

# *Quantum Dots*

## *and Modern Electronics*

*Background:* Band structure in solid state electronics, electronegativity, size. Bohr model of atomic structure.

*Other Concepts:* Solubility and miscibility.

For the past three decades, transistors used in the integrated circuit industry have been getting smaller and smaller. One result is that computers have become smaller, faster, and more reliable. Sizes have shrunk so that we are now entering the age of nano devices: devices where the dimensions are in the nanometer ( $10^{-9}$  meter, abbreviated as nm) range. To put this dimension in context, remember that atoms range in size from  $0.5\text{\AA}$  for hydrogen to  $3.3\text{\AA}$  for the largest atom, cesium. An angstrom is  $10^{-10}$  meter, so nanoparticles are on the order of ten times the size of an atom.<sup>1</sup> At this size, classical descriptions of solid state properties, e.g. conduction in terms of electron drift, breakdown and we must begin to think about electron motion in terms reminiscent of the Bohr model in atomic structure theory.

Nano structured matter is condensed matter of a size scale larger than atoms, but smaller than bulk solids. It is too big to behave like atoms or molecules but too small to act like the bulk solid. One unique property of nanoscale materials is that a large percentage of the atoms are located on the surface or at the interface. For example, a 4-nm diameter CdS particle has about 1500

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atoms. Of this number, approximately one-third are on the surface and interact with adsorbed species or gas-phase molecules. This large surface to volume ratio imparts novel properties to nano particles compared with bulk solids, while the mere existence of surface vs. bulk atoms give properties distinct from atoms or molecules.

Among small scale structures, multilayer structures have the longest history, growing out of the thin-film industry. Recently reported ultra-hard surface films created from CN and TiN is an example of a sandwiched thin film that imparts uniquely important properties to materials.

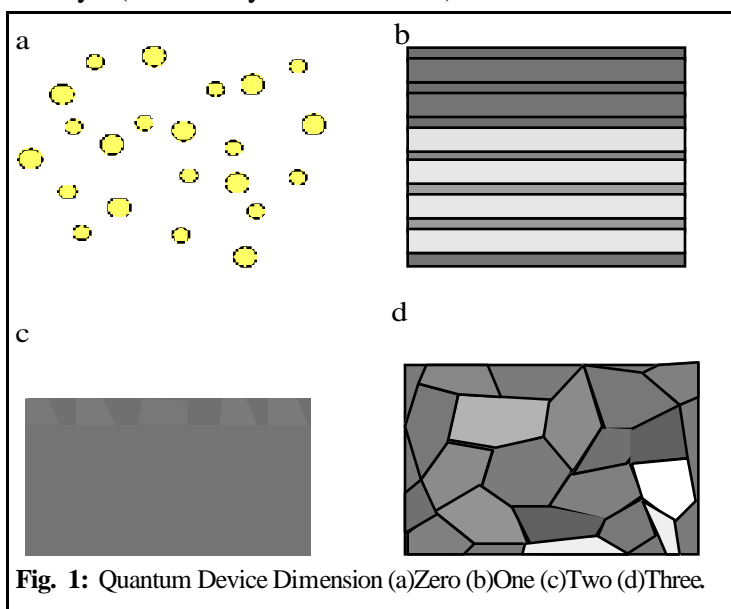
It is the technological potential of these new materials, particularly in the burgeoning electronics and computer industry that has helped fuel their advancement. The low dimensional quantum sizes in these materials makes it possible to engineer electronic and photonic properties that make devices such as high speed transistors and fast, efficient optical storage devices. Quantum-size materials are classified according to their dimension as shown in **Fig. 1**.

Quantum size effects appear when particle size becomes comparable to or smaller than the characteristic length scale responsible for that property. For example:

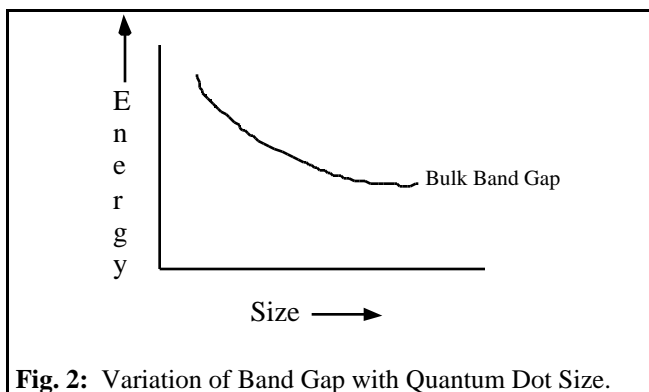
- *Light Absorption:* Due to spatial restriction of electron and hole motion, optical absorption in semiconducting clusters shifts to higher energy, i.e. the band gap increases as particle size decreases. This is

