

Nanotechnology

Zachariah Sachs (with Jeff Montgomery)

May 20, 2013

1 Purpose

In this laboratory exercise, we made several sizes of cadmium selenide nanocrystals and gold nanoparticles and then analyzed their spectral properties in solution in order to observe the novel electronic properties of semiconductors and metals of size comparable to their excitation wavelengths.

2 Theory and Methods

2.1 Semiconductor energy shift and nanocrystals

When a semiconductor nanocrystal absorbs a photon of sufficient energy, an electron-valence hole pair is created by the promotion of an electron from the valence band to the conduction band of the material. This pair maintains a charge separation, the bulk Bohr exciton radius, generally the size of the Bohr radius of the electron wavefunction in the material, for CdSe about 5.6 nm. If the bulk of the material is smaller than the corresponding diameter, the electron-hole pair cannot achieve this separation, and becomes trapped as in a quantum mechanical particle in a box, with accompanying discretization of energy levels. Discrete energy levels yield distinct electronic transitions, and thus sharper absorption and emission spectra. In particular, we are able to resolve a downshift in the transition energy from absorption to emission. This shift results as the system relaxes towards equilibrium in reaction to the location of the electron; following absorption, the internuclear distance in the crystal decreases, lowering the attractive coulombic potential energy of the electron-hole pair, and following emission, the internuclear distance expands, lowering the repulsive coulombic potential energy of the nuclei to return to the initial energy.

Assuming a uniform, spherical, singly-excitable particle with no electron probability outside, the solutions to the Schrödinger equation for just the electron gives the energies of a particle in a box:

$$E_n = \frac{h^2 n^2}{8m_e R^2}, \quad n = 1, 2, 3, \dots \quad (1)$$

where h is Planck's constant, m_c is the effective mass of the electron, and R is the radius of the nanocrystal, the boundaries of the box. However, to conserve charge, we must also include the hole. The Hamiltonian for this 2-particle box has a potential energy term consisting of a Coulomb term and a polarization term which both depend on the electron-hole separation. The lowest energy of the system, called an exciton, can be approximated assuming no correlation between the electron and hole wavefunctions, i.e.

$$\Phi_{ex}(\hat{S}_{elec}, \hat{S}_{hole}) = \Psi_1(\hat{S}_{elec})\Psi_1(\hat{S}_{hole}), \quad (2)$$

for \hat{S}_{elec} and \hat{S}_{hole} the positions of electron and hole, respectively. This gives energies

$$E_{ex} = \frac{h^2}{8R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi\epsilon_{CdSe}\epsilon_0 R} + E_{pol}(R), \quad (3)$$

for m_e and m_h the effective masses of electron and hole, respectively, ϵ_{CdSe} the dielectric constant of CdSe, ϵ_0 the permittivity of vacuum, and $E_{pol}(R)$ the polarization energy which is dominated by the kinetic and Coulomb energies. The energy of the lowest optical transition,

$$E_{np} = E_{ex} + E_g, \quad (4)$$

is the sum of the exciton and bulk band gap energies. This gives an equation which is quadratic in R and can be solved for taking E_{np} from the peak of the spectral absorption band.

2.2 Metallic nanoparticles

Conducting electrons in metallic particles of sizes smaller than excitation wavelengths resonate between available states upon absorption of visible light and are called surface plasmons. Mie theory predicts the absorbance of a dilute solution of such particles as

$$A = \log_{10} \frac{I}{I_0} = \frac{CNd}{2.303}, \quad (5)$$

where C is the absorption cross section, N is the number of particles per unit volume, and d is the path length of exciting light. The absorption cross section is dependent on the dielectric properties of substance and medium, and for radii smaller than the exciting wavelength, is given by

$$C(R, \lambda) = \frac{24\pi^2 R^3 \epsilon_m^{\frac{3}{2}}}{\lambda} \frac{\epsilon''}{(\epsilon' + 2\epsilon_m)^2 + \epsilon''^2}, \quad (6)$$

where ϵ_m is the constant dielectric permittivity of the medium and $\epsilon = \epsilon' + i\epsilon''$ is the complex dielectric function of the particle, which is further related to the complex refractive index of the metal.

