

MATERIALS AND INTERFACES

A Rapid Hot-Injection Method for the Improved Hydrothermal Synthesis of CdSe Nanoparticles

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Cadmium selenide (CdSe) quantum dots were prepared in high-temperature water via a rapid hot-injection method intended to mimic conventional synthesis in organic solvents. The nanocrystals were smaller than those previously produced hydrothermally under nonisothermal conditions when using the same process parameters. It is possible that the nucleation and growth events were greatly influenced by the present injection method. In general, the physical and optical properties of the nanocrystals were influenced by the experimental conditions. Variations in reaction temperature (200–240 °C), reaction time (1–10 min), pH (7–11), Cd:Se molar ratio (4:1–40:1) and Cd:stabilizer molar ratio (0.24–1.18) affected the mean particle size, distribution of sizes, and quantum yield. As-prepared nanoparticles exhibited quantum yields in excess of 5%.

Introduction

The upsurge in the study of CdSe nanocrystals began with the trailblazing work performed by Murray et al.¹ based in a large part on earlier studies of CdSe conducted by Steigerwald and Brus et al.,^{2,3} and CdS nanoscale dispersions by Weller et al.⁴ In this work, high quality CdSe nanocrystals were obtained, not only due to reaction conditions, but, in part because of the novel synthetic route. Their synthesis began with the injection of a cold precursor solution into a hot coordinating organic solvent, causing the formation of nuclei. Because the solvent temperature dropped, the formation of new nuclei ceased, and the system contained relatively monodisperse nuclei and enough free cadmium and selenium ions to establish a slow growth at a temperature lower than the injection temperature. Researchers^{5–11} later adapted the Murray method, producing nanocrystals with various physical attributes. Murray et al. set the precedent for a requisite strategy for obtaining high-quality, uniform nanocrystals: the separation of nucleation and growth.

In an earlier feasibility study,¹² we demonstrated the formation of CdSe nanocrystals using high-temperature water as a reaction solvent. Water is an attractive medium for this synthesis because it is nontoxic, inexpensive, and more environmentally benign than the organic solvents others have used. Additionally, the as-prepared particles could be suitable for direct use in biological applications.

Our earlier synthesis method involved loading a room-temperature mini-batch reactor with reactants also at room temperature. We refer to this earlier method as the cold-precursor loading method. The reactants and reactor were then heated together and nanoparticles formed and grew under those nonisothermal conditions. We speculated that the particle nucleation and growth, which likely occurred simultaneously, were not conducive to creating high-quality nanocrystals. In this study, we test the hypothesis that by injecting the reactants into a preheated (rather than room-temperature) reactor, we will affect nucleation and growth dynamics, possibly separating the two more than what the previous method allowed. The separation of nucleation and growth events could facilitate the

synthesis of higher quality particles. The nanoparticles should grow under nearly isothermal reaction conditions. We refer to this present method as rapid hot-injection.

This hot-injection method is both similar to and different from convention. It is similar because the reactants are immediately exposed to an elevated temperature. It is different in that we do not inject a cold fluid into a hot fluid, but, rather, into a hot metal chamber.

Though our earlier feasibility study explored the influence of the process variables (e.g., temperature, time, pH) on the mean particle size, it was necessary to explore the influence of these variables again in this work, because this study used a rapid hot-injection method. The temperature–time trajectory experienced by the growing particles in this study is quite different from that in the previous feasibility study. Therefore, one can reasonably expect differences in how the process variables influence the particle size, size distribution, and quality. Moreover, in the present work we explore the influence of the process variables over a wider range of values.

Experimental Methods

Cadmium perchlorate (Aldrich, 99%), *N,N*-dimethylselenourea (Sigma-Aldrich, 97%), sodium citrate tribasic dehydrate (Sigma-Aldrich, 99%), and 1 N sodium hydroxide (Fisher) were used as received. Deionized water served as the solvent. All experiments were carried out in 1.54 mL stainless steel batch reactors, each comprising a $\frac{3}{8}$ in. Swagelok cap, port connectors, and bellows valve. Prior to the experiments, the reactors were loaded with deionized water and heated for 1 h at 300 °C to remove any residual material from the surface.

