The Synthesis of Cadmium Sulfide Nanoparticles

In this laboratory exercise we will synthesize nanoparticles of Cadmium Sulfide, as well as a bulk sample of this semiconductor. We will then leverage the increase in the band gap of the nanoparticles, relative to that of the bulk material, to determine the radius of the nanoparticles. This increase in band gap is due to the quantum confinement of the electron-hole pairs created upon photon absorption within the nanoparticles.

Synthesis of bulk Cadmium Sulfide is fairly simple as this compound, like most other Sulfides, is insoluble in an aqueous solution. So, mixing aqueous solutions of Cadmium Chloride and Sodium Sulfide results in a Metathesis Reaction in which the product precipitates in bulk crystalline form.

\[
\text{CdCl}_2(aq) + \text{Na}_2\text{S}(aq) \rightarrow \text{CdS}(s) + 2 \text{NaCl}(aq)
\]

(Eq. 1)

The nanoparticle form of this compound is more difficult to generate as one must control the size of the resulting crystals such that they be no larger than 100 nm; the typical size limit for a material to be classified as a nanoparticle.

There are a couple of ways of controlling the size of the resulting particles and for preventing the particles from coagulating into larger aggregates. In the present case, we will use a reverse microemulsion to contain our nanoparticles. Water-in-Oil microemulsions containing each reactant will be prepared by mixing Hexane, 1-Propanol and Hexadecyltrimethyl Ammonium Bromide (CTAB). The CTAB molecule is a surfactant with a long non-polar tail and a charged, polar head.

\[
\text{CTAB}
\]

(CTAB)

In an organic solvent such as Hexane, CTAB will form small micelles with an aqueous interior.
When micelles containing Cd\(^{2+}\)(aq) and S\(^{2-}\)(aq) ions collide, the Cd\(^{2+}\) and S\(^{2-}\) will combine to form CdS particles. Because of the limited size of the micelle interior, only small nanoparticle sized precipitates will form.

As noted above, Cadmium Sulfide is a semi-conductor. When atoms of Cd and S come together to form a solid, their atomic orbitals overlap to form bonding and anti-bonding molecular orbitals.

![Cadmium Sulfide Crystal](http://en.wikipedia.org/wiki/File:Hawleyite-3D-balls.png)

When only a few atoms come together, only a few molecular orbitals are formed.
When large numbers of atoms come together, as might be found in either a bulk or a nanoparticle material, the resulting molecular orbitals form Bands of energetically very closely spaced orbitals. Lower lying orbitals filled with electrons form the Valence Band of the material while higher lying empty orbitals form the Conduction Band. If the bonding is "tight", a large gap, called the Band Gap, will exist between these bands and the material is an Insulator; it is difficult to kick electrons from the valence to the conduction band. Weak bonding results in no band gap between these bands and the material is a Metal; it is relatively easy to kick electrons into the conduction band. Materials with an intermediate band gap are classified as Semi-Conductors.

In semi-conducting materials, absorption of a photon will promote an electron from the valence band to the conduction band, leaving a positively charged "hole" behind.

The Band Gap Energy ($E_g$) is the energy needed to create the electron-hole pair, at rest with respect to the atomic lattice, and far enough apart so that their Coulombic interaction is negligible. The band gap energy for bulk Cadmium Sulfide is $3.88 \times 10^{-19}$ Joule.

In the case of nanoparticles, the electron and hole are confined to a Sphere of radius $R$. Like a Particle-in-a-Box, this quantum confinement results in quantized energy levels whose spacing increases when the sphere gets smaller. So, quantum confinement of the electron and hole to the sphere tends to widen the band gap and the resulting absorption spectrum is Blue Shifted; the absorption wavelengths decrease.
In semi-conductors, the dielectric constant ($\varepsilon$) is fairly large and the electron and hole can form a "bound state", much like a Hydrogen atom, called a Wannier exciton, with a radius that is much larger than the lattice spacing for the crystal. (For Cadmium Sulfide, $\varepsilon = 5.7 \, \varepsilon_o$, where $\varepsilon_o$ is the permittivity of free space.)