The Drude model for metals gives the dependence of the dielectric function on angular frequency $\omega = \frac{2\pi c}{\lambda}$ as

$$\epsilon' = \epsilon^\infty - \frac{\omega_p^2}{(\omega^2 + \omega_d^2)}, \quad (7)$$

$$\epsilon'' = \frac{\omega_p^2 \omega_d}{\omega(\omega^2 + \omega_d^2)}, \quad (8)$$

where ϵ^∞ is the high-frequency dielectric constant, ω_p is the bulk plasmon frequency, and ω_d is the dumping frequency, all constants.

2.3 Procedure

Initially, a solution of 13 mg cadmium (II) oxide, 0.6 ml of oleic acid, and 10 mL of octadecene was heated to 225 °C. A prepared 0.038 M solution of selenium precursor prepared with 30 mg Se, 5 mL of 1-octadecene, and 0.4 mL of trioctylphosphine was supplied. Beginning immediately after 1 mL of Se precursor was added to the heated Cd solution, 13 aliquots of the mixture were taken at intervals to generate a range of sizes of CdSe nanocrystals in solution. The timing of these aliquots was recorded on video. Initially, some of our aliquots were not sufficient to fill the cuvette of the spectrometer, so we diluted 540 μ L of each sample to final volume 1 mL with octadecene.

Absorption spectra for each sample of CdSe nanocrystals were recorded using an Ocean Optics spectrometer illuminated with the LS-1 light source hooked up to a computer with the SpectraSuite program, with integration time set to 50 ms, boxcar width set to 5, and scans to average set to 10.

Emission spectra for each sample of CdSe nanocrystals were recorded using the same spectrometer and computer program with the sample excited by a 12 V, 405 nm LED.

A solution of 20 mL of 1.0 mM HAuCl₄ was brought to a boil, at which time 2 mL of 38.8 mM trisodium citrate was added. This solution was allowed to boil for another five minutes, and then removed from heat and allowed to cool to room temperature.

An absorption spectrum for the gold nanoparticle solution was recorded with the same instruments and parameters as above. A few drops of 1 M sodium chloride solution were then added to the gold nanoparticle solution, and 12 spectra of this mixture were recorded at regular intervals over about 10 minutes.

3 Data and Plots

3.1 Cadmium selenide nanocrystals

The thirteen aliquots of CdSe nanocrystals range from visibly pale yellow through orange to pale red. These are the wavelengths the transparent samples transmit, so the complimentary colors, namely violet through green, are absorbed

The absorption spectra for the first and last aliquots of CdSe nanocrystals are included as Figures 1 and 2. The spectrometer detector was did not cleanly detect wavelengths shorter than approximately ultraviolet. The clear absorption band to the right of this noise was marked, as best as possible, at peak and FWHM and the corresponding wavelengths were recorded using MATLAB¹.

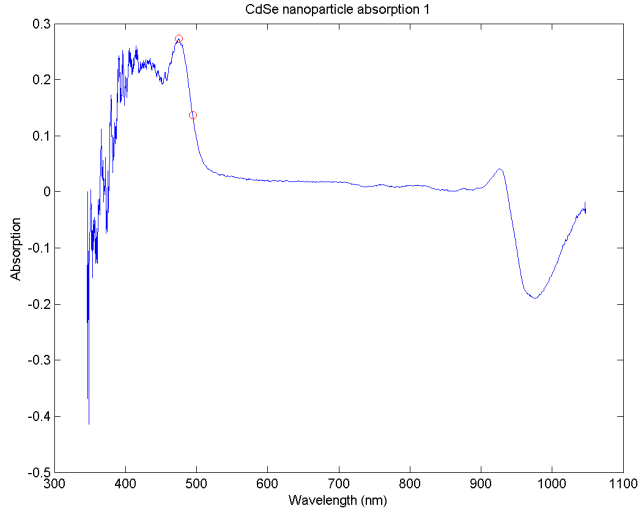


Figure 1: Absorption spectrum for the first aliquot of cadmium selenide nanocrystal solution with peak and FWHM marked.

