UC Berkeley College of Chemistry

Chemistry 125

Physical Chemistry Laboratory

Optical Properties of CdSe Nanocrystals

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1 Observations

Sample	Time Removed	Color	Color under UV
Sample 1	10.41 sec.	Yellow	Blue-green
Sample 2	20.60 sec.	Gold	Bright aquamarine
Sample 3	29.98 sec.	Orange	Green
Sample 4	87.46 sec.	Red-orange	Red-orange
Sample 5	111.90 sec.	Red-orange	Red-orange
Sample 6	118.68 sec.	Red	Red

Table 1: The colors of nanocrystal solutions under both visible and UV light, in terms of the amount of time they were allowed to react before being extracted.

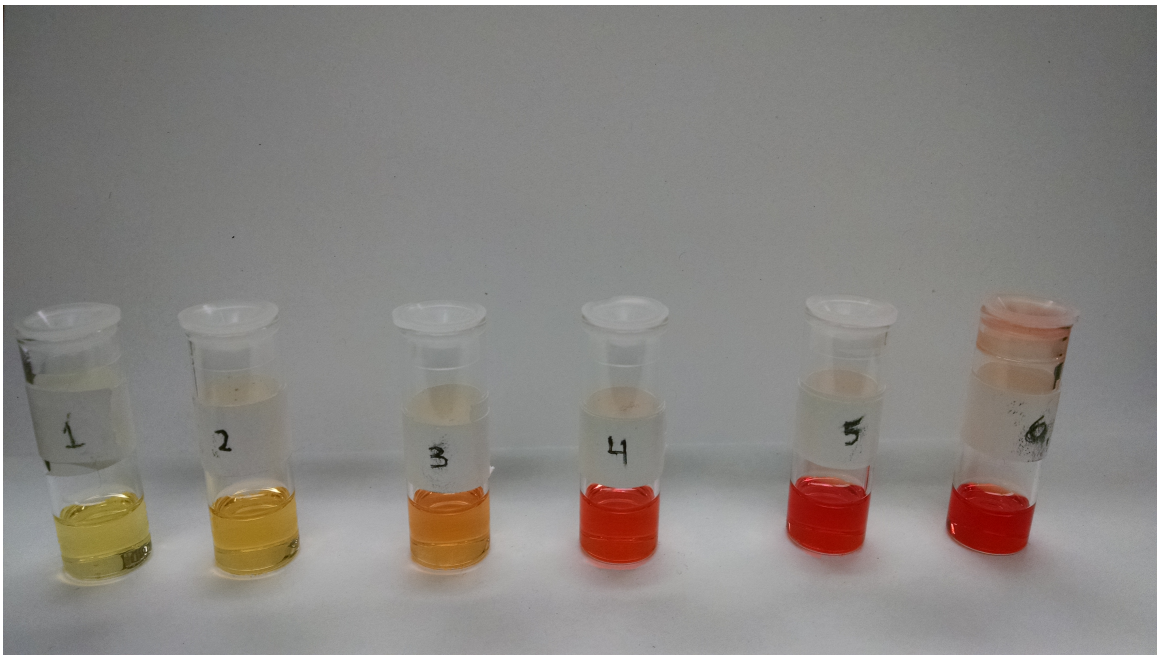

Figure 1: The nanocrystal samples, in order.