If $m_e$ and $m_h$ are the effective masses of the electron and hole moving in the lattice potential, then the Hamiltonian operator for the exciton in a "Box" model can be written as:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_h}\nabla_h^2 + V$$

(Eq. 2)

where the potential energy operator is formed using:

$$V = \begin{cases} \frac{-e^2}{\varepsilon r} & \text{if } r < R \\ \infty & \text{otherwise} \end{cases}$$

(Eq. 3)

$e$ is the fundamental charge and $r$ is the relative distance between the electron and the hole. The effective masses of the electron and hole are $1.73 \times 10^{-31}$ kg and $7.29 \times 10^{-31}$ kg respectively.

An approximate solution of the Schrödinger Wave Equation:

$$\hat{H} \psi = E \psi$$

(Eq. 4)

for the first excited state energy ($\Delta E$) is:

$$\Delta E = \frac{\hbar^2}{8R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8 \, e^2}{\varepsilon R}$$

(Eq. 5)

So, due to the quantum confinement of the electron-hole pair, the band gap of the bulk material is increased by $\Delta E$:

$$E_{g \text{ nano}} = E_{g \text{ bulk}} + \Delta E$$

(Eq. 6)
The band gap energy can be determined from the Absorption Onset of an Absorbance curve for a solution of the nanoparticles. The absorption onset occurs at a "cut-off" wavelength, which can be measured as below.

![Absorbance vs Wavelength](image)

The band gap energy is then calculated using:

\[ E_g = \frac{hc}{\lambda_{cut}} \]  

(Eq. 7)

We will generate Cadmium Sulfide nanoparticles and measure their absorbance curve. From the absorbance curve we will determine the cut-off wavelength and hence their band gap energy. This will then be used to determine the radius of the particles. Bulk Cadmium Sulfide will be generated for comparison.
**Procedure**

The organic liquids and sulfide solutions used in this experiment have irritating odors. Cadmium salts are also quite toxic. Therefore, perform this experiment in a fume hood and wear gloves and goggles at all times. Dispose of all reagents and products in an appropriate waste container.

**Preparation of Bulk Cadmium Sulfide**

1. Place 1 mL of an aqueous 0.012 M CdCl\textsubscript{2} solution in a test tube.
2. Add 1 mL of an aqueous 0.012 M Na\textsubscript{2}S solution to the test tube. Note the color change upon mixing.
3. Stir the mixture with a stir rod. Bulk CdS crystals should precipitate immediately.
4. Note the final color of the crystals and solution. Keep this solution as a reference.

**Preparation of Nanoparticles of Cadmium Sulfide**

1. Prepare three solutions, A, B and D, in separate beakers, by mixing in each beaker 12.0 mL of Hexane, 3.0 mL of 1-Pentanol and 0.60g of CTAB. These mixtures are cloudy due to the low solubility of the CTAB. Stir each microemulsion continuously with a magnetic stir bar.
2. Add 0.6 mL of an aqueous 0.012 M CdCl\textsubscript{2} stock solution to mixture A. Add 0.6 mL of an aqueous 0.012 M Na\textsubscript{2}S stock solution to mixture B. Both mixtures should become colorless and transparent.
3. Mix solutions A and B to form a slightly cloudy yellow solution; solution C. This mixture should become translucent in a few minutes. This yellow color indicates the formation of the nanoparticles.
4. A reference solution is prepared by adding 0.6 mL of Water to mixture D.
5. Measure the absorbance spectrum of solution C, using solution D as a reference.

*This procedure is adapted from Winkelmann, et al.*
Data Analysis

1. Plot the absorbance spectrum between 380 - 500 nm.

2. Note the region in the spectrum where the absorbance changes linearly. Graph the linear data and obtain the equation of the line by performing a Linear Least Squares Analysis of the data.

3. Determine the x-intercept of the line. This is the "cut-off" wavelength of the spectrum; representing the onset of absorption. Determine the photon energy for the "cut-off" wavelength.

4. Calculate the size of the nanoparticles.

5. Record all results with appropriate error estimates.
References

