Synthesis of CdSe Semiconductor Nanocrystals

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Introduction

Semiconductor nanostructures translate quantum-mechanical phenomena into unique, size-dependent, readily tunable electrical and optical properties.[1] These hold promising applications for photovoltaics and green energy, where nanocrystals have already been applied to engineer highly-efficient, economical solar cells.[2–4] Other inorganic nanostructures have also been found to catalyze CO_2 fixation,[5,6] serve as fluorescent biological imaging tags,[7,8] and even form single-electron transistors in nanoelectronics.[9] Each of these developments embody extensive potential applications in critical technologies and industries of our society.

Sadly, the presence of nanochemistry in modern research and industry dwarfs its presence in the university classroom. Despite being a topic of fierce discussion in both physics and chemistry for decades, the wide scope of nanochemistry is seldom discussed in undergraduate curricula. Even many graduate programs do not offer such courses. This set of experiments aims to change that by introducing modern synthetic techniques employed to generate nanostructures and the unique electrical and optical properties rising from the quantum phenomena they exhibit.

CdX (X = S, Se, Te) semiconductor spherical nanocrystals (i.e. quantum dots) display readily apparent optical properties, and are some of the simplest and most well-studied

nanostructures made in the laboratory. Modern syntheses involving relatively non-toxic elemental precursors have been well-established by Peng and colleagues, thus making CdX quantum dots ideal targets for study in the undergraduate laboratory.[10,11] Both shape and size are controlled simply by the CdO precursor concentration. At moderate CdO concentrations, monodisperse (i.e. similar to each other in size) spherical nanocrystals are replicably and easily synthesized. This is believed to occur due to diffusion-dependent crystal growth on certain faces of the nanocrystal upon heating.[12]

To provide a gentle introduction into the theory behind the optical properties of nanocrystals, one must first understand what happens during the absorption of a photon. It is well-established that in semiconductors, absorption of a photon results in the formation of a electron-hole pair, which can be roughly visualized as an electron (e) orbiting a positively-charged hole (h).[13,14] This is known as a Wannier-Mott exciton, and typically has a large corresponding Bohr exciton radius, far greater than that of the Bohr radii of the semiconductor's constituent atoms.

The Hamiltonian of a free Wannier-Mott exciton is trivially related by the expression

$$\hat{\mathcal{H}} = -\frac{\hbar}{2m_h}\nabla_h^2 - \frac{\hbar}{2m_e}\nabla_e^2 - \frac{e^2}{\epsilon|r_e - r_h|}, \tag{1}$$

where m_e (m_h) represents the effective mass of the electron (hole), and ϵ represents the dielectric constant of the semiconductor. This is entirely analogous to the Hamiltonian of the hydrogen atom. However, this equation must fail when the system undergoes quantum confinement, i.e. the nanocrystal radius is less than that of the exciton radius, and the exciton is no longer free. While a full derivation is beyond the scope of this paper, it suffices the mention that an additional polarization term $\hat{V}_{\text{pol}}$ must be included to account for the polarization of electric charge resulting from the formation of the exciton, which obeys a strong dependence on the radius of the spherical nanocrystal R. Following the derivation outlined by Brus, the energy of the lowest excited state of an exciton is approximated by the expression[15]

$$E = E_0 + \frac{\hbar^2\pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{\epsilon R} + \frac{e^2}{R}\overline{\sum_{n=1}^{\infty}\alpha_n\left(\frac{S}{R}\right)^{2n}}, \tag{2}$$

where E_0 is the bulk band gap, α is a constant dependent on the dielectric constant of the semiconductor and the surrounding solvent, and S is the position of the electron. The bar above the third term denotes that it should be taken as an integral over the entire wavefunction of the electron.

While this equation is complex, and can only be evaluated computationally, it is apparent that Equation (2) predicts the energy of the excited state decreasing monotonically with increasing radius. This is exactly analogous to the particle-in-a-box problem introduced in introductory physical chemistry, which also exhibits an inverse dependence between the energy E and the size of the box L.