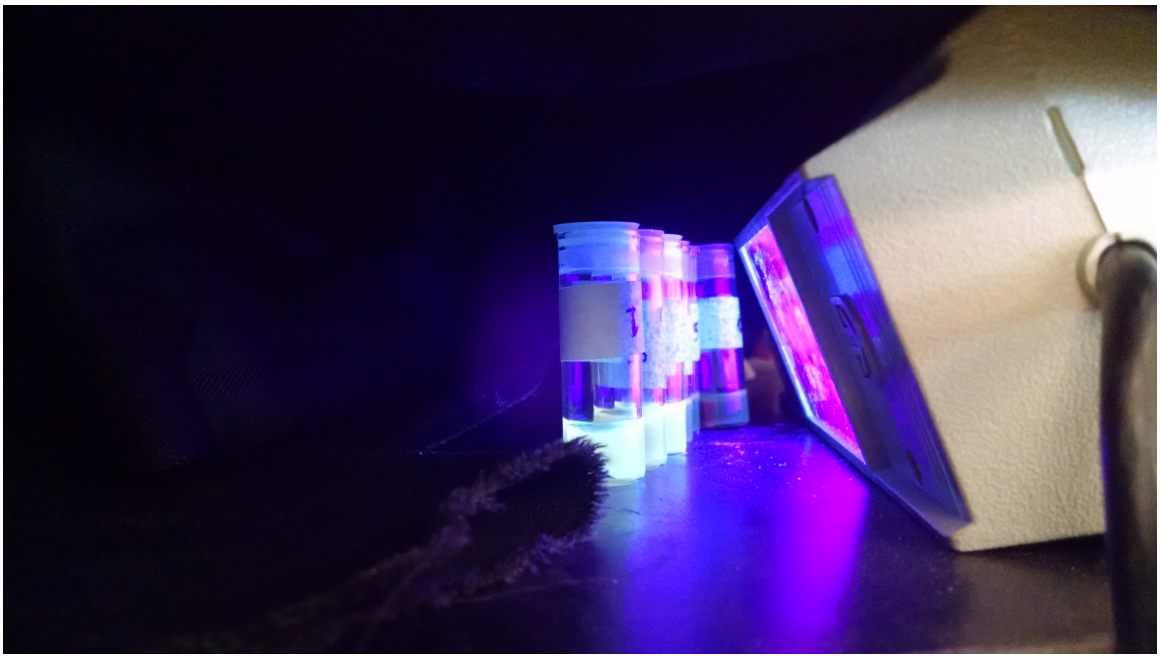

Figure 2: The nanocrystal samples fluorescing under UV radiation.

2 Raw Spectra

2.1 Absorption Spectra

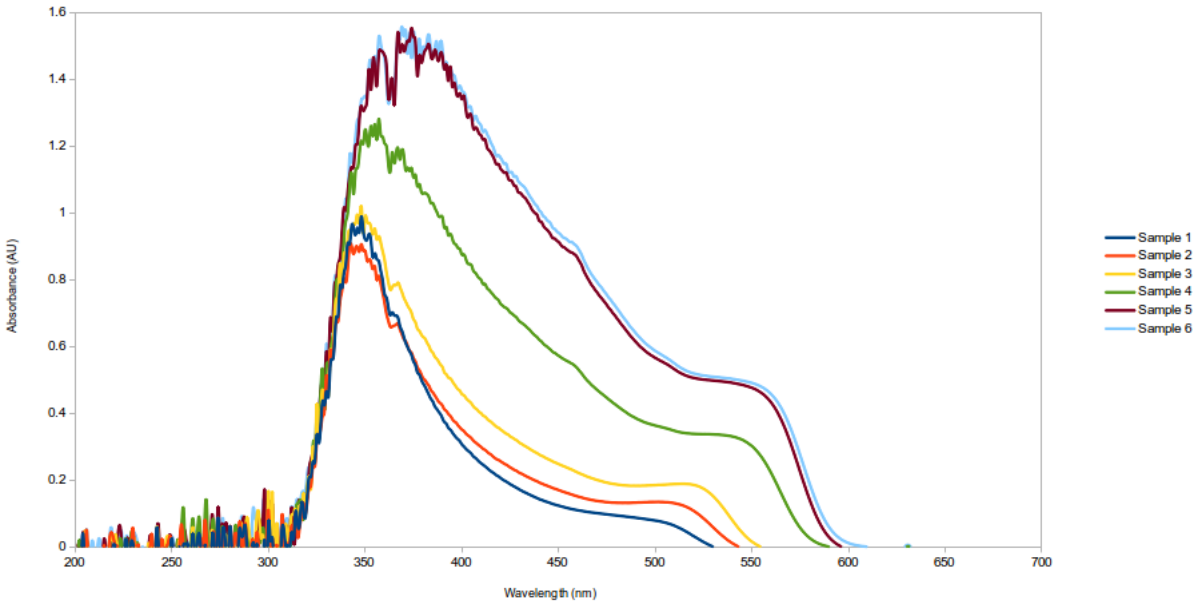

Figure 3: Absorbance spectra overlaid for all six nanocrystal samples.

