround the hydrocarbon and all are carried away when you rinse the soap off your hands.

You will prepare solutions containing micelles that limit the growth of CdS particles. One key difference between the example of soap described above and this experiment is that the solvent you use will be hexane – an organic, hydrophobic liquid – and small amounts of aqueous solutions will be added. The charged end of the surfactant will be pointed towards the center of the micelle and the nonpolar portion of the molecule will be exposed to the nonpolar solvent. Such a structure is called a reverse micelle. Figure 2 illustrates the difference between micelles and reverse micelles.

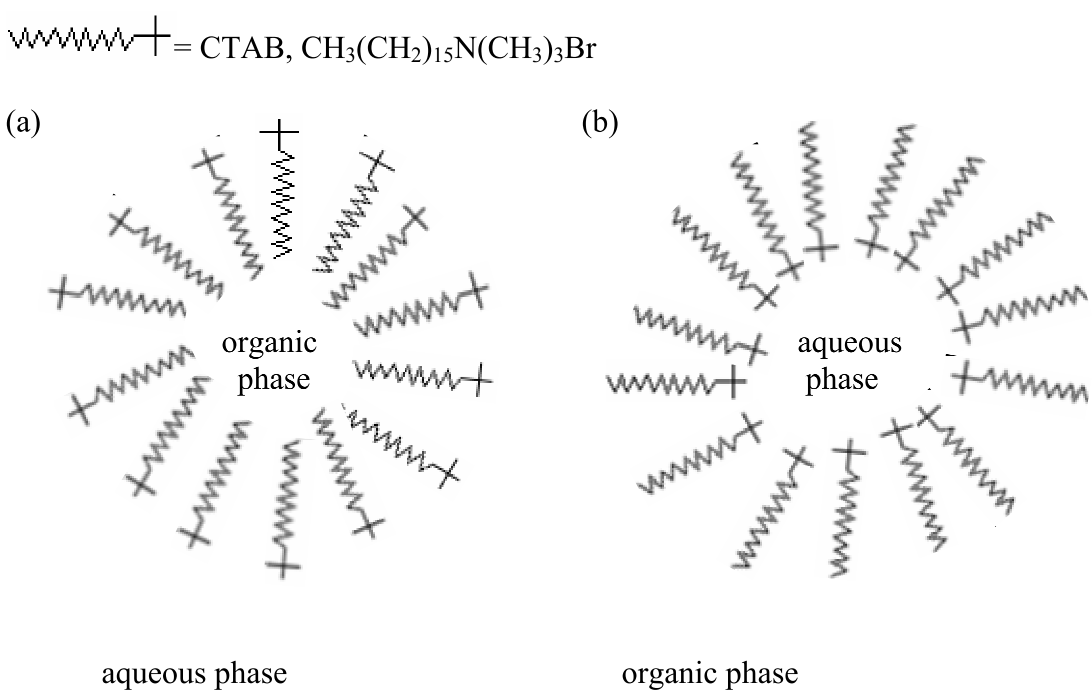


Figure 2. Diagram of (a) micelle with organic phase suspended in an aqueous solution and (b) reverse micelle with aqueous phase suspended within an organic solution.

Pre-lab Exercises

Be prepared to answer these problems before coming to lab. We will discuss the answers during the pre-lab briefing.

1. What is the relationship between wavelength and energy of light? Between frequency and energy?

2. If a substance absorbs light in the purple, blue and green sections of the visible spectrum, what color is the substance?

3. You will prepare nanometer-sized CdS particles that are yellow. If the particles were even smaller, what would be their color?

4. Rank the following in order of their expected reactivity per formula unit: a single formula unit of cadmium sulfide, one mole of CdS, a collection of 10,000 CdS formula units.

5. What are the ionic charges of cadmium and sulfide in CdS?

6. Explain the difference between micelles formed by soap in water and the CTAB micelles formed in this experiment.

7. Draw the Lewis structure of a CTAB molecule.

8. CTAB, the surfactant used in this experiment does not dissolve in hexane. Why not?

9. Would you expect the CTAB micelles to be rigid structures or flexible? Explain your reasoning.

10. Write the reaction that will occur to create CdS.

Safety

Wear your safety goggles, gloves and lab apron or lab coat. Alert the laboratory instructor if there are any spills or accidents in the lab. When you are finished, pour all chemical waste into the appropriate containers. DO NOT pour any solutions down the sink drain or throw any chemicals in the trash can.

