EXPERIMENT **2**

Nanochemistry: Synthesis and Properties of Cadmium Selenide Quantum Dot Nanoparticles

REFERENCES

a. Boatman, E. M.; Lisensky, G. C.; Nordell, K. J. “A Safer, Easier, Faster Synthesis for CdSe Quantum Dot Nanocrystals”, *J. Chem. Educ.*, **2005**, *82*, 1697-1699.
b. Yu, W. W.; Peng, X. “Formation of High Quality Semiconductor Nanocrystals in Non-Coordinating Solvents”, *Angew. Chem. Int. Ed.*, **2002**, *41*, 2368-2370.

SAFETY RECOMMENDATIONS

CAUTION: Avoid physical contact with cadmium oxide and cadmium selenide as both are carcinogens.

INTRODUCTION

a. Semiconductors

During this course we will deal with molecular species. Typical chemical bonds range between 1-3 Å (1 Å = 10 –10m). Molecules have defined structures and sizes. For materials with extended structures, like semiconductors, this is not the case. The properties of materials of this type can depend on their dimensions, particularly as particle sizes decrease.

Semiconductors have many interesting properties. One of first to be identified was their ability to conduct electricity in a way that differed phenomenologically from metals. They are less conductive than metals and their conductivity is highly temperature dependent. Electrons in a material can have various energies. When their energy is relatively low, they are “bound” to atoms in a structure. If their energy is sufficiently high, they can reside in states where they are not bound to particular atoms. This collection of states is called the conduction band. The collection of bound states is referred to as the valence band.

In physics, the energies of electrons in a system are referenced to the Fermi level, εF. This is defined as the energy at which the probability of finding an electron is 50%. At absolute zero ($T = 0$), electrons occupy all levels below εF and all energy levels above εF are empty. Because we operate in a world where $T > 0$, there is always a probability that an electron will have an energy above the Fermi level. In this case, εF can be viewed as representing average energy of the highest energy electrons in a structure.

A metal conducts electricity because its Fermi level lies in the conduction band. A semiconductor differs in that εF lies below the conduction band. Thus, energy input is required to promote electrons to states where they can move freely through the material. As T increases, the probability that electrons can have energies greater than εF increases. This leads to thermal promotion of electrons to the conduction band and creation of holes in the valence band. This is how a semiconductor conducts electricity, but the number of electrons with an appropriate energy is much lower than in a metal. In a semiconductor the energy difference between the valence and conduction bands is referred to as the band-gap energy (Eg). This is summarized in In Figure 1 below.

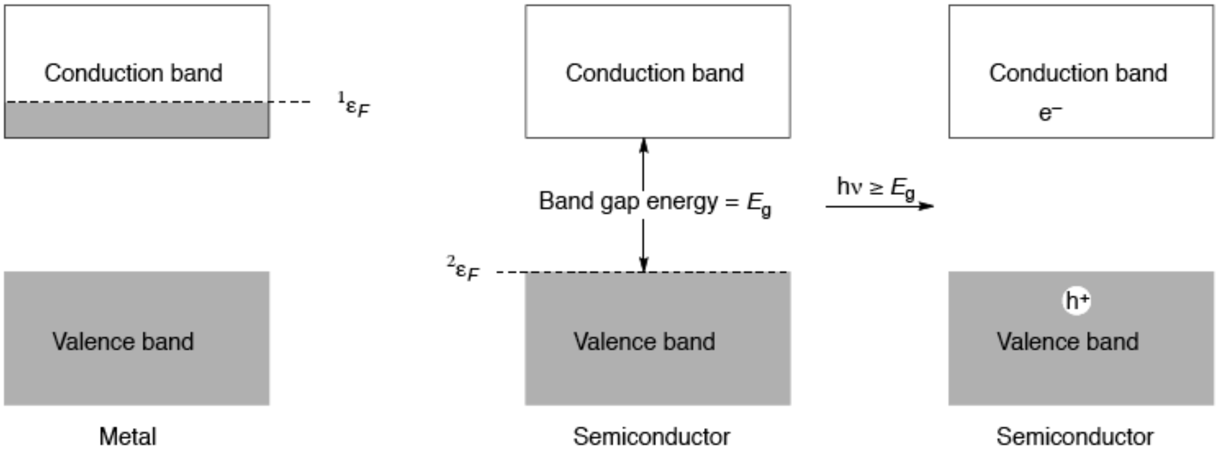

Figure 1. Electronic structures for a metal and a semiconductor illustrating the relationship between their Fermi levels and their conduction bands.

