

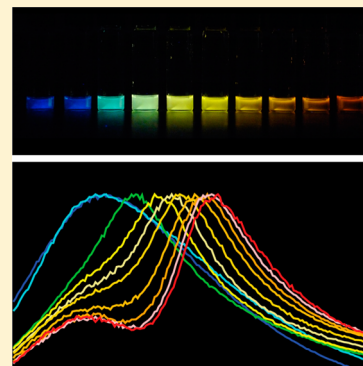
Simple Syntheses of CdSe Quantum Dots

Matthew L. Landry,[†] Thomas E. Morrell, Theodora K. Karagounis,[†] Chih-Hao Hsia, and Chia-Ying Wang*

Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States

S Supporting Information

ABSTRACT: Quantum dots are an excellent resource for demonstrating quantum phenomena. Two new methods for synthesizing quantum dots are presented. Proceeding at relatively low reaction temperatures, these exercises are safe and easy to conduct in an undergraduate student laboratory. The quantum dots prepared from the first method exhibited visible luminescence across a broad range of colors. The size-dependent spectral properties of quantum dots were examined quantitatively in the second method. Following this procedure, students in an advanced chemistry laboratory course synthesized their own quantum dots and gained experience with these important nanomaterials.



KEYWORDS: Upper-Division Undergraduate, Inorganic Chemistry, Laboratory Instruction, Physical Chemistry, Hands-On Learning/Manipulatives, Materials Science, Nanotechnology, Quantum Chemistry, Synthesis, UV-Vis Spectroscopy

Quantum dots (QDs) are semiconductor nanocrystals that display remarkable optical properties including bright luminescence, a broad excitation profile, narrow emission peaks, and exceptional photostability.¹ Absorption and emission spectra of QDs can be finely tuned by changing their size. These nanostructures have been investigated for a wide variety of applications, such as optical probes for imaging, target labeling, temperature sensing, and sensitizers for solar cells.^{1–6} Beyond their important applications, QDs are also a valuable educational tool. Because their size-dependent optical properties can be explained using a simple particle-in-a-box model, QDs serve as an excellent example to illustrate the application of quantum chemistry. In particular, QDs consisting of cadmium (Cd) and selenium (Se) absorb and emit visible radiation, which allows students to visually observe size-dependent quantum phenomena. The large Bohr radius of CdSe QDs (5.6 nm)⁷ also offers a broad range of sizes to study quantum confinement effects.

Early CdSe QDs syntheses are not suitable for an undergraduate student laboratory setting, as they are both hazardous and complicated, utilizing highly toxic and air-sensitive reagents, for example, dimethylcadmium and bis-(trimethylsilyl)selenium.^{8,9} Also, most early syntheses were conducted at high temperatures above 200 °C. Peng et al. later improved upon these procedures by employing safer chemicals, such as cadmium oxide and elemental Se.¹⁰ Based on their methods, Lisensky and co-workers developed a more accessible approach for generating CdSe QDs, which has since been adopted widely in teaching laboratories.¹¹ Their approach involves heating the Cd precursor solution to 225 °C and

adding the Se precursor solution into the Cd solution to initiate the reaction.

Over the past several years, reaction temperatures employed in QD syntheses have been gradually decreased. Very recently, Bartl and co-workers successfully synthesized high quality CdSe QDs at temperatures well below 200 °C.¹² The toxicity of the starting material is further reduced by utilizing cadmium acetate dihydrate, as well as lower concentrations of reactants as compared to the conventional high-temperature procedures. By injecting two precursor solutions simultaneously into a third growth solution containing fatty amine ligands (octylamine or octadecylamine), the authors were able to synthesize CdSe QDs under an inert gas atmosphere at temperatures ranging from 50 to 130 °C. The growth of CdSe nanocrystals is slower at lower temperatures, but the optical properties of the final products are comparable after reaction times of few hours to several days.