This experiment will involve organic liquids and a sulfide solution which may have irritating odors. As you know, chemicals are most dangerous when they are not handled carefully. This is especially true of cadmium compounds which are toxic and carcinogenic. Use care when handling them. For these reasons, perform all reaction steps in the fume hood.

Procedure

The following materials will be used:

Reagent	Formula
sodium sulfide nonahydrate	$Na_2S \cdot 9\ H_2O$
cadmium chloride hemipentahydrate	$CdCl_2 \cdot {}^5/_2\ H_2O$
1-pentanol	$CH_3CH_2CH_2CH_2CH_2OH$
hexane	$CH_3(CH_2)_4CH_3$
hexadecyltrimethylammonium bromide (CTAB)	$CH_3(CH_2)_{15}N(CH_3)_3Br$

Aqueous stock solutions of $CdCl_2$ and Na_2S will be prepared for you.

Part I: Bulk CdS

1. Place 1 mL of the $CdCl_2$ solution in a test tube.
2. Add 1 mL of the Na_2S solution to the test tube.
3. Stir the mixture with a stir rod.
4. After noting the changes in the mixture, set test tube on test tube rack.

Part II: Nanoparticle CdS

Nanoparticles are formed by mixing a hexane solution containing $CdCl_{2\ (aq)}$ in micelles (solution A) with a similar solution containing $Na_2S_{\ (aq)}$ in micelles (solution B). Upon combining the solutions, the CdS precipitates within the micelles but does not agglomerate.

As you prepare each solution, continuous stir it using the stir plate and a magnetic stir bar. Your instructor will tell you the exact amounts of hexane, 1-pentanol, CTAB and aqueous solutions to add.

1. Obtain the desired volumes of hexane, 1-pentanol and aqueous salt solutions to prepare solutions A and B.
2. Add 1-pentanol to the hexane and stir.
3. Weigh CTAB to the nearest 0.01 g. Add the CTAB to the solution prepared in step 2 and stir. Not all the CTAB will dissolve.

4. Add the $CdCl_2$ solution to the mixture from step 3. The solution should become translucent. Set this solution aside and label it "solution A."

5. Perform steps 2 through 4 again but substitute the Na_2S solution for the $CdCl_2$ solution. Label it "solution B." Solution B might remain slightly cloudy even after the aqueous Na_2S solution is added. This will not affect your results.

6. Pour solutions A and B together. Continue stirring this solution for several minutes.

7. Measure the absorbance spectrum of your CdS nanoparticle solution.

8. Clean up your work area. Dispose of any CdS mixtures in the appropriate waste jar.

9. Perform the Post-Lab exercises and turn them with your lab report in at the beginning of the next laboratory session.

Post-Lab Exercises

Use your absorbance spectrum data and any necessary Excel spreadsheet templates to perform these exercises.

1. Plot your absorbance data as a function of wavelength between 380 – 530 nm.

2. Note the region in the spectrum where the absorbance changes linearly. Graph the linear data and obtain the equation of the line.

3. Calculate the x-intercept. This is the "cut-off" wavelength of the spectrum. Convert the cut-off wavelength into units of Joules.

4. Enter the energy value from Exercise 3 into the Excel template to calculate particle size. Record the size of the CdS particles.

5. Verify that the template calculated the size correctly. Rearrange the equation in the Introduction section to solve for the particle radius.

INSTRUCTOR NOTES

Answers to Pre-Lab Exercises

1. What is the relationship between wavelength and energy of light? Between frequency and energy?

Wavelength and energy are inversely proportional. Frequency and energy are directly proportional.

2. If a substance absorbs light in the purple, blue and green sections of the visible spectrum, what color is the substance?

Its color would be orange since the transmitted colors would be yellow, orange and red.