¹MATLAB script `zs_nanocdse.m`.

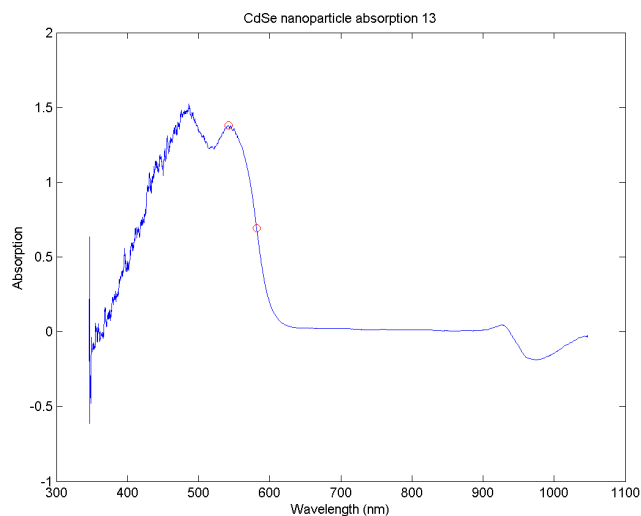


Figure 2: Absorption spectrum for the thirteenth aliquot of cadmium selenide nanocrystal solution with peak and FWHM marked.

The emission spectra for the first and last aliquots of CdSe nanocrystals are included as Figures 3 and 4. The spectrometer detector was did not cleanly detect wavelengths shorter than approximately ultraviolet. The clear absorption band to the right of this noise was marked, as best as possible, at peak and FWHM and the corresponding wavelengths were recorded using MATLAB².

²MATLAB script `zs_nanocdse.m`.

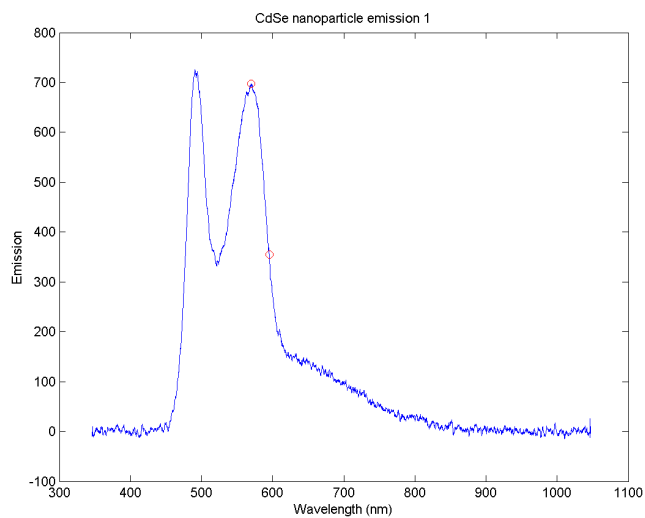


Figure 3: Emission spectrum for the first aliquot of cadmium selenide nanocrystal solution with peak and FWHM marked.

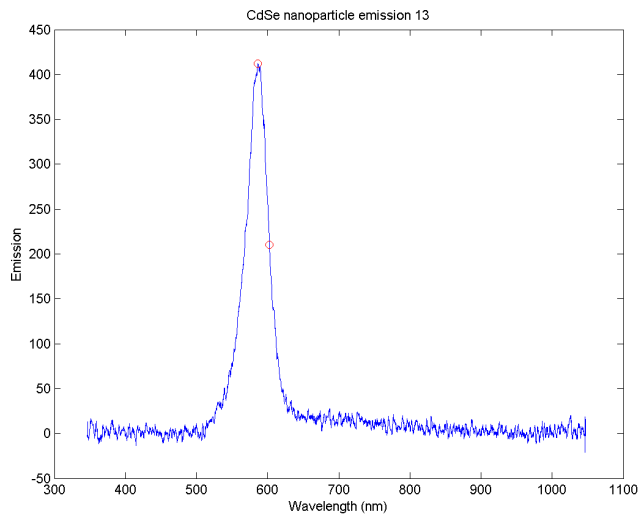


Figure 4: Emission spectrum for the thirteenth aliquot of cadmium selenide nanocrystal solution with peak and FWHM marked.

