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Materials Research Science and Engineering Center

Interdisciplinary
Education Group

Preparation of Cadmium Selenide Quantum Dot Nanoparticles

Procedure is based on E. M. Boatman, G. C. Lisensky, and K. J. Nordell, "A Safer, Easier, Faster Synthesis for CdSe Quantum Dot Nanocrystals," *J. Chem. Educ.*, *82*, 1697-1699 (2005) and W. William Yu and Xiaogang Peng, "Formation of High Quality Semiconductor Nanocrystals in Non-Coordinating Solvents," *Angew. Chem. Int. Ed. 41*, 2368-2370 (2002).

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 Samples are withdrawn from the hot solution and quenched at room temperature to produce a series of increasing particle sizes.

Clicking a thumbnail on this web page (http://mrsec.wisc.edu/Edetc/nanolab/CdSe/index.html) shows a movie of that step.

Procedure


Wear eye protection


Chemical gloves recommended


Fumehood recommended


Add 30 mg of Se and 5 mL octadecene to a 10 mL round bottom flask over a stirrer hot plate. Warning: Se is an inhalation hazard and this operation should be done in a fume hood.


Measure by syringe 0.4 mL trioctylphosphine from its Sure-Seal bottle and add to the flask.


Add a magnetic stir bar. Stir and warm the solution as necessary to completely dissolve the selenium. Cool to room temperature. This stock solution may be prepared ahead of time, has enough Se precursor for five preparations, and can be stored in a sealed container for at least several months.

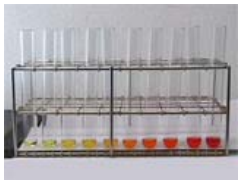

Add 13 mg of CdO to a 25 mL round bottom flask clamped in a heating mantle. Warning: CdO is an inhalation hazard and this operation should be done in a fume hood. Avoid plastic containers to reduce static problems.

To the same flask, add by pipet 0.6 mL oleic acid and 10 mL octadecene. Swirl the flask to mix the liquids. Insert a thermometer capable of measuring 225 °C.

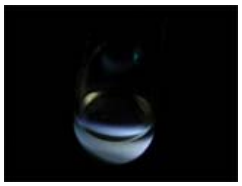

Heat the cadmium solution. (For a thermowell on high this takes about 20 minutes.) When the temperature reaches 225 °C, use a clean and dry pipet to quickly transfer 1 mL of the room temperature selenium solution to the 225 °C cadmium solution and start timing.


Remove approximately 1 mL samples at frequent intervals using a 9 inch glass Pasteur pipet as the CdSe particles grow in size. Have a partner record the times for each withdrawal, starting from the time the selenium was added. In the video the first five samples were removed at 10 second intervals.

Continue removing samples at longer intervals so there is a noticeable color change. In the video ten samples are removed within 3 minutes of the initial injection.



Record the absorbance spectra of the solutions to find the maximum wavelength peak. (Particle sizes can be estimated using the x-intercept and the calculation method shown below.)
Graph the absorbance wavelength as a function of growth time.



Record the emission spectra of the solutions to find the maximum wavelength peak. In the movie, sequential samples are placed in a beam of 400 nm wavelength light. What is the evidence for band gap excitation rather than molecular absorbance?

Option: Samples show narrower peaks in the absorption spectrum when they are quenched more quickly. Instead of collecting in test tubes, they can be collected in flasks containing liquid nitrogen.

Materials

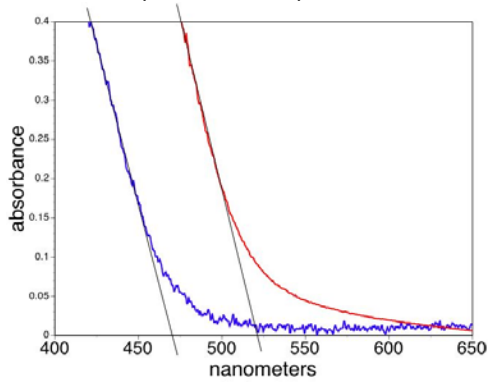
CAUTION: Avoid physical contact with cadmium oxide and cadmium selenide as both are carcinogens.
CdO, Aldrich 202894
Oleic Acid, technical grade, Aldrich 364525
Selenium, Aldrich 209651
trioctylphosphine, technical grade, Aldrich 117854
Octadecene, technical grade, Aldrich O806

Equipment

- analytical balance (0.0001 gram) in a fume hood
- 10 mL round bottom flask and stopper
- stirrer hotplate
- 1 mL syringe with needle
- 1/4" magnetic stir bar
- 25 mL round bottom flask
- 25 mL heating mantle and controller
- 1 mL graduated pipet
- 10 mL pipet
- 250 °C thermometer
- Pasteur pipets and bulbs
- test tubes
- absorbance spectrometer
- emission spectrometer

Calculations

The x-intercept of the linear portion of the absorbance as a function of wavelength graph is a measure of E_g.



$E_g = h\,c\,/\,\lambda$
h = 6.626x10^{-34} J s
c = 2.998x10^{8} m/s
e = 1.602x10^{-19} C
ε_0 = 8.854x10^{-12} C^2/N/m^2
m_0 = 9.110x10^{-31} kg

CdS
λ^{bulk} = 512 nm
ε = 5.7
m_e^* = 0.19
m_h^* = 0.80

CdSe
λ^{bulk} = 709 nm
ε = 10.6
m_e^* = 0.13
m_h^* = 0.45

ZnO
λ^{bulk} = 365 nm
ε = 8.66
m_e^* = 0.24
m_h^* = 0.59

The effective mass model suggests

$$E_g^{nano} = E_g^{bulk} + \frac{h^2}{8m_0r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 r}$$

where r is the radius of the nanoparticle. The second term is the particle-in-a-box confinement energy for an electron-hole pair in a spherical quantum dot and the third term is the Coulomb attraction between an electron and hole modified by the screening of charges by the crystal.

After multiplying by r^2, rearranging, and using the quadratic formula,

$$r = \frac{-\left(\frac{1.8e^2}{4\pi\varepsilon\varepsilon_0}\right) + \sqrt{\left(\frac{1.8e^2}{4\pi\varepsilon\varepsilon_0}\right)^2 + \left(E_g^{nano} - E_g^{bulk}\right)\frac{h^2}{2m_0}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)}}{2\left(E_g^{nano} - E_g^{bulk}\right)}$$

What is the diameter of the nanoparticles?

This page created by George Lisensky, Beloit College. Last modified July 19, 2011