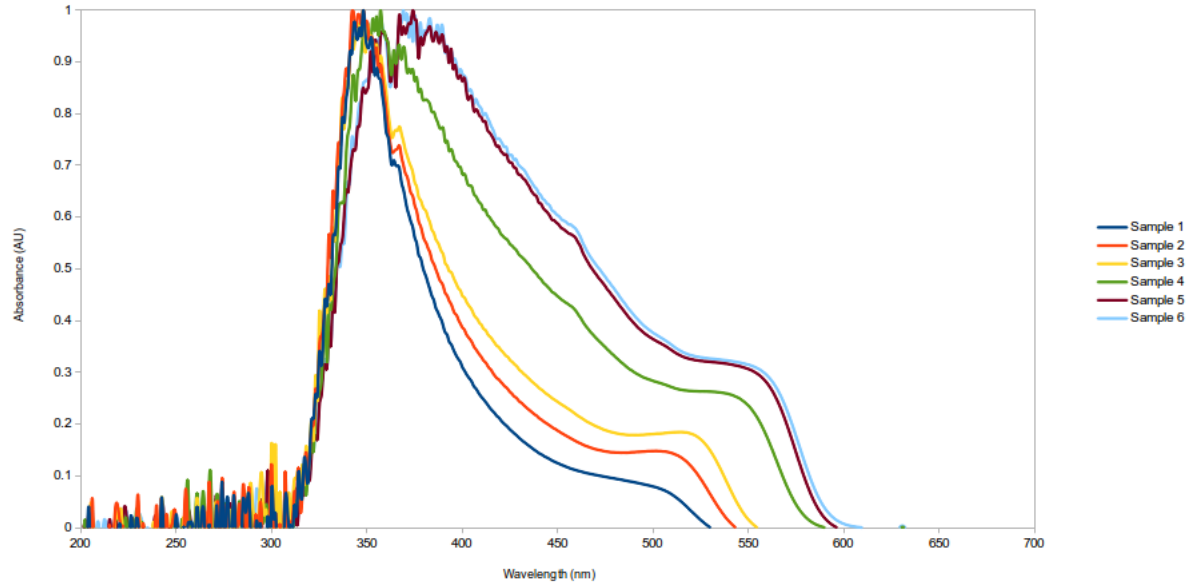

Figure 4: Absorbance spectra overlaid for all six nanocrystal samples, normalized to have the same max peak height.