The procedure to prepare the reagents for this study was identical to that performed in our earlier study¹² up to the point of pH adjustment. Briefly, we prepared separate aqueous solutions of the cadmium precursor plus stabilizer (sodium citrate) and the selenium precursor. After the sodium hydroxide was added to the cadmium/sodium citrate solution, the reactor assembly was placed in a preheated sand bath and allowed to heat for at least 3 min so that it could reach thermal equilibrium. The valve was above the level of the sand. The selenourea solution, prepared as described in the earlier study, was made

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Table 1. Summary of Experimental Conditions and Key Results

run	T , °C	t , min	pH	Cd:Se molar ratio	Cd:stabilizer molar ratio	λ_{max} , nm	fwhm, nm	QY, %
1	200	2	9	8:1	1.18	563	35	0.99
2	210	2	9	8:1	1.18	566	38	5.7
3	220	2	9	8:1	1.18	565	37	5.5
4	230	2	9	8:1	1.18	567	37	5.3
5	240	2	9	8:1	1.18	565	37	4.9
6	200	1	9	8:1	1.18	555	35	1.1
7	200	4	9	8:1	1.18	566	40	1.7
8	200	6	9	8:1	1.18	572	36	1.1
9	200	8	9	8:1	1.18	579	40	1.3
10	200	10	9	8:1	1.18	589	33	0.71
11	200	2	7	8:1	1.18	556	N/A	0.56
12	200	2	8	8:1	1.18	555	36	3.3
13	200	2	10	8:1	1.18	560	35	3.8
14	200	2	11	8:1	1.18	540	36	5.2
15	200	2	9	4:1	1.18	568	34	0.05
16	200	2	9	5.7:1	1.18	566	34	2.2
17	200	2	9	16:1	1.18	553	34	3.9
18	200	2	9	40:1	1.18	543	35	4.9
19	200	2	9	8:1	0.59	578	40	0.64
20	200	2	9	8:1	0.39	594	37	0.22
21	200	2	9	8:1	0.27	608	32	0.08
22	200	2	9	8:1	0.24	620	19	0.06

immediately before loading the reactor to minimize reaction with the oxygen in the atmosphere. Once the two precursor solutions were mixed thoroughly in a glass vial, a syringe was used to withdraw approximately 1.5 mL of solution. The contents in the syringe were immediately injected into the open port of the bellows valve in the heated reactor assembly. The valve was quickly closed (after withdrawing the syringe) and the reaction was allowed to take place. At the appointed time, the reactor assembly was quickly withdrawn from the sand bath and submerged in an ice water bath where the reactor contents were allowed to cool. The reactors were then opened and their contents were retained in glass vials and stored in a dark, cool cabinet to await analysis.

UV–vis absorption data were retrieved from an HP8453 diode array Hewlett-Packard spectrophotometer. Photoluminescence (PL) spectra were measured on a modular Fluorolog 3 SPEX spectrofluorimeter. High-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL 3011 HRTEM microscope. Images were recorded on a Gatan 794 slow scan CCD TV system. The quantum yield (QY) was determined using rhodamine B.

Results and Discussion

This section presents the results from the hydrothermal synthesis of CdSe nanoparticles at different reaction conditions under nominally isothermal conditions. We explored a range of sand bath temperatures (200–240 °C), Cd:Se molar ratios (4:1–40:1), batch holding times (1–10 min), Cd:stabilizer molar ratios (0.24–1.18) and pH values (7–11). A summary of experimental conditions and key results is listed in Table 1.

Base Case Synthesis. The conditions of run 1 ($T = 200$ °C, $t = 2$ min, pH = 9, Cd:stabilizer molar ratio = 1.18, Cd:Se molar ratio = 8:1) were chosen as the base case. Figure 1 shows the normalized photoluminescence spectrum from particles synthesized at the base case conditions. The emission spectrum does undergo a blue shift from the bulk band gap (~ 700 nm), indicating the existence of quantum confinement. This outcome is similar to what was observed in the feasibility study.¹² The location of the wavelength (λ_{max}) corresponding to the maximum of the emission curve is related to the mean size of the nanocrystal. Smaller particles have lower values of λ_{max} . The

mean size of the nanocrystals formed by the rapid hot-injection method is smaller ($\lambda_{\text{max}} = 563$ nm) than that of the nanocrystals formed by the nonisothermal method used in our previous feasibility study under the same conditions ($\lambda_{\text{max}} = 613$ nm) (Figure 1). An analysis by HRTEM (Figure 2) confirms that the mean particle size (about 3.5 nm) is indeed smaller. The cold-precursor loading method yielded a mean particle size of approximately 5 nm based on HRTEM. The mean particle sizes can also be estimated from λ_{max} by using the effective mass approximation.¹³ These values are 4.9 nm for the present rapid hot-injection method and 5.2 nm for the previous feasibility study. The effective mass approximation calculation, although not precise for small nanocrystals, does confirm the effects of quantum confinement and the rapid hot-injection method producing smaller particles.