3. You will prepare nanometer-sized CdS particles that are yellow. If the particles were even smaller, what would be their color?

Since the absorbance would be even more blue shifted, the solution will have more of a green tint.

4. Rank the following in order of their expected reactivity per formula unit: a single formula unit of cadmium sulfide, one mole of CdS, a collection of 10,000 CdS formula units.

most reactive: single CdS unit > 10,000 CdS units > 1 mole CdS units

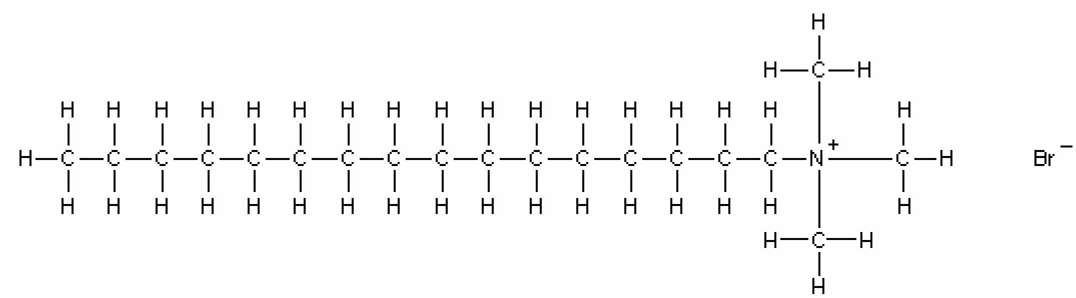
5. What are the ionic charges of cadmium and sulfide in CdS?

Cd^{2+} and S^{2-}

6. Explain the difference between micelles formed by soap in water and the CTAB micelles formed in this experiment.

Soap micelles have their hydrophilic ends pointed towards the solvent (water) while CTAB micelles have the hydrophilic ends pointed inwards towards the aqueous phase.

7. Draw the Lewis structure of a CTAB molecule.



8. CTAB, the surfactant used in this experiment does not dissolve in hexane. Why not?

The pentanol-hexane solution does not contain any sufficiently polar molecules, so there are no dipole-dipole intermolecular forces to interact with the hydrophilic portion of the CTAB molecule.

9. Would you expect the CTAB micelles to be rigid structures or flexible? Explain your reasoning.

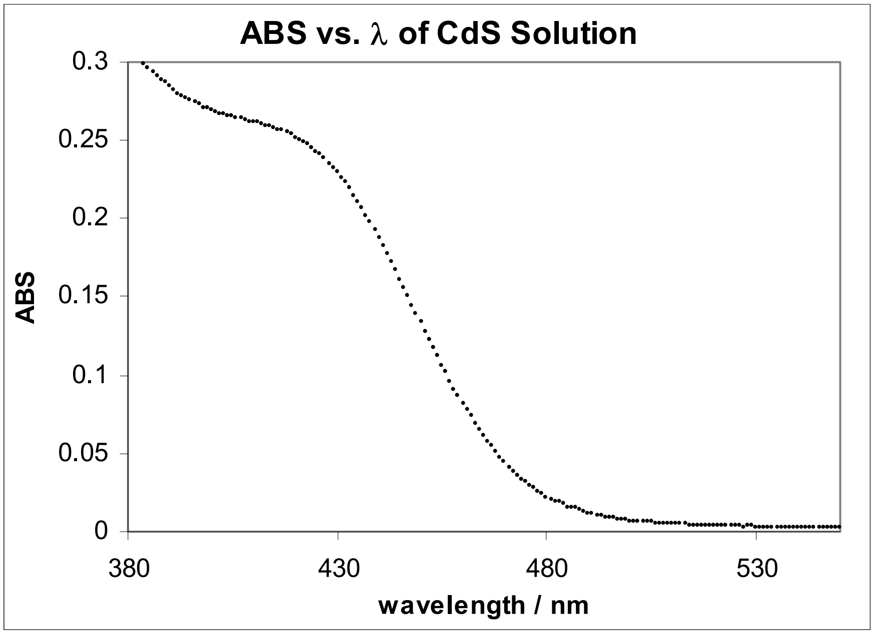
The micelles have to be flexible so that they can exchange Cd^{2+} and S^{2-} ions with each other.