Inspired by this research, we developed two robust methods for generating CdSe QDs under ambient atmosphere in an undergraduate student laboratory. An optimized reaction temperature of 165 °C is employed, so students can finish the synthesis and characterization of the QDs within a reasonable period of time. More importantly, this relatively low temperature is safe, easy to achieve, and allows the reaction to proceed at a more comfortable rate for less experienced students. In addition, both methods utilize stock solutions with a significantly reduced concentration of each metal component. These solutions can be prepared in advance and minimize the students' exposure to toxic cadmium-containing solids. The first

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method, which does not include the use of an exogenous amine ligand, produces a series of visually bright CdSe QDs spanning the full visible spectrum (from blue to orange-red). Hence, students can observe size-dependent properties even without using a spectrometer. The second method, in which a small quantity of oleylamine is added to the growth solution, produces a series of exciton-emission CdSe QDs appropriate for in-depth spectral analysis and size determination. As the syntheses only differ by one reagent, these two methods offer easily accessible options to the instructors. These simpler and safer procedures greatly improve the feasibility of synthesizing nanomaterials in an undergraduate experimental course. In fact, both procedures were first established by two third-year students as an independent project in an upper-level chemistry laboratory course. The second procedure was then implemented successfully with the entire class in following years. Working in pairs, students completed the synthesis in one 3-h laboratory session and the spectroscopic characterization in the second session. Representative results collected by students are presented in Figures 2–5.

■ SYNTHESIS OF CdSe QUANTUM DOTS

Overview

CdSe quantum dots (QDs) are produced by simultaneously injecting cadmium (Cd) and selenium (Se) precursor solutions into a heated growth solution of octadecene in ambient atmosphere. Once combined, Se and Cd form CdSe clusters that become continually growing QDs as the reaction progresses. The precursor solutions may be prepared in advance by instructors or by students at the beginning of the laboratory period. Details of the syntheses are described below. The two procedures follow essentially the same steps, except for an additional reagent, oleylamine, which is required in the second procedure. Figure 1 schematically illustrates these two procedures.

Procedure 1

The Se precursor solution was prepared by combining 99 mg of Se powder and 5.5 mL of trioctylphosphine in a 25 mL round-bottom flask. The metallic Se dissolves readily at room temperature via stirring with a magnetic stir bar.

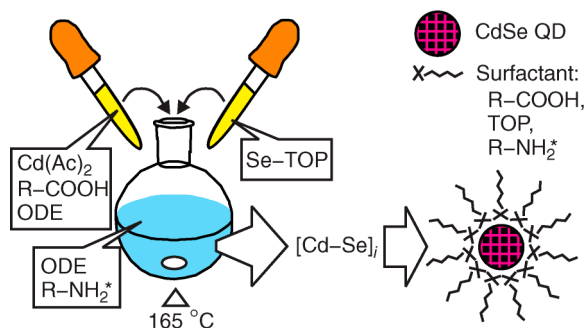


Figure 1. Experimental setup for the low-temperature synthesis of CdSe QDs. The Cd precursor solution contains cadmium acetate ($\text{Cd}(\text{Ac})_2$), oleic acid (R-COOH), and octadecene (ODE). The Se precursor solution contains Se and trioctylphosphine (TOP). ODE is the growth solution for procedures 1 and 2, whereas oleylamine (R-NH_2^*) is added for procedure 2. $[\text{Cd-Se}]_i$ represents the CdSe cluster initially formed, which then grows into the CdSe nanocrystal (CdSe QD). CdSe QDs are covered by various surfactants in the solution.

The Cd precursor solution was prepared by combining 53 mg of cadmium acetate dihydrate, 0.6 mL of oleic acid, and 5.5 mL of octadecene in a 25 mL round-bottom flask. A magnetic stir bar was added to the flask and the solution was stirred and warmed to 130°C . These two precursor solutions may be used for five syntheses.

The growth solution was prepared by adding 10 mL of octadecene into a 25 mL round-bottom flask with a magnetic stir bar. This solution was then stirred and heated to 165°C . Once the temperature of the growth solution has equilibrated, 1 mL of each precursor solution was injected into the growth solution simultaneously. The formation of CdSe clusters begins as soon as the precursor solutions are combined; so students should start the timer immediately after the addition of the precursor solutions. Over the course of 7 min, students withdrew 10 aliquots, approximately 1 mL each, of the reaction solution. The samples were withdrawn more quickly in the beginning so as to maximize the range of QD sizes (colors). Recommended withdrawal times are listed in the Instructor Notes (Supporting Information). After the aliquots have cooled, the luminescence of CdSe QDs was observed via a short-wavelength ultraviolet lamp.