2.2 Emission Spectra

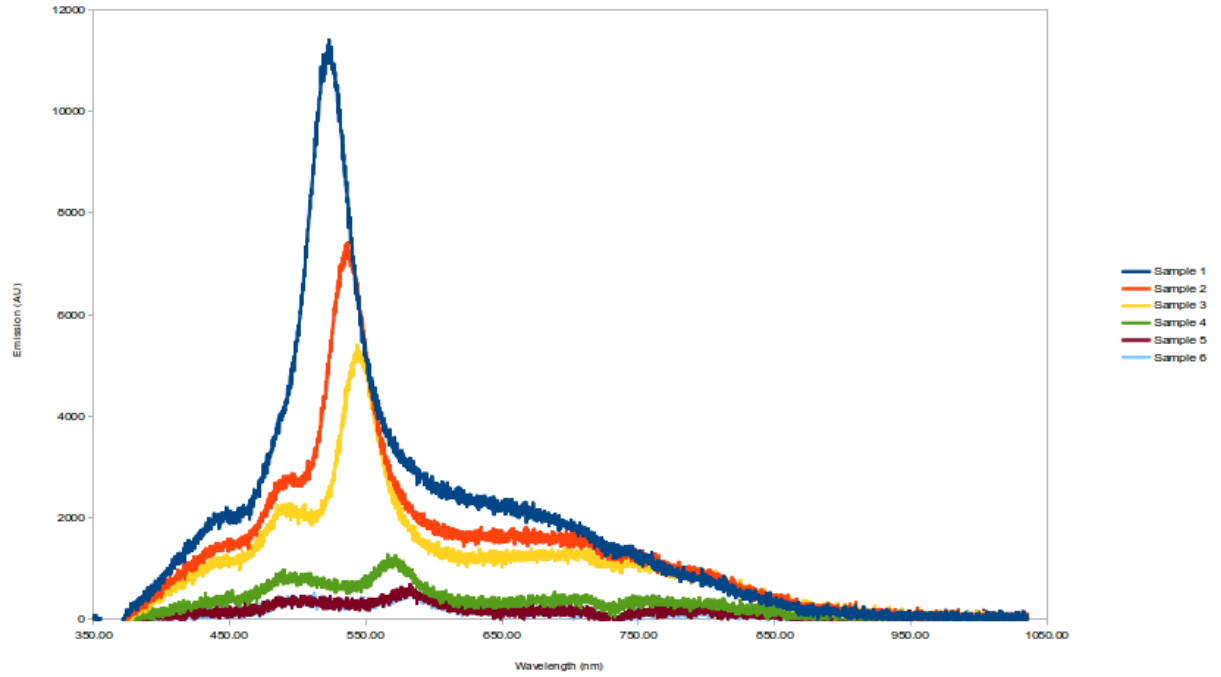

Figure 5: Emission spectra overlaid for all six nanocrystal samples.

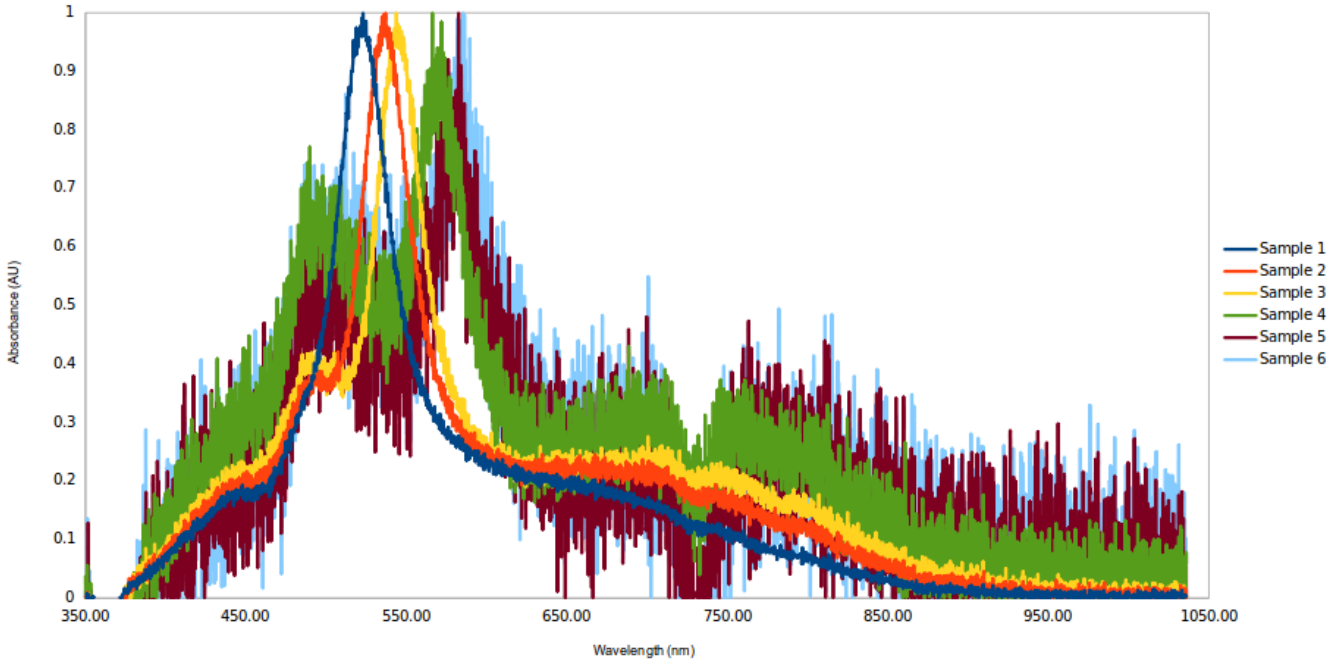

Figure 6: Emission spectra overlaid for all six nanocrystal samples, normalized to have the same max peak height. This has drastically increased the noise levels for some of the samples.