For the base case, repeat experiments resulted in an average λ_{max} of 557 ± 6.5 nm, where the uncertainty is the standard deviation. We did not repeat experiments for all conditions, but the standard deviation observed at the base case likely applies to the other experiments that were conducted.

The width of an emission peak, typically reported as the full-width-at-half-maximum (fwhm), is one common method used

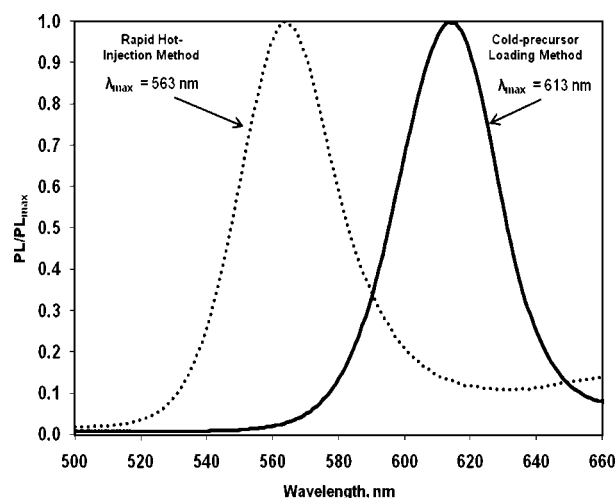


Figure 1. Normalized emission spectra for CdSe nanocrystals produced under the base case conditions.

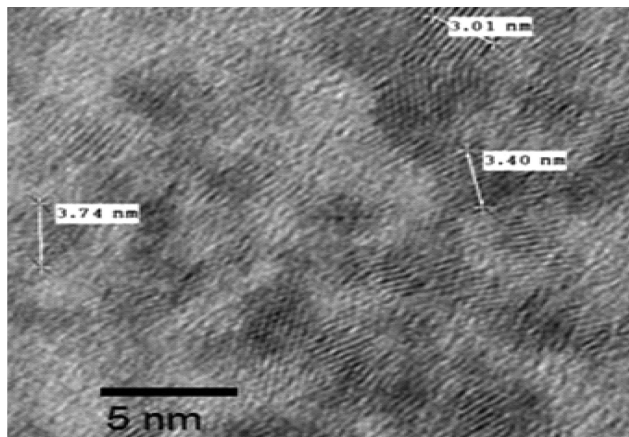


Figure 2. HRTEM image of CdSe nanocrystals produced under the base case conditions.

to evaluate the particle size distribution. The fwhm was determined from the emission spectrum to be 35 nm. The fwhm for the nanocrystals formed under the cold-precursor loading method with the same conditions is 36 nm. There does not seem to be any difference in the degree of monodispersity for the two methods. For the base case, repeat experiments resulted in an average fwhm of 35.7 ± 1.1 nm. Again, this measure of the random error is likely applicable to all other experiments that were conducted. Since a narrow size distribution can be defined as $\text{fwhm} \leq 40$ nm,¹ we can conclude that the base case for rapid hot-injection has a rather narrow size distribution.

The quantum yield (QY) for the base case was determined to be 0.99%. This is not much different from the quantum yield calculated for the base case under the earlier cold-precursor loading method (1.5%), even though the batch holding times are different (2 min for rapid hot-injection vs 1.5 min for cold-precursor loading). The lower quantum efficiency perhaps arises from either inadequate surface passivation or deep trapped emission due to surface defects. We suspect oxidation of selenium contributes to the formation of sites stimulating nonradiative recombination of electrons and holes.

Effect of Temperature. The temperature dependence of nanoparticle size and quality was investigated for a range of 200–240 °C. All other variables remained at their base case values. A normalized PL emission profile is displayed in Figure 3. Runs 1–5 in Table 1 show λ_{max} , fwhm, and the quantum yield for the particles obtained at each temperature. The temperature seems to have very little effect on the particle's mean size, as indicated by the small differences in the λ_{max} values. A temperature range of 40 °C resulted in a λ_{max} range of only 4 nm, which is definitely within the experimental uncertainty of ± 6.5 nm. It should be noted that we were able to explore a wider range of temperatures with the rapid hot-injection method than we could with our earlier method. The highest temperature at which quantum dots (rather than bulk CdSe) could be produced with the cold-precursor loading method was 215 °C. Though that temperature range was only 15 °C, we observed a 20 nm range in λ_{max} in the previous study. This behavior clearly differs from that observed with rapid hot-injection method used in the present work.