Pedagogy

In this experiment, students will learn how to perform hot injection synthesis of CdSe quantum dots, arguably the most important synthetic technique in nanochemistry today. Students will encounter important topics in nanochemistry such as nanocrystal size, shape control, band gaps, and monodispersity. Furthermore, students will analyze the collected absorbance and fluorescence emission spectra to answer questions regarding the relationship between the semiconductor band gap and nanocrystal size, and the theoretical underpinnings of such behavior as discussed in the introduction and explained more extensively by Brus.[15] Students will also revisit concepts discussed during physical chemistry, such as the Stokes shift and selection rules, and draw connections between those concepts and the collected spectra.

Hazards

Octadecene is both viscous and flammable, and thus should be carefully handled near flames or sparks. Trioctylphosphine is especially corrosive and air-sensitive, and should only be transported via syringe from its packaging (typically in a Sure-Seal bottle). Oleic acid is air and light-sensitive, and is also an irritant. Both elemental Se and CdO are acutely toxic, and exposure can occur through inhalation, ingestion, or direct contact. All laboratory work should be handled in a well-ventilated fume hood with usage of standard PPE, including lab coats, nitrile gloves, and goggles. Waste should be disposed of as heavy metal waste. Glassware should be cleaned with soap and water.

Experimental Procedures

The synthesis of CdSe nanocrystals is adapted from Boatman and Kippeny and their respective coworkers.[16,17] To a three-necked 50 mL round-bottom flask is charged 13 mg CdO, 0.6 mL oleic acid, and 10 mL 1-octadecene (tech., 90%). Rubber septa should be placed on the side necks, and a thermal couple should be inserted through the rubber septum on a side neck. Insertion of the thermal couple can be difficult, and a small hole may be cut into the septum using a large needle or a scalpel. This thermal couple should then be connected to a heating mantle controlling the temperature of the round bottom flask. If a thermal couple is unavailable, a thermometer capable of measuring up to 300 °C can be used as a substitute, but this is less ideal.

The Se precursor is made with 30 mg ground Se, 5 mL of 1-octadecene, and 0.4 mL trioctylphosphine in a glass scintillation vial with a stir bar. This is to be heated and stirred until the Se is fully dissolved.

Next, the round-bottom flask is stirred vigorously and heated to 225 °C, after which 1 mL of the Se precursor is injected into the flask. Immediately, the solution should immediately turn a cloudy black and rapidly progress towards a clear, highlighter-yellow. Ten 1 mL

samples are taken with a Pasteur pipette within 3 minutes of injection, with more samples being taken early in the reaction. A stopwatch should be used to record the time intervals following injection. These samples are then supposed to be stored in glass scintillation vials, and the nanocrystals are allowed to ripen overnight to maximize monodispersity.[18]

The CdSe aliquots should all then be transferred into centrifuge tubes, and precipitated with 5 mL acetone. The aliquots are then to be centrifuged at 10000 rpm for 10 minutes. As many of the students have not used a centrifuge prior, it is imperative that the instructors emphasize the importance of balancing the centrifuge rack to prevent damage to such expensive instrumentation. The supernatant is to be discarded, and the nanocrystals should be re-dispersed in 1 mL hexane. This removes excess reagent and impurities formed during the synthesis, and minimizes background of subsequent spectra. UV-vis and fluorescence (400 nm excitation) spectra of each aliquot should then be taken in glass cuvettes.

Results and Discussion

It is expected that students complete this experiment over two separate lab periods, the first involving the synthesis and the second involving the purification and spectrum acquisition. The first lab period is expected to take roughly 90 to 120 minutes, including the glassware cleaning afterwards. The second lab period is expected to take at least 90 minutes as well, because students will likely have to queue to use the centrifuge.