Procedure 2

The Se and Cd precursor solutions were prepared as explained in procedure 1. The growth solution contains 10 mL of octadecene and 0.67 mL of oleylamine. When the growth solution has reached 165°C , the Cd and Se precursor solutions were added to start the formation of CdSe QDs. Following similar time intervals, ~ 1 mL of aliquots were withdrawn consecutively. Afterward, samples were allowed to cool and were transferred to a 1-cm cuvette. The absorption and emission spectra were measured directly without further dilution. An excitation wavelength of 400 nm was used for all emission spectra. The recommended wavelength scan range for the emission measurement is between 410 and 700 nm.

■ HAZARDS

Standard laboratory safety precautions should be used during the syntheses, including the wearing of nitrile gloves, protective clothing, and safety goggles. It is important to note that all the preparations and syntheses should be executed in a well-ventilated fume hood. Octadecene and oleic acid vapors should not contact skin or eyes or be inhaled. Trioctylphosphine and oleylamine cause skin burns and eye damage; they should be handled exclusively with a syringe. Metallic selenium is toxic if inhaled and may be harmful if swallowed or absorbed through skin. Cadmium acetate dihydrate is toxic if inhaled or swallowed and is known to be carcinogenic to humans. Any cadmium-containing solutions should be collected in a separate waste container for proper disposal.

■ RESULTS

Procedure 1: Bright Visible Luminescence

Under ambient light, the synthesized CdSe QDs from both procedures appear colorless to reddish orange. When irradiated with a short-wavelength ultraviolet lamp, the colorless samples from procedure 1 glow blue to green and the colors of the yellow, orange, and red QDs become more pronounced, as shown in Figure 2. The colors of luminescence change with reaction times. This change in color indicates the varying sizes of the QDs. This ultra bright luminescence may result from the emission of surface-trapped states of the QDs, which renders

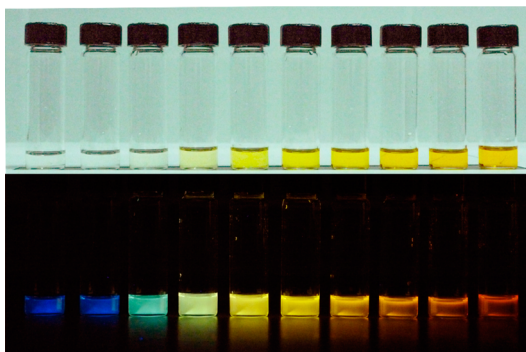


Figure 2. Visible light illuminated (top) and short-wavelength UV light illuminated (bottom) CdSe QDs from procedure 1. The reaction time increases from left to right.

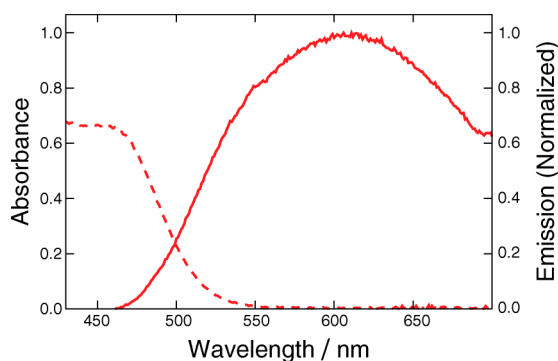


Figure 3. Absorption (left, dashed-line) and normalized emission spectrum (right, full-line with 400 nm excitation) of a CdSe QDs sample collected near the end of reaction from procedure 1. The large red shift and the dramatic broadening of the emission peak are consistent with the trap-state emission.

their emission spectra very broad and significantly red-shifted relative to their absorption peaks (see an example in Figure 3). Full spectra of all samples are provided in Figures S1 and S2 (Supporting Information).

