

A Safer, Easier, Faster Synthesis for CdSe Quantum Dot Nanocrystals

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Properties that vary with particle size are an important feature of nanoscale materials. CdSe quantum dot nanocrystals vary in color from green–yellow to orange–red and luminesce from blue to yellow, where shorter wavelength, higher energy, electronic transitions correspond to smaller crystal sizes. CdSe quantum dot nanocrystals are a visually engaging way to demonstrate quantum effects in chemistry, since their transition energies can be explained as a “particle in a box,” where a delocalized electron is the particle and the nanocrystal is the box. Readers are referred to the article by Kippeny and coworkers in a previous issue of this *Journal* that contains additional background information and a theoretical discussion (1). CdSe nanocrystal solutions are also an example of colloidal suspensions where nanocrystals do not settle out of solution and cannot be readily filtered.

The synthesis provided here has several advantages over the previous method (1). Others note that the starting materials in that preparation, especially dimethyl cadmium, are extremely toxic, expensive, unstable, explosive, or pyrophoric, making the system difficult to control or reproduce (2–4). Peng and others (4–9) have pioneered the kinetic synthesis of CdSe nanocrystals from CdO and elemental Se as an example of green chemistry, where relatively safe materials are used, although the hazards associated with the CdO and Se should not be overlooked. This procedure is suitable for students who can exercise careful handling of reagents and is most applicable in an inorganic or physical chemistry course.

Additional advantages of the method reported here are that inert atmosphere techniques are not required and that the resulting crystals are grown at a significantly lower temperature (225 °C). Lab preparation and synthesis of a series of CdSe nanocrystals can be easily accomplished within one hour, producing a similar CdSe absorption series as that reported by Peng and Peng (4). The resulting CdSe nanocrystal solutions yield high quality absorbance and emission spectra with particle sizes (10) ranging from approximately 1.8 nm to 4.0 nm and emission wavelengths ranging from 490 nm to 580 nm.

CdSe Nanocrystal Synthesis

CdSe nanocrystals are synthesized from CdO and elemental Se using a kinetic growth method where particle size depends on reaction time.

A stock solution of Se precursor may be prepared ahead of time by combining 30 mg of Se and 5 mL of 1-octadecene (tech., 90%) in a 10-mL round-bottom flask clamped over a stirrer hot plate. A syringe is used to measure 0.4 mL of trioctylphosphine from its Sure-Seal bottle to the same 10-

mL flask. A magnetic stirbar is added and the solution is stirred. It may be warmed as necessary to speed dissolution of the Se. The stock solution is stored at room temperature in a sealed container and has enough Se precursor for five preparations.

Each student prepares his own Cd precursor by adding 13 mg of CdO to a 25-mL round-bottom flask clamped in a heating mantle. To the same flask 0.6 mL of oleic acid and 10 mL of octadecene are added. A thermometer capable of measuring 225 °C is inserted, the temperature to which the flask is then heated. When the temperature reaches 225 °C, 1 mL of the room-temperature selenium solution is transferred to the 225 °C cadmium solution. Because the characteristics of the products depend on reaction time, one should begin timing when the selenium solution is added. A 9-inch Pasteur pipet is used to remove and quench approximately 1-mL samples at frequent time intervals, as quickly as possible in the beginning and when noticeable color change is detected at later times. Obtain nine or ten samples within two to three minutes (Figure 1).

The visible absorption and emission spectra of individual samples are recorded to find maximum wavelength peaks. An excitation wavelength of 400 nm can be used for all emission samples. The concentration of reaction solutions is appropriate for measurements in 1-cm glass or polystyrene small-volume cuvettes with no further sample preparation.

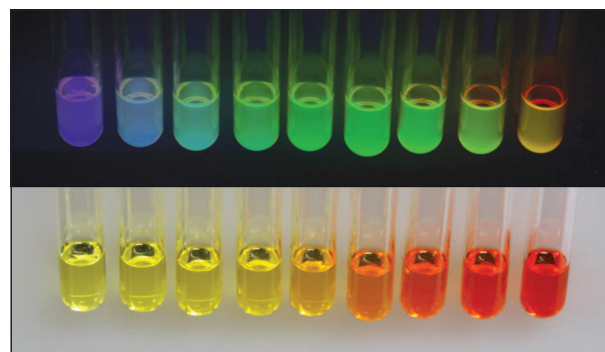


Figure 1. Colloidal suspensions of CdSe quantum dots of increasing size from left (approximately 1.8-nm diameter) to right (approximately 4.0-nm diameter). Bottom: Samples viewed in ambient light vary in color from green–yellow to orange–red. Top: The same samples viewed under long-wave ultraviolet illumination vary in color from blue to yellow.