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known as quantum confinement. Optical properties of these clusters are exciting both from a fundamental scientific and a technological point of view. From a fundamental science point of view, nano particles represent a bridge between atomic and solid state theories. They can be modeled using an extension of the Bohr model used to understand atomic properties or a modification of band theory. (See Theory section below.)



**Fig. 1:** Quantum Device Dimension (a)Zero (b)One (c)Two (d)Three.



**Fig. 2:** Variation of Band Gap with Quantum Dot Size.

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- *Mechanical Properties: Metals* Materials that are normally soft, strengthen when the grain size falls below about 50 nm. At this size, sources of dislocations become difficult to activate with conventional forces. For example, bulk Cu is fairly soft and bendable due to the large number of easily moved defects and the large number of close packed planes in copper's face centered cubic structure. One method for strengthening copper is to limit mobility of defects by terminating them on other defects as in work hardening it. Another method is to assemble "bulk" Cu from nanoparticles of 5-7 nm size range. Solid copper made in this way has a hardness and yield strength up to 500% greater than conventionally produced Cu.<sup>2</sup>
- *Mechanical Properties: Insulators* Ceramics, are normally quite brittle due to directed, localized bonding. Fractures, once started, tend to grow catastrophically due to the thermodynamic energy released as the bonds break. Plastic deformation of ceramics is extremely limited due to repulsion of like charged ions forced into close proximity. However, ceramics become ductile when assembled from clusters of size below about 15 nm.<sup>3</sup>
- *Electrical Resistance:* Layered structures of materials with different magnetic properties can be used to create a material with a dramatically lowered electrical resistance. Application of a magnetic field to layered materials causes a cooperative-ordering, regularity to the material. Since regularity is greatly

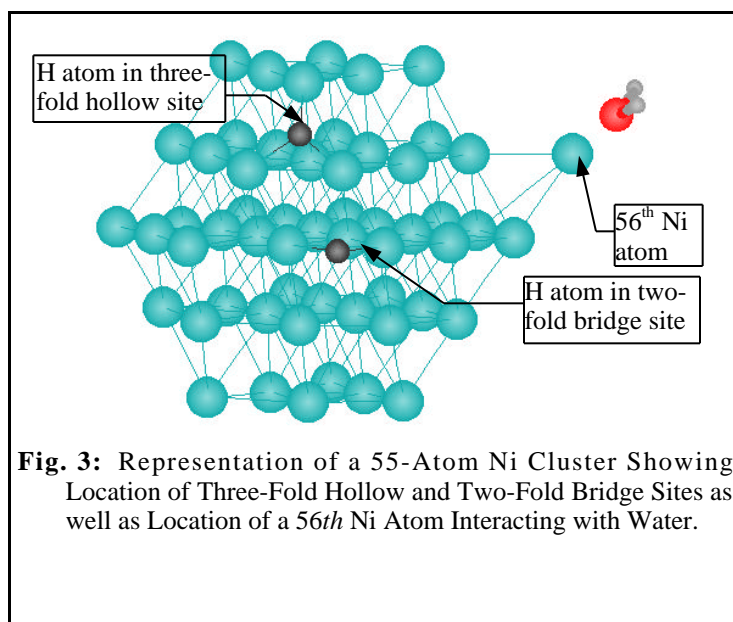
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increased, scattering of electrons, which is the basis of resistance, is greatly decreased. This magnetoresistance is the basis for development of low noise, high signal read heads in the recording industry. The issues remaining include maintenance of the magnetoresistance effect to room temperature and “turning” on the low resistance with lower magnetic fields.

It is very early in the development of applications and creation of these new materials. Although understanding of the optical properties appears to be well on the road, control of the mechanical properties including the optimal elements to be incorporated in the cluster is still very much in its infancy.