Though the temperature does not affect the nanocrystal's size for the rapid hot-injection method, we recognize that the reaction time was only 2 min. It is possible that this reaction time may not be long enough to exhibit any significant differences in temperature-dependent growth. We will report on this topic in a future article. It is also possible that the rapid-injection method

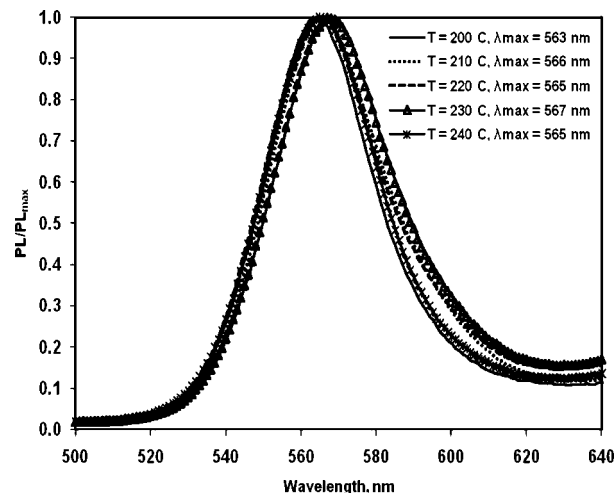


Figure 3. Normalized emission spectra for nanocrystals produced at different sand bath temperatures.

may have contributed to this phenomenon if the nucleation is temperature dependent. Dushkin et al.¹⁴ assert that the nucleation event can, and does, define the subsequent growth behavior. Bullen et al.⁸ studied nucleation and growth of CdSe nanocrystals in a noncoordinating solvent, observing effects of temperature, among other variables. They observed smaller nuclei and final particle sizes as the temperature increased. They suggest that at higher temperatures, nucleation events are faster, nuclei concentration increases, and growth kinetics are less strongly dependent on temperature. This scenario may help explain the results we obtained. If the concentration of CdSe nuclei increases with an increase in temperature, the availability of monomer decreases. With a lack of material to add to existing nuclei, further growth may be slowed.

Table 1 shows that the temperature has very little effect on the size distribution or the quantum yield within the experimental temperature range. An exception is that the quantum yield for $T = 200$ °C is considerably lower than those for the remaining temperatures. It is important to note that this rapid injection method did achieve quantum yields for the as-synthesized particles much higher than those obtained for the base case from the previous method (QY = 1.5%). Although we did not measure quantum yields for all cases in the cold-precursor loading method, it is likely that the yields would not have increased with an increase in temperature since the nanoparticle size increased dramatically.

It has long been recognized^{1,15} that the growth stage following a nucleation event, if controlled, can increase the quantum yield due to thermal annealing. It is believed that the growth of the nanoparticle allows the surface to restructure through the addition of material. The surface can reorganize by adding ligands needed to passivate dangling cadmium ions and by eliminating trapped surface charges to allow for proper electron–hole recombination. Because we observed no appreciable increase in the mean size of the nanocrystal at higher temperatures, we would not expect the quantum yield to change very much with temperature. The temperature increase may have only served to create additional nuclei, rather than alter the nanoparticle's surface properties. This scenario is consistent with the quantum yields at 210–240 °C in Table 1 being essentially independent of temperature.

The injection temperature of the system is crucial in the overall growth and final size of CdSe nanoparticles, as the rapid hot-injection method indicates compared with the cold-precursor loading method. Injection of a cold fluid into a hot solvent led

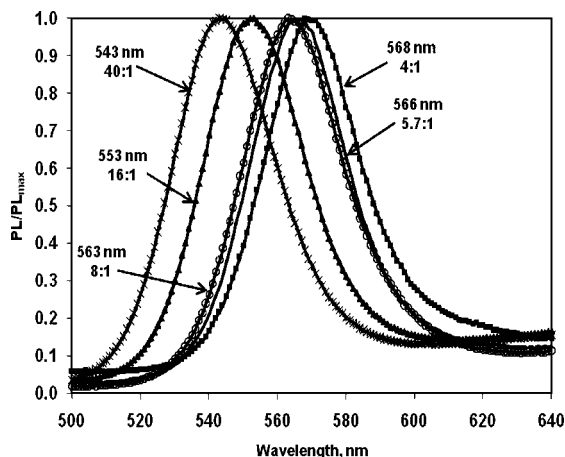


Figure 4. Normalized emission spectra for nanocrystals produced at different Cd:Se molar ratios. Each curve is labeled with its λ_{max} and the Cd:Se ratio.

to the instantaneous formation of CdSe nuclei.¹ The subsequent drop in temperature, due to injection of the cold precursor solution, helped to prevent formation of new nuclei. Consequently, a manual increase in the temperature led to a slow growth of the nanoparticles. One difference in our system is that we did not inject the cold precursor solution in a hot solvent, but rather into a hot empty metal reactor. We speculated that a nucleation event was induced simply because of the temperature. The reactor temperature probably decreased upon injection, which limited subsequent nucleation. As for the growth, it occurred at roughly the same temperature as the injection. Based on the success of others' hot-injection synthetic routes, we hypothesize that nucleation and growth were more discrete events in this hot-injection method than in the nonisothermal cold-precursor loading method used in our earlier study.