Procedure 2: Exciton Emission

In Procedure 2, an additional reagent, oleylamine, is included in the growth solution, which may alter the surface properties of the CdSe QDs and reduce the trap-state emission. As a result, the luminescence of QDs synthesized in procedure 2 is dominated by the exciton emission. As exciton emission is less intense than the trap-state emission, the QDs prepared from procedure 2 are only mildly luminescent under UV light (Figure S3). As evident in Figure 4, the exciton emission spectra exhibit narrower peaks compared to those from procedure 1. As the reaction time increases, the peak position shifts to longer wavelengths (from 465 to 530 nm). This phenomenon is in accordance with the particle-in-a-box model, which states that larger boxes have smaller energy gaps between adjacent energy levels. Consequently, larger QDs emit longer wavelengths as they increase in size. A minor peak near 460 nm appears on the spectra of later samples, which suggests the formation of small clusters at later times. The attribution of the minor peak to the emission of small clusters is supported by the observation that this lower-wavelength peak disappears following the precipitation of the sample (Figure S4). Details of the purification process are explained in the Supporting Information. Peaks in the absorption spectra exhibit a similar

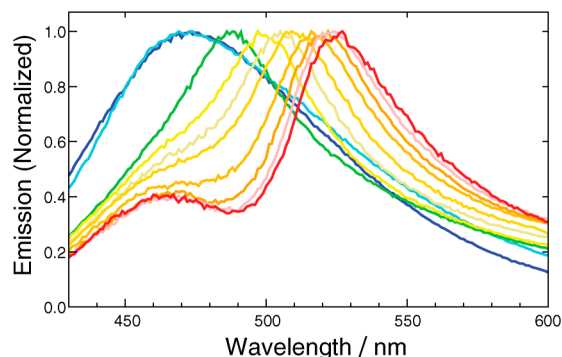


Figure 4. Normalized emission spectrum of CdSe QDs from procedure 2 with a 400 nm excitation wavelength. Samples obtained at longer reaction times are shown to the right. The change of the peak position demonstrates the growing of the QDs. Spectra were acquired from an Agilent Cary Eclipse fluorescence spectrophotometer.

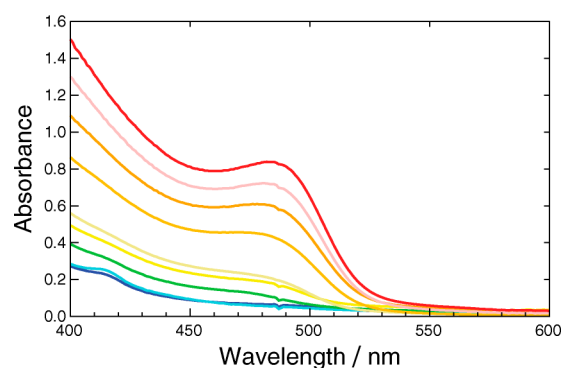


Figure 5. UV–Vis absorption spectrum of CdSe QDs from procedure 2 utilizing a HP 8452 UV–Vis spectrophotometer. Samples withdrawn at longer reaction times are shown on the top. The peak position shifts to longer wavelength following the progress of reaction, indicating the growth of QDs.

size-dependent shift, as shown in Figure 5. In addition, the peak positions are at shorter wavelengths than their corresponding peaks in the emission spectra (refer to Figure 4). This phenomenon is known as the Stokes shift, which is attributed to the nonradiative relaxations of the excited states.

DISCUSSION

Upon irradiation, electrons (e^-) in QDs are excited to the conduction band and form excitons with the pairing holes (h^+) in the valence band, as illustrated in Figure 6. Exciton or band edge emission is generated from the recombination of electrons and holes. For small QDs that have large surface-to-volume ratios, it is possible for the holes to be trapped in the midgap states existing on the surface.^{13,14} Emission from these trapped states is intensive, very broad, and significantly red-shifted relative to the absorption peaks.^{14–16} These features of trap-state emission have been exploited in CdSe QDs as potential illuminating sources.¹⁵ An energy diagram illustrating both exciton and trap-state emissions is sketched in Figure 6. Trap-state emission appears to dominate the luminescence of CdSe QDs synthesized in procedure 1 (Figure 3). The origins of the surface traps and the mechanisms of consequent emission are complicated and still under investigation by the research community, so that it would be difficult for students to quantitatively analyze the emission spectrum of QDs from procedure 1. However, the vivid color change with reaction