**Cluster Characterization:**

It is instructive to ask, how the atomic level structure of these clusters have been characterized. After all cluster optical properties vary with cluster size and shape, so until the connection between size and shape and optical absorption was established, optical methods could not be used. Conventional solid state techniques also could not be used because, by definition, quantum size particles are too small to show regularity of atomic arrangement on a long-range scale. An elegant solution to this problem is to use chemical activity. As atoms are added to the surface of a small cluster, the ability of the cluster to interact with surrounding molecules changes depending on the atomic structure of the surface.



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For example, the structure of 55 Ni or Co atoms is that of an icosahedral sphere. This structure can bind 44 hydrogen atoms in triangular-hole and two-atom-bridge sites. Addition of a 56th Ni or Co atom, puts this atom outside of the sphere, sticking out. This 56<sup>th</sup> atom shows a high affinity for binding of water or ammonia in a coordinate covalent bond.<sup>4</sup>

Comparison of clusters formed with similar elements is also instructive. For example, Co and Ni clusters of the same size form similar cluster structures, but with important differences. The cluster structure changes as the size changes with some size ranges forming the more closely packed face centered cubic (Ni) or hexagonal close packed (Co) structure of the bulk solid. However, the propensity for forming the icosahedral structure is greater for Ni. This is consistent with the decrease in *d*-electron bonding in Ni relative to Co.

Recall that the extent of *d* orbital bonding in the solid affects the density in all three transition series. In the first transition series, up to Mn, the number of *d* orbital electrons involved in bonding is roughly equal to the number of *d* orbitals. Past Mn, this number decreases through Zn. After Zn the *d* orbital electrons are essentially not involved in bonding.

### ***Goal of the Experiment:***

This exercise represents an excursion into cutting-edge technology. Both the theory and experimental construction methodology will undoubtedly change as the field develops. The purpose of this exercise is to demonstrate how fundamental principles of solubility and band-gap energy are involved in these very exciting

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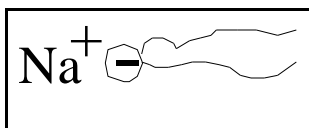
materials. In the process you will gain experience with excluding oxygen from a synthetic system as well as careful execution of experimental procedure. As you perform this experiment, be particularly attentive to water. Keep this in mind as you read how to create nano particle size materials.

This could be an open ended experiment that you can follow through for a “problem of the semester” exercise. Suggestions for further development will be given at the end of the exercise.

#### ***The Confinement System:***

One of the technological challenges of dealing with quantum-size materials, both in synthesis and application, is to limit the size of growing clusters and to prevent them from interacting with each other. If clusters do interact, they condense and collapse into the bulk solid. This interaction must be prevented for the clusters to exhibit quantum confinement properties. In this exercise, you will limit cluster size by two methods; growing them in ultra-small vessels called inverse micelles, and in the small, included volume in a coiled polymer, polyvinyl alcohol. Once formed, cluster must be prevented from interacting when assembled into a liquid or solid media for application. That is, they must be stabilized without destroying quantum confinement properties. In this exercise, we shall not stabilize the clusters. However, as a follow up problem of the semester, you might experiment with systems for stabilizing the micelles or capping the clusters.

**Micelles:**



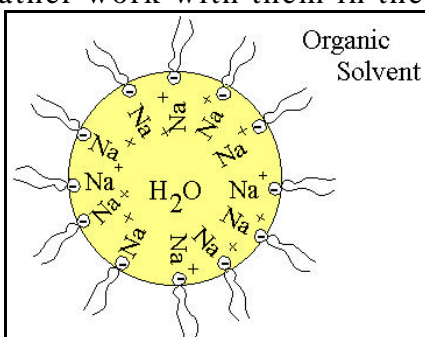
**Fig. 4:** A Surfactant Molecule Showing the Polar Head and Long Chain Groups.

To understand the formation of micelles, it is necessary to understand the structure of surfactants. Surfactants are also known as soap. Although soaps differ in their detailed structure, all

consist of a long chain organic portion attached to an ionic group known as the head group. In water, collections of these molecules conglomerate with polar head-groups pointing toward the water and the long chain organic portion imbedded in any organic based grease or dirt. This unit consisting of a cluster of surfactant molecules with ionic head groups pointed toward bulk water is known as a micelle.