Effect of Cd:Se Molar Ratio. Since the surface of the nanocrystal plays such a crucial role in affecting the overall quality of the nanocrystal, a systematic control of the ratio of metal precursors could in turn control and improve the photoluminescence qualities.^{10,15} Figure 4 shows normalized emission spectra for CdSe nanocrystals synthesized at different Cd:Se molar ratios. Runs 1 and 15–18 in Table 1 further show the effect of the different molar ratios on the fwhm and the quantum yield.

Our results reveal that the initial Cd:Se molar ratio is a determining factor for the emission properties of the synthesized nanocrystals. The size and quantum yield were strongly correlated with the increase in the Cd:Se molar ratio. Figure 4 reveals a decrease in nanoparticle size as the Cd:Se molar ratio increases. This is expected with our system since we did not change the number of cadmium ions for each experiment. Thus, the Cd:stabilizer molar ratio remained constant, but the selenium concentration decreased. With less selenium monomer available for particle growth, the size of the nanoparticle should decrease.

Table 1 also shows that while the fwhm is virtually unaffected by the initial Cd:Se ratio, the quantum yield increases. It is possible that the smaller particles have fewer dangling Se bonds, fewer trapped emission sites, and, therefore higher quantum yields.^{10,16}

Our results are in stark contrast to those produced from the cold-precursor loading method,¹² where a more cadmium-rich environment yielded larger nanocrystals. This trend could have arisen in the previous study if the cold-precursor loading method promoted Ostwald ripening. With decreasing amounts of selenium monomer, the critical particle size required to maintain

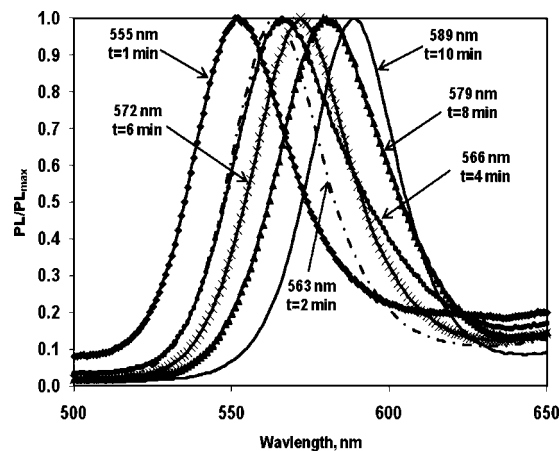


Figure 5. Normalized emission spectra for nanocrystals produced at different reaction times. Each curve is labeled with λ_{max} for the given reaction time.

equilibrium increased so any particles that remained in solution were at least slightly larger than the critical size. Peng et al.¹⁷ even discuss the importance of injecting additional monomer in order to shift the critical size of the nanoparticle back to a smaller value.

Numerous researchers have studied the characteristics of CdSe grown in excess selenium.^{10,15,18} A selenium-rich environment promoted a faster nucleation process, higher quantum yields, and narrower size distributions. Conversely, cadmium-rich systems resulted in fewer nuclei formed, slow nucleation and low quantum yields.¹⁰ We did not carry out experiments in excess of selenium because the selenium precursor reacted with oxygen from the air. In spite of this limitation, our results do suggest that the surface chemistry, as modified by changing the Cd:Se molar ratio, is indeed a major influence on the nanoparticle's quality.

Effect of Batch Holding Time. Time, as a synthesis condition, has been studied to assess its effects on nanoparticle size and overall quality. With all other parameters remaining constant, one would expect the size of the nanocrystals to increase with an increase in reaction time. This is because more material is allowed to add to existing nanoparticles. Figure 5 shows the temporal evolution of nanoparticle size (as inferred from λ_{max}) in a time range of 10 min. As indicated by the increase in λ_{max} , appreciable growth occurs throughout the entire 10 min time span.

Table 1 (runs 1, 6–10) shows the effect of reaction time on λ_{max} , the fwhm, and the quantum yield. The fwhm values show a modest change, with the largest value at 4 min and at 8 min. It is unclear whether there is a true increase in fwhm from $t = 1$ –4 min and then a decrease from $t = 4$ –10 min. We did not observe any effect of time on the fwhm in the previous study and we are reluctant to declare the existence of any trend under the rapid hot-injection method used here.