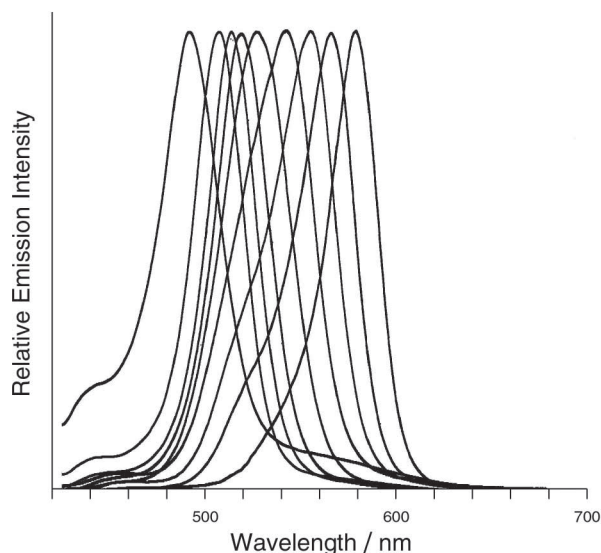


Figure 2. Normalized emission spectra of the samples in Figure 1 using 400-nm excitation. The samples were withdrawn from the reaction mixture in order from left to right at an initial time of 8 seconds after selenium addition to a final time of about two minutes after addition. Longer wavelength, smaller energy emission corresponds with larger particle sizes.

Hazards

Octadecene vapor should not be inhaled, and contact with skin and eyes should be avoided. Trioctylphosphine is corrosive and causes burns; it should be transferred exclusively by syringe from its Sure-Seal bottle. Oleic acid is air, light, and heat sensitive and irritating to eyes, the respiratory system, and the skin. Elemental selenium is toxic by inhalation, by absorption through the skin, and the effects of ingestion are cumulative. Cadmium oxide is highly toxic and cadmium compounds are known to be human carcinogens if inhaled or swallowed. All work should be carried out in a fume hood with careful handling of reagents to especially prevent inhalation of solids. Wear nitrile gloves. Leftover cadmium, selenium, and CdSe octadecene solutions should be collected in a waste container for proper disposal. Glassware cleans up readily with soap. Additional hazards information is available in ref 11.

Results and Discussion

A major goal in synthesizing nanocrystals is the production of monodisperse particles. Monodisperse means the particles exhibit a relatively narrow size distribution, resulting in narrow absorbance and emission peaks. Such particles are preferred for labeling studies where different quantum dot sizes are used as different labels. One excitation wavelength causes many different-sized nanoparticles to fluoresce at their respective peak emission wavelengths with narrow and non-overlapping emission spectra enabling multiple labels to be simultaneously observed (12).

Experimental emission spectra for 400-nm excitation possess a highly pronounced and relatively narrow peak, ~35 nm at full-width, half-maximum (Figure 2). The peaks move

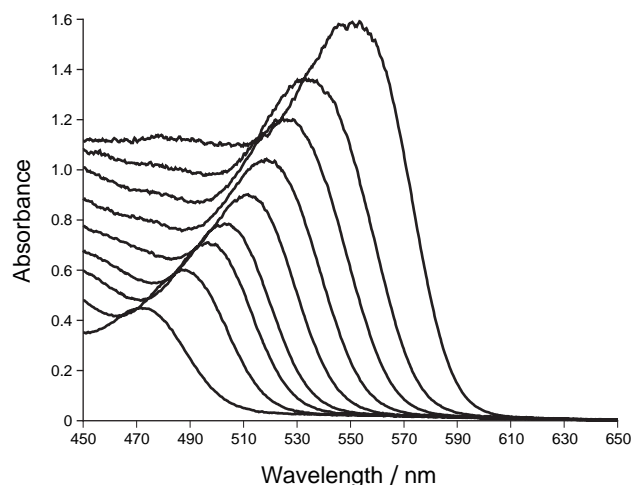


Figure 3. Visible absorption spectra of the samples in Figure 1. The samples were withdrawn from the reaction mixture in order from left to right. Longer wavelength, smaller energy emission corresponds with larger particle sizes.

toward the red end of the visible spectrum with growth time, as expected from the “particle in a box” theoretical prediction where longer time corresponds with larger crystals, lower energy electronic emission, and longer wavelengths. TEM measurements of CdSe nanocrystals by others suggest that such wavelengths correspond to 2–4 nm diameter crystals (10) with at most a few hundred atoms. **As nanocrystals grow, their peak emission quickly approaches the band gap of bulk CdSe (730 nm).**

While the absorbance spectra are less clear, there is still an observable peak maximum that shifts from violet to green with increasing crystal size (Figure 3). The absorption spectra show peak maxima with additional absorption at lower wavelengths due to starting materials and oleic acid polymerization. Fortunately the experiment finishes within several minutes at 225 °C; heating oleic acid and octadecene alone yields increasing visible absorption at increasing wavelengths over time as the effects of oleic acid polymerization become noticeable.