In the present case, we also want small drops in a solution. However, we do not want an organic drop in an aqueous solution, but rather an aqueous drop containing the material of interest in an organic solution. Hence, the units that we will create are referred to as *inverse* micelles. We shall not cap the micelles to stabilize them, but rather work with them in the synthetic solution.

The surfactant used is referred to as AOT and is dioctyl sulfosuccinate, sodium salt. It is called AOT in reference to the



**Fig. 5:** Schematic of an Inverse Micelle.



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solution or the PbS in the surfactant solution. Comment on your results if you choose to do this.

### *The Cluster Material:*

You will work with both CdS and PbS. Both of these materials are semiconductors in the bulk. The band gap of bulk CdS is 2.6 eV. The band edge for bulk CdS is therefore 476 nm, absorption occurs in the violet and the bulk solid appears the complementary color, or yellow-orange. In keeping with quantum confinement, as the size of these particles decrease, the band gap increases. Since the CdS band gap is nearly out of the visible to begin with, the color change is not dramatic. How will you be able to detect formation of quantum dots rather than bulk solid? Answer: using light scattering. Since quantum particles are smaller than the wavelength of light in the visible region of the spectrum, they do not scatter light as the bulk solid, which has much larger dimensions, does. Thus, a solution containing the bulk solid appears turbid due to scattering of light. In contrast, a solution of the quantum size particles is clear. If your solution is turbid, think about how the confinement system is created and recheck your technique.

In agreement with the general principal that band gap decreases as size of atoms in a semiconductor increases, the band gap in PbS is 0.41 eV. This is on the opposite end of the visible spectrum compared with CdS, in the infrared. As a result PbS absorbs throughout the visible and appears black to dark brown. A solution of quantum dot PbS is clear and reddish-brown due to

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transmission of the red end of the spectrum as the band gap moves into the visible.

### ***Pre Lab Questions:***

1. PbS and CdS are referred to as II-VI semiconductors. Suggest a reason for this terminology.
2. Based on reactivity and stability, suggest a reason for the exclusion of O<sub>2</sub> from the synthesis apparatus.
3. Look up or predict the band gap in CdSe and CdTe. (Predict the size of the gap relative to CdS and PbS.)
4. Could CdSe or CdTe be used to form quantum-size, semiconductor particles? Why or why not?
5. Could PbSe or PbTe be used? Why or why not?
6. Could the well known semiconductors Ge and Si be used to form quantum size semiconductors? Would the synthetic procedure differ substantially from that used in this exercise? Why or why not?
7. Think about the role of surfactant, water, and heptane in this exercise. Which concentrations are critically important and why?

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***Procedure:***

1. Obtain the following from the store.  
Glassware: two 125-mL round bottom flasks  
two 125-mL Erlenmeyer flasks  
four 250  $\mu$ L syringes  
two 150-mL beaker  
two transfer pipettes  
one 100-mL graduated cylinder  
Chemicals: 50-mL heptane/surfactant solution  
10-mL 4% polyvinyl alcohol solution  
Other: one two-hole stopper and two solid stoppers

***Surfactant Method, CdS:***

2. The apparatus is shown in **Fig. 7**. Add 50 mL surfactant/heptane solution to a scrupulously clean and dry round-bottom flask. Insert the pipette attached to a N<sub>2</sub> purge, purge and stir vigorously for 10 minutes.
3. Add 250  $\mu$ L H<sub>2</sub>O. Again, stir vigorously and purge for at least 10 minutes or until clear.
4. Add 25  $\mu$ L of Cd(NO<sub>3</sub>)<sub>2</sub> to the solution while continuing to stir for another 5 minutes
5. *Slowly* add 25  $\mu$ L Na<sub>2</sub>S to the solution while stirring. Continue to stir for another 5 min.
6. Stop stirring. Remove the purge tube and stopper tightly. Wait 15 minutes.

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7. Remove an aliquot of the solution and put into a cuvette for the HP diode array spectrometer and record the spectrum.
8. Repeat steps 2-6 using 50  $\mu$ L of  $\text{Cd}(\text{NO}_3)_2$  and 50  $\mu$ L  $\text{Na}_2\text{S}$  in steps 4 and 5. Compare your solutions.