There is very little effect on the quantum yield as the reaction time increases. The size of the nanoparticle does not seem to influence the quantum yield. Since low values of quantum yield indicate surface-trapped emission, it is possible that the passivation due to the sodium citrate alone is inadequate and that modification of the crystal's surface may have a greater effect on its optical integrity. It does appear that the smaller fwhm values correlated with the lower quantum yields.

The previous feasibility study and this study did reveal similar trends (increase in time yielded an increase in size), but this study produced smaller nanoparticles. With the cold-precursor

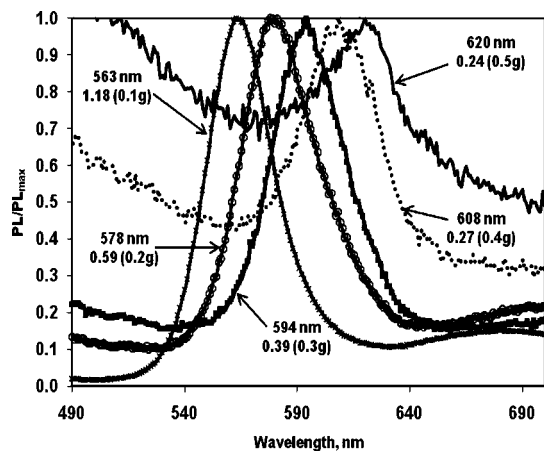


Figure 6. Normalized emission spectra for nanocrystals produced at different Cd:stabilizer molar ratios. The curves are labeled with λ_{max} for each ratio. The values in parentheses represent the quantity of stabilizer used to obtain the given molar ratio.

loading method, a 2.5 min reaction time produced nanoparticles with $\lambda_{\text{max}} = 619$ nm. An additional increase in time ($t \geq 3$ min) resulted in brownish-red precipitate forming, indicating larger bulk CdSe particles. With the rapid hot-injection method, we were able to react for 10 min and produce nanoparticles with $\lambda_{\text{max}} = 589$ nm. This outcome may be a function of the synthesis method as we allowed contact of the cold precursor solution with a hot metal surface. Small bubbles may have formed on the surface of the reactor, acting as the sites for nuclei on which the nanocrystals would grow.

Effect of Stabilizer Concentration. We reported earlier that, under the cold-precursor loading method, larger amounts of stabilizer increased the particle size. We observed an identical trend with the rapid-injection method. Surprisingly, as the stabilizer amounts decrease, the mean particle size (as inferred from λ_{max}) decreases (Figure 6), which is contrary to most, if not all studies of methods of nanoparticle synthesis.¹⁹ The particles formed at the highest stabilizer loadings exhibit a low photoluminescence peak intensity. Therefore, the signal-to-noise ratio in Figure 6 is lower for these low-quality particles.

The data from Table 1 (runs 1, 19–22) show that dispersity increases initially, and then decreases as the nanoparticle size increases. There does not seem to be a consistent monotonic trend between the fwhm and the amount of stabilizer, although at higher stabilizer amounts, the fwhm does trend downward. Reasons for this trend in the fwhm could be due to there being a small number of particles. The presence of more citrate ions in the solution may be hindering the formation of many CdSe nuclei, but at the same time, the citrate could rapidly complex to the cadmium ion as any nuclei form. Bullen et al.⁸ observed this phenomenon while synthesizing CdSe nanoparticles in hot octadecene. They noticed that the number of nuclei decreased linearly as more oleic acid (capping agent) was added.

The decrease in the quantum yield with increasing amount of stabilizer may be a result of limited overgrowth to reconstruct the surface during the growth stage.¹⁵ The excess citrate may provide a steric hindrance to the selenium monomer as it tries to move through the bulk to the nanocrystal's surface. This hindrance would increase the chance of there being dangling cadmium bonds and would adversely affect the quantum efficiency.

Effect of pH. The results obtained from experiments using the cold-precursor loading method showed that a higher basicity yielded smaller particles.⁹ We observed a similar trend for the

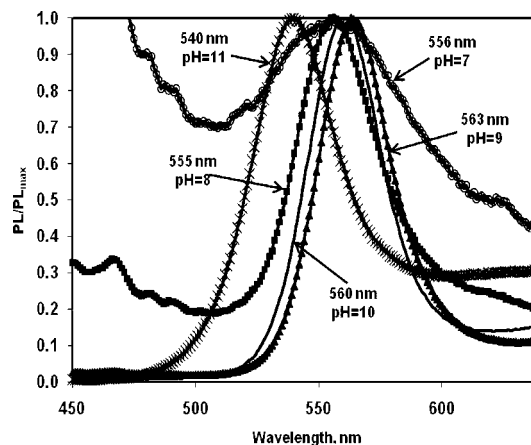


Figure 7. Normalized emission spectra for nanocrystals produced at different pHs. The curves are labeled with λ_{max} for each pH.

rapid hot-injection method (Figure 7). Nanoparticles synthesized at higher pH values exhibit more intense emission and generate well-defined peaks. The nanoparticle size decreases from the base case condition (pH = 9) as pH increases. Additionally, the quantum yield increases with the increase in pH from the base case condition.