10. Write the reaction that will occur to create CdS.

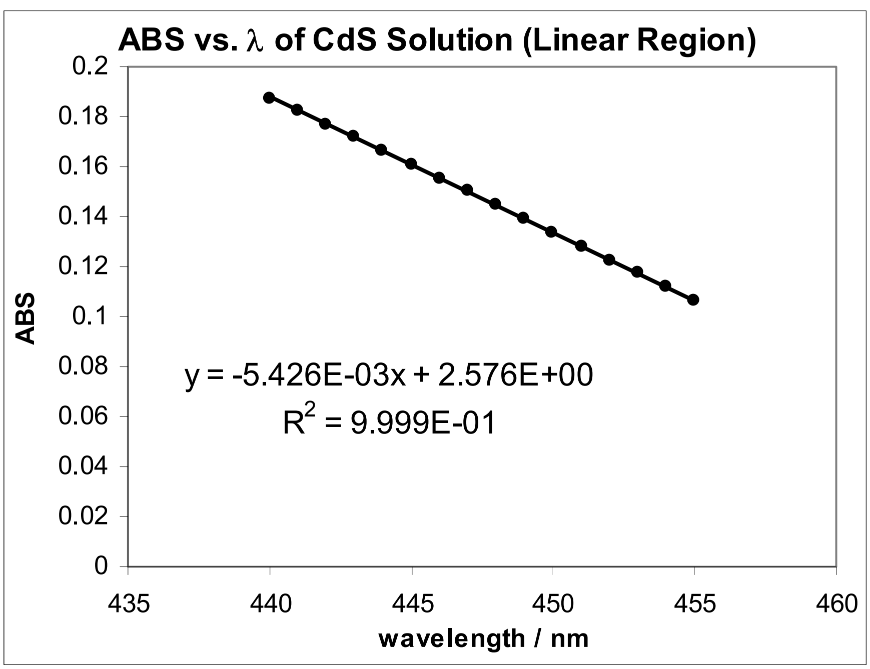
$CdCl_{2\,(aq)} + Na_2S_{(aq)} \rightarrow 2\ NaCl_{(aq)} + CdS_{(s)}$

Answers to Post-Lab Exercises

1. Plot your absorbance data as a function of wavelength between 380 – 530 nm.



2. Note the region in the spectrum where the absorbance changes linearly. Graph the linear data and obtain the equation of the line.



3. Calculate the x-intercept. This is the "cut-off" wavelength of the spectrum. Convert the cut-off wavelength into units of Joules.

x-intercept = - b / m = - 2.576 / (-0.005426 nm^{-1}) = 474.8 nm

$$\frac{1}{474.8 \times 10^{-9}\ \mathrm{m}} \times \frac{2.998 \times 10^{8}\ \mathrm{m}}{\mathrm{s}} \times 6.626 \times 10^{-34}\ \mathrm{J\ s} = 4.184 \times 10^{-19}\ \mathrm{J}$$

4. Enter the energy value from Exercise 3 into the Excel template to calculate particle size. Record the radius of the CdS particles.

r = 2.58 × 10^{-9} m

5. Verify that the template calculated the size correctly. Below is the equation for determining the band gap of the nanometer-sized CdS particle. Rearrange that equation to solve for the particle radius. Use the values of physical constants listed below to calculate the radius of your particles.

$$r^2(E_g^{nano} - E_g^{bulk}) + \frac{1.8e^2 r}{4\pi\varepsilon\varepsilon_o} - \frac{h^2}{8}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) = 0$$

$$r = \frac{-\dfrac{1.8e^2}{4\pi\varepsilon\varepsilon_o} + \left\{\left(\dfrac{1.8e^2}{4\pi\varepsilon\varepsilon_o}\right)^2 - 4(E_g^{nano} - E_g^{bulk})\left[-\dfrac{h^2}{8}\left(\dfrac{1}{m_e^*} + \dfrac{1}{m_h^*}\right)\right]\right\}^{1/2}}{2(E_g^{nano} - E_g^{bulk})}$$