### ***Polymer Method, PbS:***

9. Combine 10 mL polyvinyl alcohol solution and 88 mL water in scrupulously clean and dry round-bottom flask. Insert the pipette attached to a  $\text{N}_2$  purge, purge and stir vigorously for 10 minutes.
10. Add 25  $\mu$ L of  $\text{Pb}(\text{NO}_3)_2$  to the solution while continuing to stir vigorously. Stir for another 5 minutes.
11. *Slowly* add 25  $\mu$ L  $\text{Na}_2\text{S}$  to the solution while stirring. Continue to stir for another 5 min.
12. Stop stirring. Remove the purge tube and stopper tightly. Wait 15 minutes.
13. Remove an aliquot of the solution and put into a cuvette for the HP diode array spectrometer and record the spectrum.

### ***Bulk Solutions:***

14. To compare quantum dots to a bulk solid, add 50 mL of water, 25  $\mu$ L  $\text{Cd}(\text{NO}_3)_2$  and 25  $\mu$ L  $\text{Na}_2\text{S}$  and swirl. Record your observation and compare it with your quantum dots.

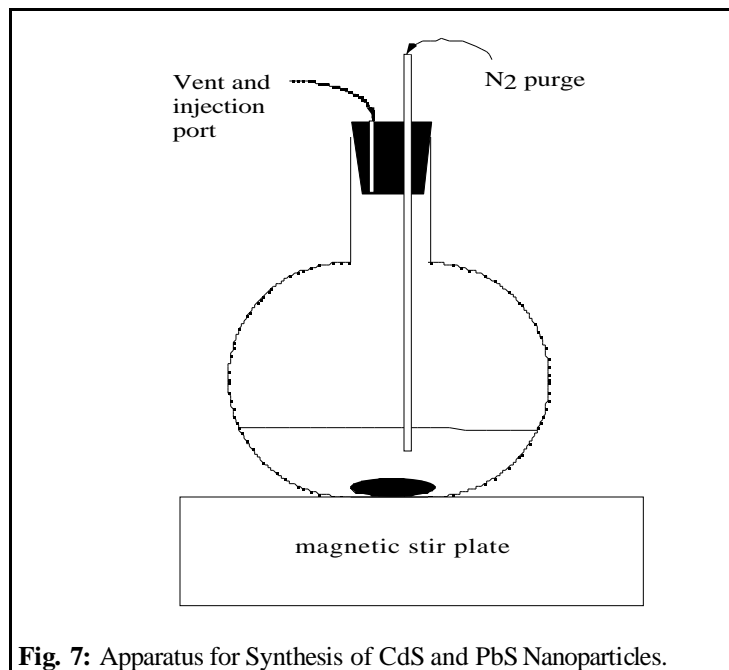
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15. Repeat 14 with  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Na}_2\text{S}$ .

*Hints for Success:*

- Keep stirring as vigorously as possible without the stir bar going crazy.
- Make sure all glassware is very clean and *dry*.
- Measure all quantities very precisely. This experiment deals with relatively small quantities and is sensitive to even minor changes.
- If a precipitate is found on the bottom of the flask then it is possible no quantum dots formed since this is the bulk product. (What might have gone wrong? Review your technique and ask your instructor for assistance!)

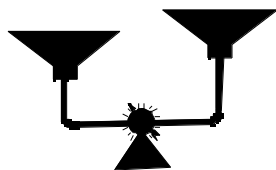
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***Post Lab Report:***

1. Report any observations that you made while performing the synthesis. Include your spectra. Compare your spectra with your colleagues in lab. Are there any differences? Discuss the effect of water on quantum dots.
2. Could you make quantum particles with any of the following:  $K_2S$ ,  $CaS$ ,  $CoS$ ,  $SnS$ . Why or why not? Note: If you have not yet discussed solubility in class, then ask your instructor which of these are soluble in water and think about the solubility of the cadmium and lead salts used in this experiment to answer this question.
3. Could quantum particles be formed with  $CdO$ ,  $PbO$ ,  $CaO$ ? Why or why not? (See note in 2.) What color are the bulk materials? What color would the quantum particles be?
4. Suppose that one wanted a quantum dot which absorbs in the blue region of the spectrum. What color would it appear? What material would you choose to make it with?