3.2 Gold nanoparticles

The absorption spectra for the original gold nanoparticles is included as Figure 5³. The spectrometer detector did not cleanly detect wavelengths shorter than approximately ultraviolet.

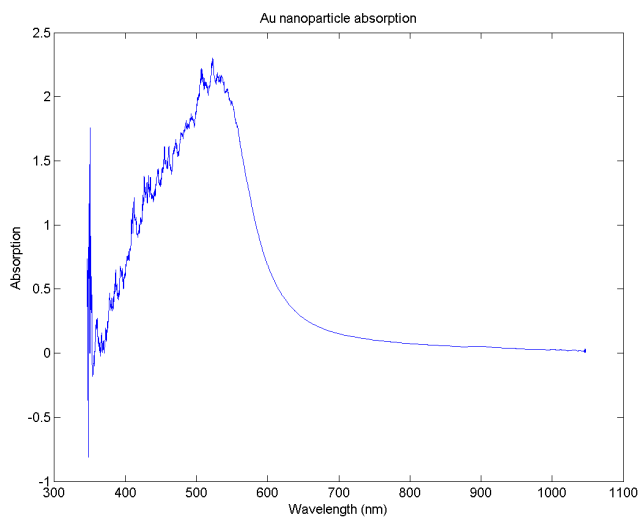


Figure 5: Absorption spectrum of the original gold nanoparticle solution.

The first and last absorption spectra taken after the addition of sodium chloride to the gold nanoparticle solution are included as Figures 6 and 7.

³MATLAB script `zs_nanoau.m`.

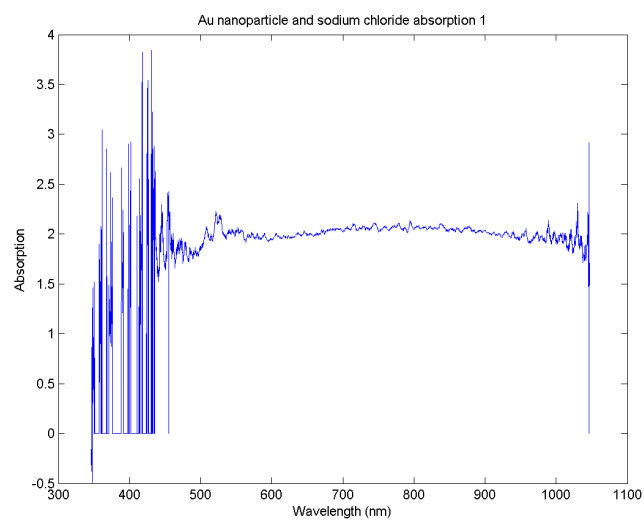


Figure 6: First absorption spectrum of gold nanoparticle solution treated with sodium chloride.

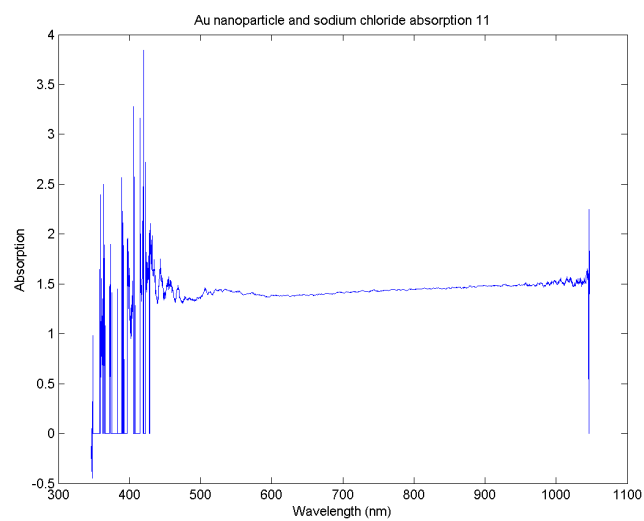


Figure 7: Eleventh absorption spectrum of the gold nanoparticles solution treated with sodium chloride.