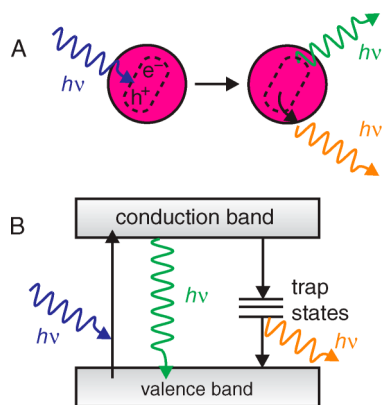


Figure 6. (A) Depiction of exciton formation in QDs after photoexcitation (blue), followed by the exciton emission (green) and/or the trap-state emission (orange). The black arrow inside the QD denotes radiationless relaxations. (B) Diagram of energy levels in QDs corresponding to the transitions in (A). The black arrow pointing up shows the process of absorption. The black arrows pointing down represent two possible transitions due to the trap states. Originating from smaller energy-level spacings, the trap-state emission radiates at longer wavelengths than the exciton emission.

time provides a simple, yet powerful, visual demonstration of size-dependent properties. Procedure 1 can be considered for laboratories with limited access to spectrometers or time constraints. This procedure greatly reduces the time necessary for a laboratory experience involving the synthesis of QDs, as spectra acquisition can be cumbersome if multiple groups of students are required to collect many spectra. Moreover, these CdSe QD solutions can be prepared by the instructors and demonstrated in the lectures of lower-level courses for general discussions of light–matter interactions.

The addition of oleylamine to the growth solution in procedure 2 results in observable exciton emission. Substitution of various ligands on the surface of QDs has been shown to modulate the relative contribution of the exciton emission and the trap-state emission to the total luminescence.^{14,17} Capping the QDs with a second layer of different materials, namely, core–shell QDs, is another way to suppress the trap-state emission.^{18,19} Additionally, a shell such as ZnS preserves the otherwise air-sensitive CdSe core and shields Cd toxicity.¹⁹

Comparison of the emission (Figure 4) and the absorption (Figure 5) spectra for CdSe QDs illustrates the Stokes shift. Previous studies on the origins of Stokes shifts in CdSe QDs have revealed that electron–hole exchange interaction causes a splitting of the active exciton states.^{7,20} Upon excitation, electrons are promoted to the higher of these two excited states, decay nonradiatively to the lower of the excited states, and then emit a photon (luminescence) as they relax to the ground state and recombine with the holes. The CdSe QDs from procedure 2 provide spectra that enable upper-level undergraduate students to perform quantitative analysis and to study quantum confinement effects in the advanced physical chemistry or inorganic chemistry laboratory.

There are a number of methods to evaluate the size of the CdSe QDs. With the absorption spectra, the peak position λ (nm) was determined by fitting the normalized and background subtracted absorption spectrum with a Gaussian function. The fitting result was utilized to calculate the diameter of QDs, D (nm), based on the empirical equation of $D(\lambda)$ reported by Mulvaney and co-workers.²¹ The details of analysis is provided

in the Supporting Information and examples are shown in Figures S5 and S6. The diameters are estimated to vary from 1.62 to 2.09 nm for QDs synthesized in procedure 1 at reaction times of 1.5–6.5 min (Figures S1 and S5). The diameters of QDs acquired from procedures 2 at similar reaction times are found to range from 2.12 to 2.27 nm (Figures 5 and S6). It should be noted that these values are averages over various sizes of QDs in each sample, rather than representing one single size of QDs. The size distribution contributes to the widths of the absorption and emission spectra. Because exciton emission peaks are usually sharper than the corresponding absorption peaks, they can be located graphically and are more convenient for undergraduate students to analyze. Consequently, educational articles often focus on the examination of emission spectra in studying the size-dependent properties and applying the particle-in-a-box model (more accurately, a particle-in-a-sphere model for the 3-D QDs).^{22,23} The theoretical equation relating the energy gap (the transition wavelength) and the QD radius derived from the particle-in-a-sphere model is included in Student Procedure 2 (Supporting Information). However, it is important to note that this model, which utilizes the individual effective mass of the electron and the hole as an approximation, is only applicable to larger QDs.^{24,25} The deviation between the calculated sizes and the experimental measurements has been shown to become more significant with decreasing QD dimensions.^{9,25} Alternatively, an empirical correlation between the QD size and the emission peak position has been established experimentally.^{26,27} The exciton emission spectra of CdSe QDs prepared from procedure 2 (Figure 4) were evaluated using the fitting equation reported by Peng and co-workers,²⁷ as detailed in the Supporting Information. The diameter of QDs calculated from the emission maximum is 1.82 nm for the 1.5 min sample and 2.39 nm for the last sample of 6.5 min reaction time.