### ***Appendix A:***

Suggestions for further work as problem of semester:

- A. Work on stabilizing the micelles, perhaps with a polymer so that they do not fuse into the bulk on removal of the solvent.
  
- B. Investigate the feasibility of controlling the band edge using different cations and anions.

### ***Appendix B:***

THEORY OF BAND GAP IN QUANTUM DOTS:

***Extension of the Bohr Model:*** The energy of the band gap in quantum particle consists of a term due to confinement of the electron and hole to the sphere plus a contribution from the Coulombic attraction of the negatively charged electron for the positively charged hole:

$$E_g = \frac{\hbar^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{18e^2}{R}$$

Here  $E_g$  is the change in energy of the band gap,  $R$  is the particle radius,  $\epsilon_0$  is the permittivity of free space,  $\hbar$  is Planck's constant divided by  $2\pi$ ,  $e$  is the charge on the electron and  $m_e$  ( $m_h$ ) is the effective mass of the electron (hole). In PbS, these are  $m_e=0.19m$  and  $m_h=0.8m$  where  $m$  is the mass of the electron. See Nedeljkovic, *J. Chem. Ed.*, **70**, 342 (1993).

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For large sizes, the  $1/R$  term dominates and the band gap is given by the Coulombic term. As  $R$  decreases, the first term grows in importance and the confinement term dominates as the particle size gets into the 40nm and smaller range.

***Modification of Band Theory:*** In the molecular orbital view, electronic bands arise due to interaction of a large number of individual orbitals resulting in states so close in energy that they overlap into a continuous band of allowed states bounded by a band of non-allowed states. The total number of states for the solid is equal to the number of atomic orbitals which interact. For every atom removed from a bulk solid, a corresponding number of extended orbitals is removed from the allowed bands of states. Due to the extremely large number of atoms in a typical solid (on the order of  $10^{20}$  even for a small sample) this removal of states is not detectable.

However, when the total number of atoms in the solid is a much smaller number, e.g. on the order of  $10^3$ , the total number of states is also correspondingly smaller. Some of this large number of missing states come from near the top of the valence band while others come from the bottom of the conduction band. Since the band-gap energy is the energy difference between the bottom of the conduction band and the top of the valence band, it increases when states are missing from these regions.

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### *Notes and References:*

<sup>1</sup>  $1\text{\AA}=10^{-10}$  meter. In SI (Standard International) units,  $1\text{\AA}=0.1$  nanometer or 100 picometers. Currently atomic radii often are given in SI units.

<sup>2</sup> G. W. Nieman, J. R. Weertman, R. W. Siegel, *J. Materials Res.* **6**, 1012 (1991).

<sup>3</sup> M. J. Mayo, R. W. Siegel, A. Narayanasamy, W. D. Nix, *J. Materials Res.* **5**, 1073 (1990).

<sup>4</sup> T. D. Klots, B. J. Winter, E. K. Parks, S. J. Riley, *J. Chem. Phys.* **92**, 2110 (1990) and **95**, 8919 (1991).

The AOT method procedure was adapted from R. R. Chandler, S. R. Bigham, and J. Coffey, *J. Chem. Ed.*, **70**, A7 (1993).

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### **needed**

For each group:

50 mL surfactant solution (25.6 g AOT per liter heptane, AOT is dioctyl sulfosuccinate, sodium salt)

10-mL, 4% polyvinyl alcohol solution, polyvinyl alcohol is 124,000-186,000 molecular weight. Heat water to ~80°C, stir vigorously, add PVA *slowly*. Continue to maintain 80°C with stirring for a couple of hours. Solution should be nearly clear.

25 \_L 0.6 M  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

25 \_L 0.6 M  $\text{Pb}(\text{NO}_3)_2$

50 \_L 0.6 M  $\text{Na}_2\text{S}$

two 125-mL Round-Bottom Flasks

two 125-mL Erlenmeyer Flasks

$\text{N}_2$  for purge

2 stoppers for round-bottom flasks

1 two hole stopper

1 cuvette for HP spectrophotometer

250-\_L syringe for

$\text{Cd}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ , and  $\text{Na}_2\text{S}$  solutions

2 transfer pipettes

Magnetic stir plate and stir bar

$\text{N}_2$  tank with regulator for purge

For the Lab: one HP diode array spectrometer.