4 Analysis

4.1 Cadmium selenide nanocrystal diameter and color

The CdSe nanocrystal diameters can be calculated by finding the roots of Equations (3) and (4), which generate a quadratic equation in R , and taking the maximum real part. Taken from the absorption peak wavelengths, the diameters range from 3.89 nm for the first aliquot to 4.18 nm for the last aliquot. The wavelengths of the corresponding absorption peaks range from 475 nm to 538 nm, corresponding to the absorption of blue to green light and the transmission of yellow to red light, as expected.

Assuming a Gaussian distribution for the absorption/emission bands of CdSe crystals, from the estimated full-width-half-maximum (FWHM) plotted above, we calculate a standard of deviation, or a variance, of about 44.9 nm.

4.2 Cadmium Selenide nanocrystal absorption/emission energy shift

The peak absorption wavelength versus the peak emission wavelength for CdSe nanocrystals is plotted⁴ in Figure 8 with a superimposed linear fit. The constant term of -299 nm gives the energy shift from emission to absorption described above.

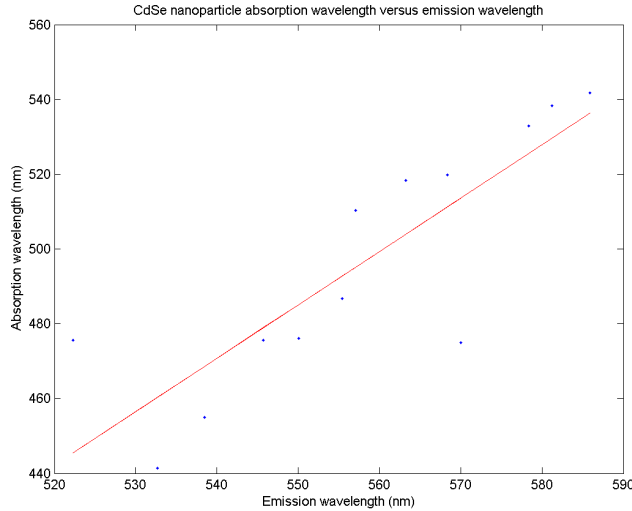


Figure 8: Relation between peak absorption and peak emission wavelengths for CdSe nanocrystals.

⁴I would plot this with error bars corresponding to the Gaussian variance from above, but I don't know how. This would indicated the quality of the coming linear fit.

4.3 Cadmium Selenide nanocrystal absorption/emission energy shift

The CdSe nanocrystal diameter versus absorption peak energy is plotted below in Figure 9. I attempted a least square curve fitting using Equation (1) with initial guesses $n = 1$ and m_c half the rest mass of an electron. Clearly, the shape of the curve and the data parallel each other, but something has not been accounted for. For one, Equation (1) assumes only an electron trapped in a box, and not an electron-hole pair.