Our results imply that, in the presence of increased alkalinity, cadmium citrate complexes are more strongly bound, stabilizing growth (smaller nanocrystal) and electronically passivating the surface (stronger emission peak). Furthermore, cadmium adsorption to the nanocrystal may be stronger, since cadmium ions tend to desorb at low pH values.²⁰ This increased affinity for the surface would aid in creating a more optimal surface structure and, with the cadmium's increased affinity to the citrate, eliminate dangling bonds.

Gao et al.²¹ observed enhanced fluorescence for CdTe nanoparticles prepared in low pH in aqueous solution. They conclude that the particle surface coverage with thiol ligands is increased in acidic CdTe solutions. They suggest that a thick layer of cadmium thiol complexes is formed on the nanoparticle's surface and can be considered as a wide-band gap material, making it analogous to CdS or ZnS passivation shell around the CdTe core. Although our nanoparticles are prepared in the presence of a higher pH and cadmium citrate complexes, some similar type of pH-sensitive phenomenon might be occurring in our system.

For pH values above 9, we observed a reaction after the selenium precursor was injected into the cadmium and citrate solution. The color of the solution began to change while remaining optically clear, indicating the formation of CdSe. Thus, it seems that a chemically induced nucleation event occurred. Subsequent injection of the solution into the hot reactor likely prompted a separate thermally induced nucleation event. Smaller particles could have resulted at these higher pH values if the initial CdSe nuclei were shrouded with cadmium citrate complexes that delayed any additional material being adsorbed onto the particle during the thermal growth event. The thermally induced nuclei may not have had much material addition due to fewer free cadmium and selenium ions available for appreciable growth.

Conclusions

This study highlights the results of using a rapid hot-injection method for hydrothermal synthesis of CdSe quantum dots. This method mimics that used in conventional methods with organic

solvents. Our investigation revealed that a rapid hot-injection produces a smaller nanocrystal ($\lambda_{\max} = 563$ nm) and a similar particle size distribution (fwhm = 35 nm) compared with those from the cold-precursor loading method ($\lambda_{\max} = 613$ nm; fwhm = 36 nm) under the same experimental conditions. The QY determined for the rapid hot-injection method at the base case was 0.99%. This value is not much different from the QY of 1.5% from the cold-precursor loading method under the same experimental conditions except for time, which differed by 30 s.

We surveyed the effects of experimental parameters on the mean particle size (represented by λ_{\max}), size-distribution (represented by fwhm), and QY. An increase in reaction time increased the size, while an increase in the Cd:Se molar ratio, pH, and Cd:stabilizer ratio decreased the size. An increase in the reaction temperature did not affect the nanocrystal size at the reaction time investigated. An increase in the reaction temperature, Cd:Se molar ratio, and pH did not affect the size distribution. There seemed to be no consistent trend of the dispersity with the stabilizer loading in general, but at higher stabilizer loadings, the fwhm tended to decrease, implying a narrower particle size distribution. An increase in the Cd:Se molar ratio, pH, and Cd:stabilizer molar ratio increased the QY, but an increase in the reaction temperature and time had no appreciable effect on QY.

These results demonstrate the viability of high-temperature water as a medium for CdSe synthesis. In particular, quantum dots with quantum yields of about 5% can be prepared via rapid hot-injection in a one-pot aqueous-phase synthesis. Quantum dots with quantum yields even higher than those reported here may be available from hydrothermal synthesis at high Cd:Se molar ratio, high pH, and high Cd:stabilizer ratio.