Reporting nanocrystal yields is seldom performed in literature due to its impracticality and complexity. This is because of the competing differences in size, shape, ligand type, and ligand distribution of each nanocrystal. Thus, a simple mass-based calculation of reaction yield is ultimately meaningless, and is not expected of the students. However, students should be able to estimate the nanocrystal diameter and quality of each aliquot based on absorbance and fluorescence spectra.
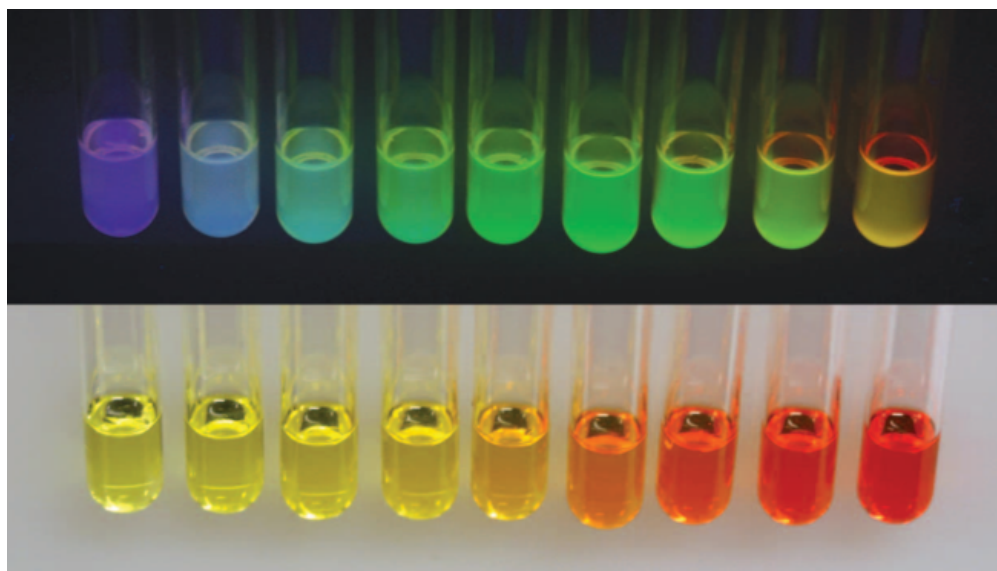
Figure 1: Various aliquots of CdSe nanocrystals, arranged from left to right in order of increasing size. Below: Color of CdSe quantum dots under ambient conditions. Above: Color of CdSe quantum dots under a UV blacklight. Reprinted from Boatman and colleagues.[17]

**(a)**   **(b)**
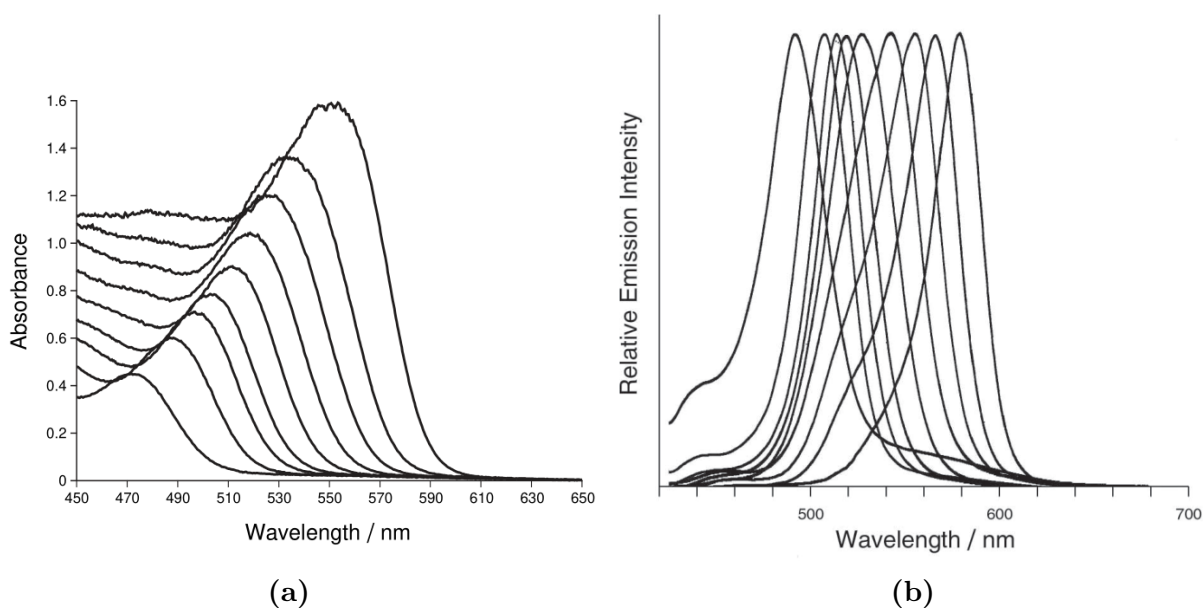
Figure 2: Absorbance spectra (a) and fluroescent emission spectra at 400 nm excitation (b) of CdSe nanocrystals of various sizes. Larger nanocrystals correspond to higher wavelength absorbance and emission. Reprinted from Boatman and colleagues.[17]

Rather than using yield as the basis of reaction quality, monodispersity should be used.