An electron can also be promoted to the conduction band when a semiconductor absorbs a photon whose energy $E = h\nu \geq E$g. This process also creates an electron-hole pair. Electron holes and pairs can recombine and release energy by emitting photons. They can also recombine by passing through a circuit that is connected to a load. Recombination in this fashion allows the energy from the photon to be converted to electrical or chemical energy (Figure 2). In a semiconductor, the electron-hole pair (exciton) is bound within a volume of a characteristic radius called the exciton Bohr radius (*a*B). As long as the shortest dimension of the material is greater than *a*B, the band-gap energy Eg remains constant. If the dimensions of the material are smaller than *a*B, the hole-pair is confined and Eg will increase.

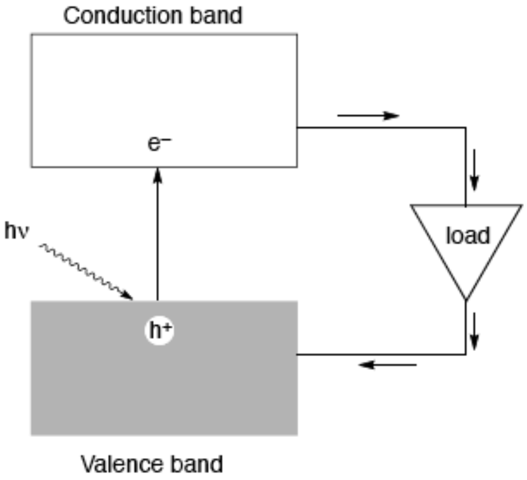

Figure 2. A schematic for a semiconductor photovoltaic device. Electrons and holes can recombine through a circuit were the energy of the photon performs work or is stored as electrical or chemical energy.

Cadmium selenide (CdSe) is a semiconductor with *E*g ~ 1.7 electron-volts (eV) with *a*B = 56 Å. In this module, you will synthesize cadmium selenide (CdSe) nanoparticles whose radii are less than *a*B and characterize them by UV-Vis spectroscopy.

b. Cadmium Selenide Semiconductors

The visible absorption and photoluminescence of CdSe nanoparticles depend on the size of the particle. Octadecene is used as a non-coordinating, high-boiling solvent. A sudden injection of room temperature selenium solution into the hot cadmium solution produces seed crystals which then grow quickly. Samples are withdrawn from the hot solution and quenched at room temperature to produce a series of increasing particle sizes.

PROCEDURE

A 25 ml roundbottom flask equipped with a stir bar is loaded with 13 mg of CdO powder, 0.6 mL of oleic acid, and 10 mL of 1-octadecene. The reaction flask is immersed in a silicon oil bath on a hotplate that was set to the highest temperature setting. The oil bath is surrounded with aluminum foil so the temperature can reach 225 °C, which will take ~ 1 h. Some hot plates may heat up faster and the experiment can be performed sooner.

As the CdO solution is heating, the Se solution should be prepared. Five student can share the Se solution, since only 1 mL is required for each reaction. A 25 mL round-bottom flask equipped with a stir bar is loaded with 30 mg of Se and 5 mL of 1-octadecene and allowed to stir at room temperature. To this stirred solution was added 0.4 mL of trioctylphosphine via syringe. The mixture will turn homogeneous. At this point it is ready for the next step.

Once the CdO solution has reached a temperature of about 225 °C, add 1 mL of the Se solution. After about five minutes of addition, the solution should turn yellow. At this time, remove ~ 1 mL of the solution via pipette and into a test tube. Pipette ~ 1 mL samples into separate test tubes every 5 to 10 minutes. During this time, the reaction solution will change color from clear yellow to orange to blood red.

Pipette the 1 mL samples into a glass cuvette and dilute with pentane to a constant volume and record their UV-Vis spectra. The solutions collected in test tubes can be stored overnight in the hood or drawer without decomposition if there is not enough time to record UV-vis spectra.

In lieu of a formal report, attach your to a sheet where you answer the following questions:

1. What reaction is occurring when the selenium dissolves after trioctylphosphine is added.
2. Write balanced reactions for the nanoparticle synthesis
3. From your UV-Vis data, what color light do the yellow and red solutions absorb, respectively?
4. What wavelength light does bulk CdSe absorb?
5. Estimate the radii of your particles from their absorption spectra.