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Literature Cited

- (1) Murray, C. B.; Norris, D. J.; Bawendi, M. G. Synthesis and characterization of nearly monodisperse CdE (E = S, Se, Te) semiconductor nanocrystallites. *J. Am. Chem. Soc.* **1993**, *115*, 8706–8715.
- (2) Brennan, J. G.; Sigrist, T.; Carroll, P. J.; Stuczynski, S. M.; Brus, L. E.; Steigerwald, M. L. The preparation of large semiconductor clusters via the pyrolysis of a molecular precursor. *J. Am. Chem. Soc.* **1989**, *111*, 4141–4143.
- (3) Steigerwald, M. L.; Alivisatos, A. P.; Gibson, J. M.; Harris, T. D.; Kortan, R.; Muller, A. J.; Thayer, A. M.; Duncan, T. M.; Douglass, D. C.; Brus, L. E. Surface derivatization and isolation of semiconductor cluster molecules. *J. Am. Chem. Soc.* **1988**, *110*, 3046–3050.
- (4) Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. Photochemistry of colloidal semiconductors. 20. Surface modification and stability of strong luminescing CdS particles. *J. Am. Chem. Soc.* **1987**, *109*, 5649–5655.
- (5) Qu, L. H.; Peng, Z. A.; Peng, X. G. Alternative routes toward high quality CdSe nanocrystals. *Nano Lett.* **2001**, *1*, 333–337.
- (6) Peng, X. G.; Manna, L.; Yang, W. D.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. Shape control of CdSe nanocrystals. *Nature (London)* **2000**, *405*, 59–61.
- (7) Peng, X. G.; Wickham, J.; Alivisatos, A. P. Kinetics of II–VI and III–V colloidal semiconductor nanocrystal growth: “Focusing” of size distributions. *J. Am. Chem. Soc.* **1998**, *120*, 5343–5344.
- (8) Bullen, C. R.; Mulvaey, P. Nucleation and growth kinetics of CdSe nanocrystals in octadecene. *Nano Lett.* **2004**, *4*, 2303–2307.
- (9) Qu, L. H.; Yu, W. W.; Peng, X. P. In situ observation of the nucleation and growth of CdSe nanocrystals. *Nano Lett.* **2004**, *4*, 465–469.
- (10) Qu, L. H.; Peng, X. G. Control of photoluminescence properties of CdSe nanocrystals in growth. *J. Am. Chem. Soc.* **2002**, *124*, 2049–2055.
- (11) Talapin, D. V.; Rogach, A. L.; Kornowski, A.; Haase, M.; Weller, H. Highly luminescent monodisperse CdSe and CdSe/ZnS nanocrystals synthesized in a hexadecylamine-triethylphosphine oxide-triethylphosphine mixture. *Nano Lett.* **2001**, *1*, 211–214.
- (12) Williams, J. V.; Adams, C. N.; Kotov, N. A.; Savage, P. E. Hydrothermal synthesis of CdSe nanoparticles. *Ind. Eng. Chem. Res.* **2007**, *46*, 4358–4362.
- (13) Brus, L. E. Electron–electron and electron–hole interactions in small semiconductor crystallites—The size dependence of the lowest excited electronic state. *J. Chem. Phys.* **1984**, *80*, 4403–4409.
- (14) Dushkin, C. D.; Saita, S.; Yoshie, K.; Yamaguchi, Y. The kinetics of growth of semiconductor nanocrystals in a hot amphiphile matrix. *Adv. Coll. Inter. Sci.* **2000**, *1*, 37–78.
- (15) Donega, C. D.; Hickey, S. G.; Wuister, S. F.; Vanmaekelbergh, D.; Meijerink, A. Single-step synthesis to control the photoluminescence quantum yield and size dispersion of CdSe nanocrystals. *J. Phys. Chem. B* **2003**, *107*, 489–496.
- (16) Underwood, D. F.; Kippeny, T.; Rosenthal, S. J. Charge carrier dynamics in CdSe nanocrystals: implications for the use of quantum dots in novel photovoltaics. *Eur. Phys. J. D* **2001**, *24*, 1–244.
- (17) See ref 7.
- (18) Peng, Z. A.; Peng, X. G. Nearly monodisperse and shape-controlled CdSe nanocrystals via alternative routes: Nucleation and growth. *J. Am. Chem. Soc.* **2002**, *124*, 3343–3353.
- (19) Murray, C. B.; Sun, S. H.; Gaschler, W.; Doyle, H.; Betley, T. A.; Kagan, C. R. Colloidal synthesis of nanocrystals and nanocrystal superlattices. *J. Res. Dev.* **2001**, *1*, 47–56.
- (20) Lee, M. K.; Saunders, J. A. Effects of pH on metals precipitation and sorption: field bioremediation and geochemical modeling approaches. *Vadose Zone J.* **2003**, *13*, 7–185.
- (21) Gao, M.; Kirstein, S.; Mohwald, H.; Rogach, A. L.; Kornowski, A.; Eychmuller, A.; Weller, H. Strongly photoluminescent CdTe nanocrystals by proper surface modification. *J. Phys. Chem.* **1998**, *102*, 8360.

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