The absorption maxima occurs at higher energies than the emission maxima, Figure 4. Because molecules with excited electrons normally have weaker bonds than molecules with electrons in the ground state, fluorescence is normally of lower energy (longer wavelength) than absorbance. The difference between the excitation and emission wavelengths is known as the Stokes shift and **for the particle sizes prepared here remains relatively constant as suggested by the slope of nearly one in Figure 5.** When small molecules are used in fluorescence labeling studies the Stokes shift indicates the ability to separate the excitation peak from the emission peak. Because of additional nearby energy levels, semiconductor nanoparticles can be excited by photons with greater than or equal to the minimum absorption energies (Figure 6). For example, the same excitation wavelength of 400 nm is used for all samples in Figure 2, demonstrating the effective Stokes shift can be hundreds of nanometers. Thus when different size quantum dots are used for multiple labels, all the labels can be excited and detected simultaneously.

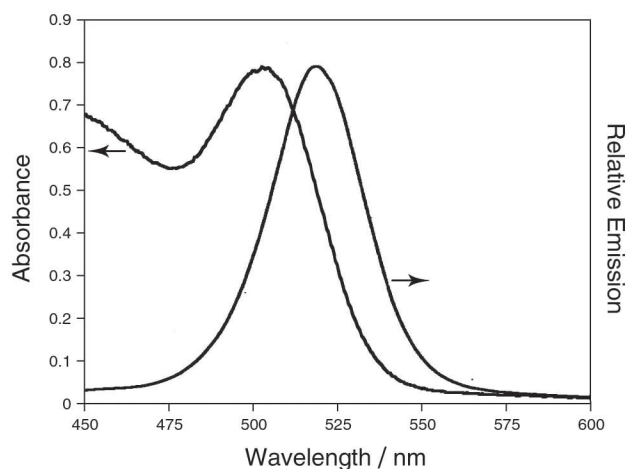


Figure 4. For a given size quantum dot the absorption maximum (peak at left) occurs at higher energy than the emission maximum (peak at right).

As a colloidal solution, the CdSe nanocrystals will stay suspended in solution and cannot be filtered out. The oleic acid acts as a surfactant, binding to the exterior of the crystal lattice and allowing for the crystals to remain soluble in the octadecene (13).

Acknowledgments

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Supplemental Material

Instructions for the students and notes for the instructor are available in this issue of *JCE Online*.

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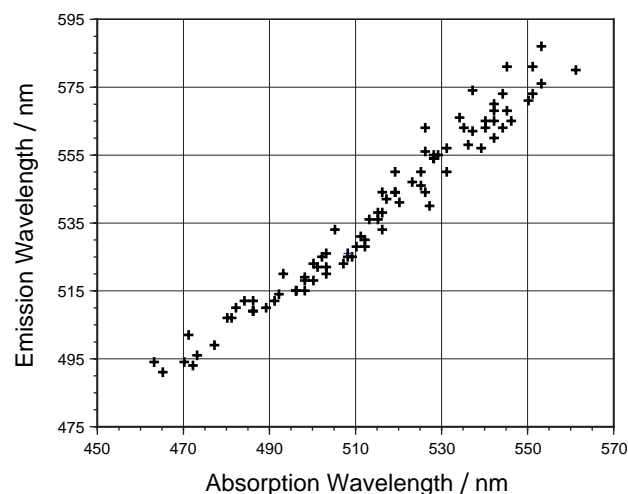


Figure 5. Absorption maxima correlate with emission maxima for CdSe quantum dots.

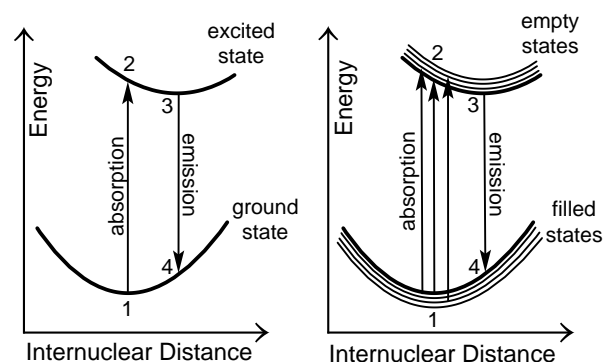


Figure 6. Relationship between absorption and emission energies for discrete molecules (left) and for semiconductor nanoparticles (right). When a photon is absorbed thereby exciting an electron from the ground state (1) to an excited state (2) the bond order decreases and the atoms relax to a longer internuclear distance (3) before emission of a photon (4) and relaxation to the ground state (1). In semiconductor nanoparticles the process is the same (steps 1–4) but there are more possibilities for the energy of the excitation photon to match an electronic energy transition.

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