3 Collated Emission/Absorption Peak Values

Sample	Max Absorbance (nm)	Max Emission (nm)
Sample 1	487(3)	523(1)
Sample 2	504(3)	537(1)
Sample 3	515(2)	543(1)
Sample 4	528(2)	566(1)
Sample 5	534(2)	582(2)
Sample 6	537(2)	585(2)

Table 2: Peak absorbance and emission values for all six nanocrystal samples. Uncertainties in the last decimal place, in parentheses, were defined by instrumental parameters.

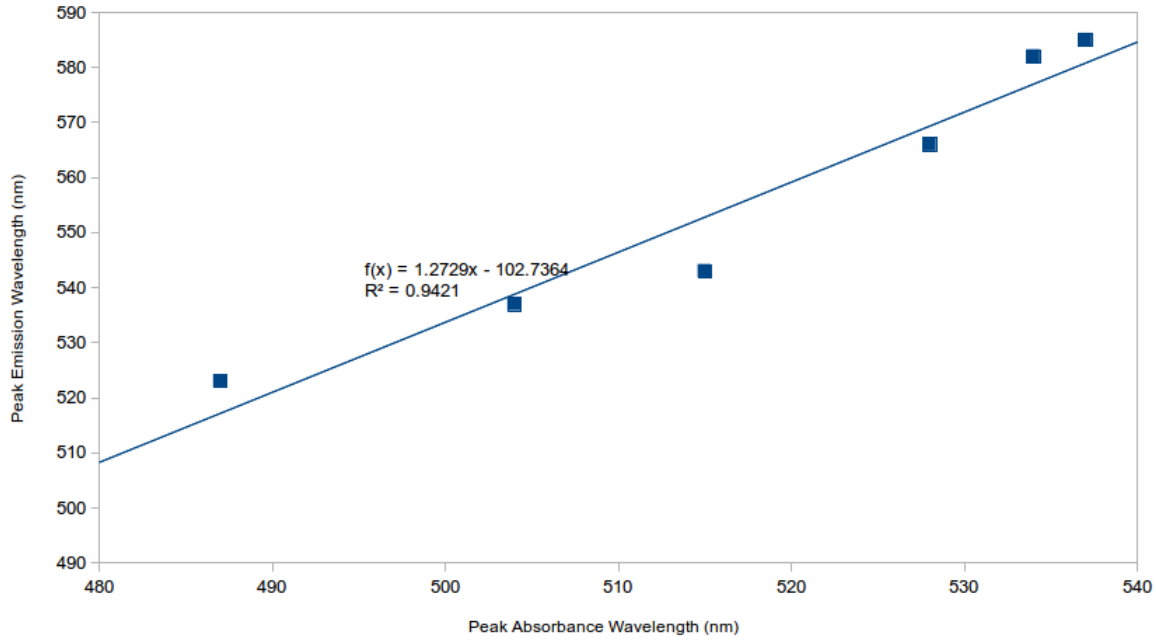

Figure 7: A plot of absorbance vs. emission data for all six nanocrystal samples, with a fit by Excel's LINEST().

4 Nanoparticle Size Calculation

The following polynomial fit for CdSe nanocrystal size was determined experimentally in Yu et. al.[1]:

$$D = 1.6122 \times 10^{-9}\lambda^4 - 2.6575 \times 10^{-6}\lambda^3 + 1.6242 \times 10^{-3}\lambda^2 - 0.4277\lambda + 41.57,$$

where D is the diameter of the nanocrystal in nanometers, and λ is the wavelength of the nanocrystal's first absorbance peak.