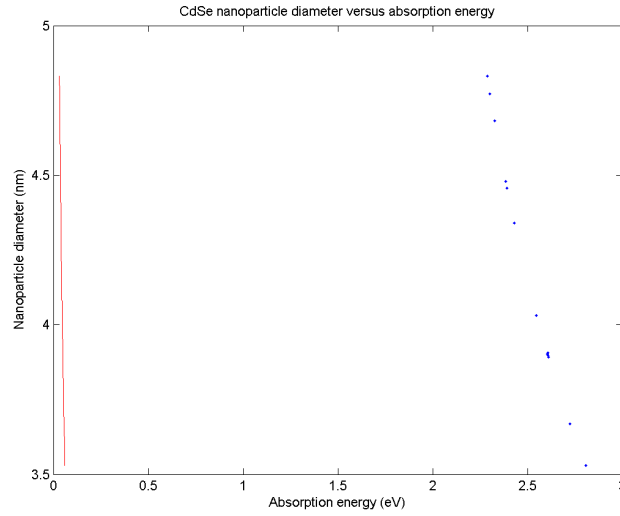


Figure 9: Relation between nanoparticle diameter and absorption energy for CdSe, fit with a particle in a box equation.

4.4 Simulated absorption spectrum for gold nanoparticles

The average number of gold atoms in a nanoparticle are given by

$$N = \frac{\pi \rho d^3}{6M} N_A, \quad (9)$$

where N_A is avogardo's constant, M is the atomic mass of gold, ρ is the density of gold, and d is the average diameter. This can be plugged into the following equation to give the molar concentration of gold as

$$C_m = \frac{N_T}{NVN_A}, \quad (10)$$

where N_T is the total number of gold atoms added in the procedure as HAuCl_4 , and V is the volume of the reaction solution. The extinction coefficient for the

gold nanoparticles at a particular wavelength is then given by

$$\epsilon(\lambda) = 3.0 \times 10^{-3} \frac{C(R, \lambda)}{\pi R^2} \frac{1}{C_m 4 \cdot 2.303 R}, \quad (11)$$

where C is the absorption cross section computed using Equations (6), (7) and (8). Using literature⁵ values for all the constants, most importantly an average gold nanoparticle radius of 6 nm, a simulated gold nanoparticle absorption spectrum⁶ is plotted below in Figure 10.

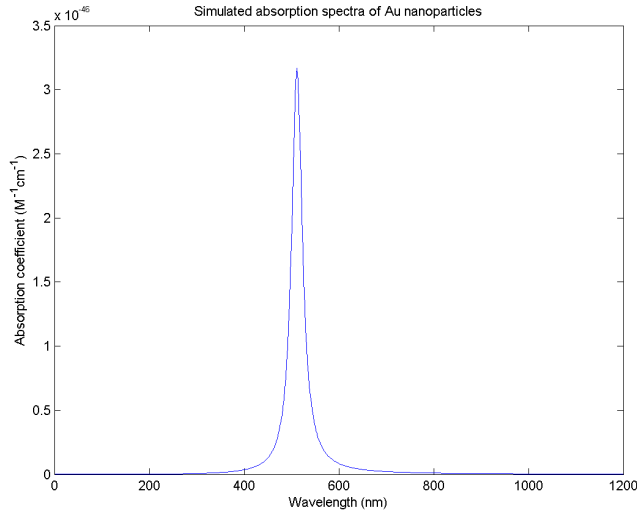


Figure 10: Simulated absorption spectra for gold nanoparticles.

It is possible to use MATLAB and the above equations to actually fit the extinction coefficient spectrum adjusted by the concentration of the solution to the gold nanoparticle spectrum using some sort of curve fitting. Given the giant size of the equations involved, I have simply included the simulated spectrum to give an idea of the theoretical shape.

5 Discussion

The citrate ions present in the gold nanoparticle solution forms a hydrophilic shell around the neutral metallic nanoparticles. The three carboxylic acid regions of the ion protect the particle. Addition of sodium chloride drastically increases the cation concentration. Aqueous chloride ions are much smaller and

⁵See procedure.

⁶The orders of magnitude of the units for the extinction coefficient may be off, but the shape is correct

more stable than giant citrate ions, so the sodium binds to it and draws the citrate off of the nanoparticles. I imagine gold, a heavy metal, has a poor index of refraction on it's own, so it transmits nothing when it aggregates. Thus, we see almost total absorbance above in Figures 6 and 7.

This lab has presented another view of quantum effects that show visible changes. It has also clarified the process by which we quantify and measure said somewhat subjective visual.