$$r = 2.58 \times 10^{-9}\, m$$

Background and Experimental Notes

A presentation of quantum effects should begin with reminding students about the quantized energy levels in atoms. Overlap of two atomic orbitals creates a bonding orbital and antibonding orbital. Inclusion of more atomic orbitals creates more bonding orbitals of lower energy and more higher-energy antibonding orbitals. This causes the band width to "spread" and become a continuum of energy levels. When this happens to two separate bands, the energy difference between the bands decreases. For instructors who desire more details of this phenomenon, consult pages 502 - 505 in Peter Atkins' "Physical Chemistry", 5th edition published by W. H. Freeman and Company in New York.

Quantum confinement can be explained qualitatively in another way based on the particle in a box model. In this case, the particle (the electron) is confined within a sphere of radius r. As the dimensions of the box or sphere increase, the energy difference between adjacent levels decreases until the band gap energy of the nanoparticle approaches that of the bulk material. In effect, the electron is confined to a small volume that causes a greater difference in its quantized energy levels. More advanced nanoscience texts provide a thorough explanation of this topic. References for the full derivation of the Brus equation (Equation 1) are given in the Lab Summary *(7, 8)*.

A surfactant is a molecule with a long, nonpolar, hydrocarbon "tail" and a polar or ionicly charged "head" group. Hexadecyltrimethylammonium bromide (CTAB) is the surfactant used in this experiment. Above a certain concentration (the critical micelle concentration), these molecules organize themselves into nanometer-sized spheres to maximize intermolecular attractions with the solvent. The concentration of CTAB in this experiment is several orders of magnitude larger than its critical micelle concentration. If the micelles form within a polar solvent, such as water, the charged/polar head groups form the surface of the micelle and the nonpolar tails point towards the center of the sphere. Other nonpolar molecules can be contained within the micelle, thereby reducing the thermodynamically unfavorable interactions between the polar solvent and the nonpolar solute. Soap contains salts of long-chain fatty acids that clean by forming micelles that surround the small amounts of oil and grease. The micelles are then rinsed away, removing the undesired materials. Reverse micelles form when the solvent is a nonpolar liquid. In this environment, the surfactant's nonpolar tail extends out into the solvent while the polar/charged head groups are located in the middle of the micelle.

The concentration of CTAB, the molar ratio of 1-pentanol : CTAB (P_o) and the molar ratio of water : CTAB (W_o) determine the stability of the surfactant mixture. Values of P_o between 9 and 18, values of W_o between 5 and 60 and [CTAB] $\approx$ 0.1 M were found to consistently yield kinetically stable and translucent solutions. The amounts listed in the Lab Summary fall within these ranges. The instructor will find the Excel spreadsheet included in the Supplemental Materials useful for determining the amount of each solution component needed for given values of P_o, W_o, [CTAB] and [CdS]. It may be instructive for students to calculate these values themselves, perhaps as a pre-laboratory exercise. Cadmium sulfide surfactant solutions are stable for at least one day but the water and organic phases will begin to separate with the CdS suspended between the two layers. Solutions that do not contain any CdS in the aqueous phase, which are used as references for UV/vis analysis, are stable for at least several weeks.

In this experiment, 1-pentanol acts as a co-surfactant that stabilizes the CTAB reverse micelle in two ways. Despite the fact that the nonpolar end of the surfactant is directed towards the hexane phase, CTAB does not form micelles (or even completely dissolve) in hexane alone. An alcohol, such as 1-pentanol, helps to stabilize the packing of the surfactant molecules and allows them to arrange into micelles. Stable micelles have a larger radius of curvature so a larger micelle sphere can form. In addition to stabilizing the micelle, 1-pentanol prevents the surfactant molecules from packing closely together, which would form a rigid micelle structure. A surfactant solution containing CTAB, 1-pentanol and hexane contains micelles with a more dynamic composition – surfactant molecules can move somewhat freely between the micelle and solvent. When two micelles come into contact with each other, there is some mixing of the aqueous phases. This can result in CdS particle formation if the aqueous phases contain Cd^{2+} and S^{2-} ions. Although the micelle walls are somewhat flexible, they do prevent the nanoparticles from immediately agglomerating into bulk crystals.