The uncertainty propagation equation for this equation is

$$\sigma_D = \sqrt{(4(\frac{\sigma_\lambda}{\lambda})(1.6122 \times 10^{-9}\lambda))^2 + (3(\frac{\sigma_\lambda}{\lambda})(2.6575 \times 10^{-6}\lambda))^2 + (2(\frac{\sigma_\lambda}{\lambda})(1.6242 \times 10^{-3}\lambda))^2 + ((\frac{\sigma_\lambda}{\lambda})(0.4277\lambda))^2}$$

Using this equation, the following nanocrystal radii and uncertainties can be determined:

Sample	Nanocrystal Radius (nm)
Sample 1	1.12(1)
Sample 2	1.19(1)
Sample 3	1.25(1)
Sample 4	1.33(1)
Sample 5	1.38(2)
Sample 6	1.40(2)

Table 3: Nanocrystal radii, calculated from their absorbance peaks and an experimentally-determined polynomial.

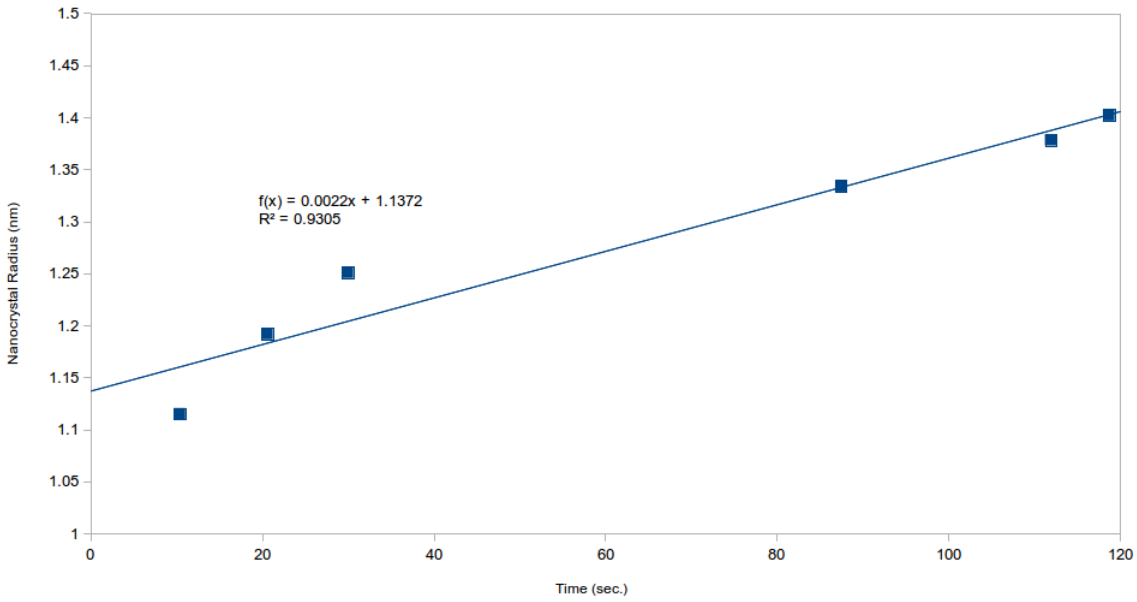

Figure 8: A plot of nanocrystal radius against the time each sample was reacted for (Table 1 on page 1).

5 Nanocrystal Excitation Energy Calculation

The lowest-energy excitation for the nanocrystals synthesized can be calculated using the following modified particle-in-a-box equation:

$$E_{ex} = \frac{h^2}{8R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1.8e^2}{4\pi\varepsilon_{\text{CdSe}}\varepsilon_0 R} + E_{pol},$$

where, in addition to an array of fundamental constants, E_{ex} is the excitation energy of the nanocrystal, R is the radius of the nanocrystal, m_e is the mass of an electron in a CdSe exciton (approximately 0.13 times the free-electron mass), m_h is the mass of a hole in a CdSe exciton (approximately 0.45 times the free-electron mass), $\varepsilon_{\text{CdSe}}$ is the bulk dielectric constant for CdSe (approximately 10.6), and E_{pol} is a complex function that accounts for the polarization of a nanocrystal by an internal point charge that can be reverse-evaluated from the following computationally-determined plot:

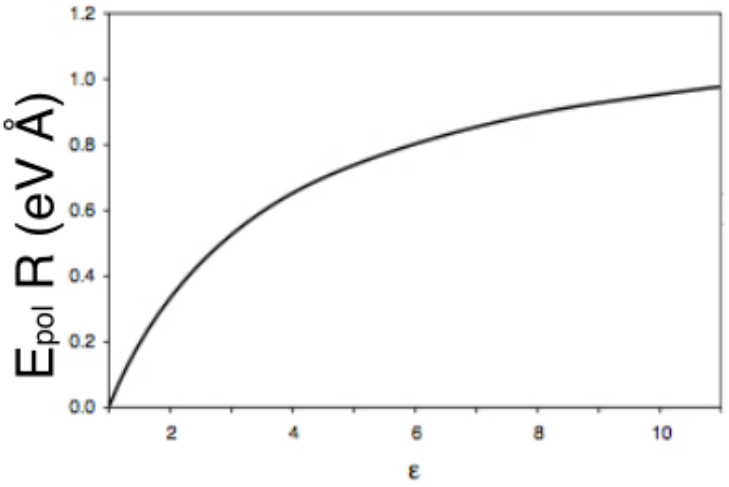

Figure 9: A plot of polarization energy times nanocrystal radius against $\varepsilon = \frac{\varepsilon_{\text{CdSe}}}{\varepsilon_{\text{outside}}}$, where $\varepsilon_{\text{outside}}$ is the permittivity of the solvent around the nanocrystal (in this case, octadecene, for which $\varepsilon_{\text{outside}} = 1.9$[3]).

Using $\varepsilon_{\text{CdSe}} = 10.6$ and $\varepsilon_{\text{outside}} = 1.9$ and looking at Figure 9, we can determine that $E_{pol}(\text{eV}) \approx \frac{0.8}{R(\text{Å})}$. Plugging everything into the two equations and summing the two terms, we can calculate the minimum excitation energies per particle:

Sample	**Radius (nm)**	E_{pol} **(eV)**	$E_{ex} - E_{pol}$ **(eV)**	E_{ex} **(eV)**
Sample 1	1.12(1)	0.071(2)	2.8(3)	2.9(4)
Sample 2	1.19(1)	0.067(3)	2.4(2)	2.5(1)
Sample 3	1.25(1)	0.064(2)	2.2(1)	2.3(1)
Sample 4	1.33(1)	0.060(1)	1.9(1)	2.0(1)
Sample 5	1.38(2)	0.058(1)	1.8(1)	1.8(1)
Sample 6	1.40(2)	0.057(1)	1.7(1)	1.8(1)

Table 4: Nanocrystal excitation energies, calculated from their radii and an extension of the particle-in-a-box equation.

The uncertainty propagation equation for this equation is

$$\sigma_{E_{ex}} = \sqrt{\left(\left(\frac{h^2}{8}\left(\frac{1}{m_e}+\frac{1}{m_h}\right)\right)\left(\frac{\sigma_R}{R}\right)(2R)\right)^2 + \left(\left(\frac{1.8e^2}{4\pi\varepsilon_{\mathrm{CdSe}}\varepsilon_0}\right)\left(\frac{\sigma_R}{R}\right)(R)\right)^2},$$

taking into account only errors in the radius and assuming all fundamental constants, literature values, and computational estimates have no intrinsic error.

References

[1] Yu, W. W., Qu, L., Guo, W., Peng, X. *Chem. Mater.* 15:2854 (2000)

[2] Kippeny, T., Swafford, L. A., Rosenthal, S. J.*J. Chem. Ed.* 79:1094 (2002)

[3] *List of common solvents by dielectric constant and refractive index.* http://www.stenutz.eu/chem/solv23.php

[4] Shoemaker, Garland, Nibler. *Experiments in Physical Chemistry, 8th ed.*; 2008.