Instructors notes:

Bulk CdS band gap = 2.53 eV

PdS = 0.41 eV

bulk PbS is nearly black due to absorption of all colors

quantum size PbS is wine-red to brown - tea colored

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### ***Answers to Pre Lab Questions:***

1. PbS and CdS are referred to as II-VI semiconductors. Suggest a reason for this terminology.

**Answer:** The common ionization states for Pb and Cd is +2, while that of S is +6: hence II-VI.

2. Based on reactivity and stability, suggest a reason for the exclusion of O<sub>2</sub> from the synthesis apparatus.

**Answer:** Since oxygen is more reactive than sulfur, it may interfere with the synthesis of a sulfide by forming the oxide or a mixed oxide/sulfide.

3. Look up or predict the band gap in CdSe and CdTe. (Predict the size of the gap relative to CdS and PbS.)

**Answer:** The band gap in CdSe and CdTe are smaller than that in CdS, and CdTe is smaller than CdSe. Both CdSe and CdTe have larger gaps than PbS, although this prediction is not so straight forward. (It has to do with the very large size of Pb<sup>2+</sup>).

4. Could CdSe or CdTe be used to form quantum-size, semiconductor particles? Why or why not?

**Answer:** Both CdSe and CdTe could form quantum dots utilizing a procedure similar to the one in the laboratory. Both CdSe and CdTe are insoluble, and Na<sub>2</sub>Se and Na<sub>2</sub>Te are soluble. Both have been made, but the need to rigorously exclude oxygen is even stronger for these materials.

5. Could PbSe or PbTe be used? Why or why not?

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**Answer:** PbSe and PbTe also form quantum dots. They could be used, but again oxygen would have to be excluded. In these cases, the dots would be black since the band gap is even smaller than that of PbS which is already in the infrared. (PbS is reddish because the quantum size particle transmits a bit of the red due to its small size.)

6. Could the well known semiconductors Ge and Si be used to form quantum size semiconductors? Would the synthetic procedure differ substantially from that used in this exercise? Why or why not?

**Answer:** Both Ge and Si could be used. The synthetic method would have to be different since these are not binary solids.

7. Think about the role of surfactant, water, and heptane in this exercise. Which concentrations are critically important and why?

**Answer:** Since heptane is in great excess (as the solvent) its concentration is not critical. Water and Surfactant are both critical since it is the water/surfactant ratio that determined the pool size and therefore the dot size.

### *Answers to Post Lab Questions:*

1. Report any observations that you made while performing the synthesis. Include your spectra. Compare your spectra with your colleagues in lab. Are there any differences? Discuss the effect of water on quantum dots.

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**Answer:** Report results and observations. The effect of water is very important. If the vessels are not completely dry, the pools or reaction vessels inside the micelles are large and precipitate is formed rather than quantum dots.

2. Could you make quantum particles with any of the following:  $K_2S$ ,  $CaS$ ,  $CoS$ ,  $SnS$ . Why or why not? Note: If you have not yet discussed solubility in class, then ask your instructor which of these are soluble in water and think about the solubility of the cadmium and lead salts used in this experiment to answer this question.

**Answer:**  $K_2S$  and  $CaS$  are both quite soluble, so the method we used would not work.  $CoS$  is reasonably insoluble and  $SnS$  is very insoluble, hence should work.

3. Could quantum particles be formed with  $CdO$ ,  $PbO$ ,  $CaO$ ? Why or why not? (See note in 2.) What color are the bulk materials? What color would the quantum particles be?

**Answer:**  $CdO$  and  $PbO$  are insoluble, so could be used.  $CaO$  is probably too soluble.  $CdO$  is brown and  $PbO$  is yellow. Both would make colorful quantum dots, though the  $PbO$  would be pale.

4. Suppose that one wanted a quantum dot which absorbs in the blue region of the spectrum. What color would it appear? What material would you choose to make it with?

**Answer:** A quantum dot that absorbs in the blue region of the spectrum would appear orange. To absorb in the blue region, the band gap would have to be somewhat larger than that of  $CdS$  which absorbs in the violet

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region. CdSe is a candidate. The bulk is red, so a quantum dot might well be orange. A second candidate is HgS, also red in the bulk.