To improve the applicability to the student laboratory, these two procedures have been developed under ambient atmosphere. The presence of water and oxygen has been shown to affect the optical properties of CdSe QDs,²⁸ and these factors have also been utilized to assist in shaping the CdSe nanocrystals.^{29,30} Accordingly, growth of nanocrystals exposed to air are not as well controlled as those under inert conditions. Size, shape, and surface components of the final products may be more complex. Nevertheless, as shown in Figure 5, the widths of absorption spectra are approximately 50 nm, indicating a reasonable size distribution within each aliquot of various reaction times. To further examine the quality of the CdSe nanocrystals, a sample from procedure 2 (withdrawn at a reaction time of 6.5 min) was inspected using a Philips CM100 transmission electron microscope (TEM). As illustrated in Figure 7, the QDs are mostly in spherical shape and exhibit only moderate size variations.

SUMMARY

Two simple and reliable procedures for the synthesis of CdSe QDs have been developed. Both procedures were carried out by a group of third-year students and the second procedure has been executed effectively in an upper-level undergraduate chemistry laboratory.

These two new protocols offer several advantages. Both procedures consume less cadmium per experiment than conventional high temperature syntheses. The replacement of cadmium oxide with the less hazardous cadmium acetate dihydrate is a considerable improvement. Cadmium oxide is

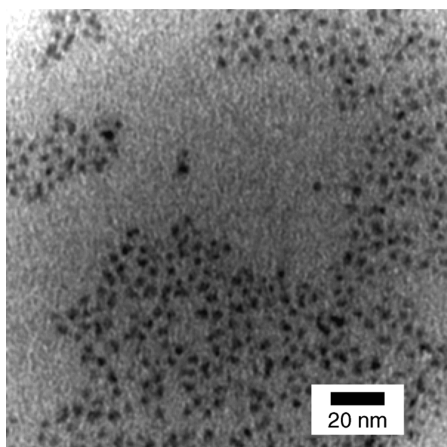


Figure 7. TEM image of purified CdSe QDs collected at the reaction time of 6.5 min in procedure 2. The scale bar is 20 nm.

fatal if inhaled, whereas cadmium acetate is toxic, but not lethal.³¹ The inhalation hazard of cadmium oxide is exacerbated by the fact that it is a powder, as opposed to the crystalline form of cadmium acetate dihydrate. Furthermore, these procedures are conducted at lower temperatures, eliminating the requirement of specialized heating apparatus. Stock solutions containing the metal reagents can be prepared in advance, so that students do not have to handle the toxic cadmium compounds.

In addition to the above-stated safety benefits, these low-temperature syntheses take place at slower reaction rates that require less hectic aliquot withdrawals. Students extracted aliquots over the period of 6.5 min, with the first withdrawal occurring at 15 s and subsequent withdrawals occurring at progressively longer intervals. The first procedure produced CdSe QDs with a full spectrum of colors (blue to reddish-orange). The intensely visible luminescence enabled students to observe the size-dependent properties of the QDs without having to use a spectrometer. These QDs can also be prepared by instructors and serve as an excellent visual demonstration in lectures. The second procedure allowed for quantitative analysis of the spectral properties of the QDs. These new procedures present an easier, safer, and robust means to synthesize QDs in an undergraduate student laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Instructor notes and student laboratory procedures. This material is available via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: chiawang@princeton.edu.

Notes

The authors declare no competing financial interest.

[†]These authors are undergraduate students.

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