Both the size of the micelles (the microstructural effect) and their lack of rigidity (the dynamic effect) increase with the P_o value and result in the formation of larger CdS particles *(5)*. However, the CdS clusters prepared using this procedure were larger and their size showed less dependence on P_o compared to the results of Agostiano *et al. (5)*. In this procedure, increasing the value of P_o showed a slight but statistically insignificant increase in particle size based on a confidence interval > 95%. For example, solutions with $P_o = 9$ and 16 yielded nanoparticles with radii of 2.4 ± 0.1 nm and 2.7 ± 0.2 nm, respectively. The most likely reason for differences between this procedure and that of Agostiano is that those experiments employed a lower concentration of $CdCl_2$ and Na_2S that produced less intensely colored solutions. A vivid color change was considered important for this experiment, so the concentrations were increased from 1×10^{-4} M to

2.5×10^{-4} M. However, the effect of ion concentrations is just a hypothesis that we did not test. Varying the W_o value had no effect on the CdS particle size.

Formation of CdS occurred during mixing so slight variations in the speed that students combined and stirred their solutions led to slightly different results. Particle diameters varied by 5-10% even when identical solutions were used in repeated trials performed by the same student. Stirring solution C with a glass stir rod instead of a magnetic stirrer did not produce consistent results and should be avoided. A slightly different procedure was used when students originally performed this experiment in class. In that instance, small amounts of aqueous Na_2S and $CdCl_2$ solutions were added dropwise to a hexane-pentanol-CTAB mixture. This method yielded 5 - 6 nm diameter particles but the results were less reproducible. The procedure presented in this laboratory was not tested by a class of students but instead by two undergraduate research students (Noviello and Brooks) working independently.

Hazards

Cadmium compounds, sodium sulfide, pentanol and hexane are toxic and should be handled with extreme care. Cadmium sulfide and cadmium chloride are carcinogens. Hexane and pentanol are flammable liquids. Due to the presence of organic vapors and the odor of the Na_2S solution, students should perform this experiment in a fume hood. Students should wear gloves, goggles and lab aprons or lab coats. All solutions and precipitates should be disposed of properly.

Excel Spreadsheets

The amounts of reagents listed in the Lab Summary can be used to prepare CdS nanoparticles (P_o = 17, W_o = 20). A "Microemulsion Parameters Template" Excel file allows the instructor to change the amount of aqueous solution, CTAB, 1-pentanol and hexane if desired. To do so, answer the questions in the yellow colored cells of the Excel file. Results are calculated at the bottom of the worksheet. Analysis of the CdS microemulsion absorbance data can be performed by students using the Data Analysis Template. Within that template, the Experimental Data worksheet acts as an "electronic lab book" where students can record their observations and calculate experimental values of [$CdCl_2$], [CTAB], etc. The Spectra Data worksheet provides space to cut and paste the wavelength vs. ABS data. An absorbance vs. wavelength graph will automatically appear in the graph to the right of the data. The second graph plots the linear portion of the absorbance data. Since data sets will be slightly different, students will need to modify the selection of data points to be plotted. Below the graphs is a table of physical constants that are used to calculate the size of the CdS nanoparticles. If these spreadsheets are made available to students, it is recommended that cells containing mathematical formulas and physical constants be "locked" so that students do not accidentally erase or modify the contents.

CAS REGISTRY NUMBERS

Chemical Name	Chemical Formula	CAS Registry Number
1-hexane	C_6H_{14}	110-54-3
1-pentanol	$C_5H_{12}O$	71-41-0
water	H_2O	7732-18-5
cadmium chloride hemipentahydrate	$CdCl_2 \cdot {}^5/_2H_2O$	7790-78-5
sodium sulfide nonahydrate	$Na_2S \cdot 9H_2O$	1318-84-4
cadmium sulfide	CdS	1306-23-6
hexadecyltrimethylammonium bromide	$C_{19}H_{42}BrN$	57-09-0