Monodispersity can be qualitatively determined by the peak width (full-width, half-maximum)

of the absorbance and fluroescence spectral peaks, with thinner peaks indicating a higher degree of monodispersity. Instructors may also provide spectra of nanocrystals both before and after ripening, and ask students to interpret differences between the spectra.

Absorbance and fluorescence spectra should reveal that larger CdSe nanocrystals (taken from aliquots which underwent a longer reaction time) have correspondingly redshifted absorbance and emission peaks. This is in agreement with the theoretical Wannier-Mott exciton band gap detailed in the introduction and summarized in Equation (2), which predicts a lower band gap for larger nanocrystals. These spectra should resemble those presented in Figure 2, but with less background at lower wavelengths due to the removal of impurities during centrifugation.
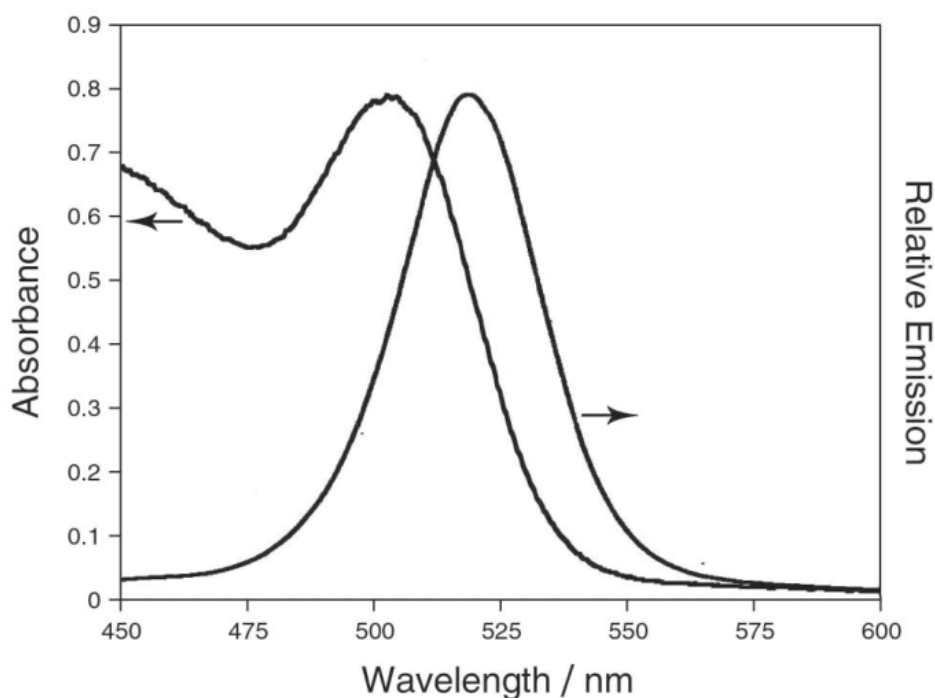
Figure 3: Stokes shift observed for a given size CdSe quantum dot. Reprinted from Boatman and colleagues.[17]

There should also be a noticable Stokes shift between the wavelengths of the absorbance and emission peaks, coupled with a lower peak width of emission peaks, as shown in Figure 3. Especially gifted students should be able to explain these two phenomena in terms of

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non-radiative transitions and selection rules. Finally, if possible, TEM imaging of students'
samples should also be collected, to demonstrate the monodispersity and spherical shape
control of this technique.

Conclusion

In conclusion, this experiment aims to introduce undergraduates to the frontier of nanochem-
istry and demonstrate the hot-injection technique employed to synthesize CdSe nanocrystals.
Students are asked to discuss the relationship between nanocrystal size and the peak loca-
tion and width in the absorbance and fluorescence spectra. Furthermore, topics such as
Wannier-Mott excitons, band gaps, and polarization energies should be discussed to further
emphasize the theoretical underpinnings of the relationship between spectra and theory.

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