

Chapter 7: Discussion and Conclusions

Synthesis Rate Control Mechanisms

One of the key assumptions used to develop the diffusion model was that organometallic synthesis was a diffusion-limited process. Evidence that supports and evidence that challenges this assumption will be reviewed. Diffusion rates and reaction rates can both be characterized by activation energies, so demonstrating Arrhenius temperature dependence did not determine which control mechanism was dominant. The magnitudes of activation energies, Q , the magnitudes of growth rates, the variation of Q with solvent molecular weight, and the focusing of size distributions, when taken together point more towards dual control rather than either diffusion control or reaction control.

In stearic acid, the synthesis activation energy ($Q_{SA} = 0.6 \pm 0.1$ eV) agrees well with the activation energy for the self-diffusion of liquid sodium stearate (0.607 eV) at typical synthesis temperatures.⁶⁷ To some degree, this agreement supports the hypothesis that synthesis in stearic acid is controlled by diffusion.

However, the synthesis diffusion rate ($D/L_{syn.} \sim 3.5 \times 10^{-7}$ cm/s) is orders of magnitude slower than expected for the diffusion of liquid cadmium stearate, ($D/L_{liq.SA} \sim 6 \times 10^{-3}$ cm/s). For these calculations, $D/L_{syn.}$ was estimated by modeling the growth of CdSe quantum dots in stearic acid at a metal bath temperature of 235 °C, as shown in Figure 7-1, using the method described in the Chapter 6 for Figure 6-33. To calculate $D/L_{liq.SA}$, diffusivity parameters for cadmium stearate were assumed to be similar to experimental measurements of D_o and Q for sodium stearate by Blinc,⁶⁷ as summarized

on page 52. In the expression ($D = D_o \exp\{-Q/RT\}$), the actual reaction temperature, T , was assumed to be 225 °C when the metal bath was 235 °C. A generous liquid diffusion length of 2.42 μm was used, which is about 100 times longer than the stearic acid molecule. These assumptions should be sufficiently conservative for an order of magnitude estimate of a lower limit on $D/L_{\text{liq.SA}}$. These calculations imply that rapid diffusion through the liquid solvent could not be the slowest step in synthesis, in agreement with the thrust of arguments made by Bullen.⁵⁹

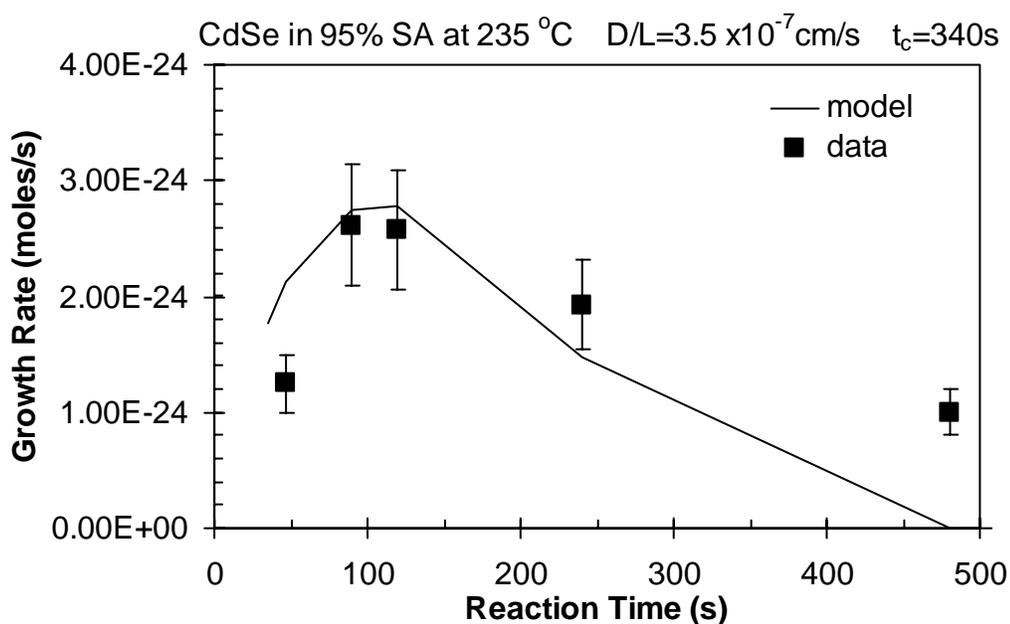


Figure 7-1. Growth rates used to estimate D/L for synthesis in stearic acid. Similar analysis methods were used to produce Figure 6-33.

However, one should not rule out the possibility that the slow growth rates observed during the organometallic synthesis of CdSe quantum dots could be limited by slow diffusion through the ligand layer. Since ligands are attached on one end to the nanocrystal surface, incoming cadmium stearate molecules may have difficulty moving past the ligands. With such constraints, if the ligands behave more like a solid than a liquid, one would need to compare D/L using diffusivity parameters for solid cadmium stearate, but at temperatures far above its melting point. Although such measurements may be hard to find in the literature, analysis of the organometallic synthesis of quantum dots may provide access to this behavior.

Replacing stearic acid ($W_{SA} = 284.47$ g/mole) with a larger branched molecule such as trioctylphosphine oxide ($W_{TOPO} = 386.65$ g/mole) resulted in a higher effective synthesis activation energy ($Q_{TOPO} = 0.96 \pm 0.26$ eV), which was proportional to the solvent molecular weight in this case, when compared to stearic acid ($Q_{SA} = 0.6 \pm 0.1$ eV). This suggests that the physical size and shape of the solvent molecule affect Q .

However, Q did not always increase with the solvent's molecular weight. For example, the activation energy in dodecylamine ($Q_{DA} = 1.05 \pm 0.1$ eV) was similar to that of TOPO ($Q_{TOPO} = 0.92 \pm 0.26$ eV), even though the molecular weight of DA ($W_{DA} = 185.35$ g/mole) is much smaller than that of TOPO ($W_{TOPO} = 386.65$ g/mole). This suggests that another contribution to Q , perhaps chemical in nature, compensated for the decrease in chain length from TOPO to DA. The solvents used in this study are thought to form metal-organic complexes with Cd, so that each Cd^{+2} ion can have two ligands.³⁶ Since one of these ligands must be broken off to form CdSe on the surface of a nanocrystal, it is reasonable that a chelate "bond" energy could contribute to Q .

This work demonstrated that the activation energy for organometallic synthesis of CdSe quantum dots can be tailored by the choice of solvent. All three solvents chosen have different functional groups at the chelate site, and different carbon chain structures, as illustrated in Figure 7-2. TOPO also has branched carbon chains, whereas SA and DA both have flexible linear carbon chains. These limited comparisons suggest that both the physical structure and the chelate interaction energy can affect Q . However, the relative contributions to Q have not been determined.

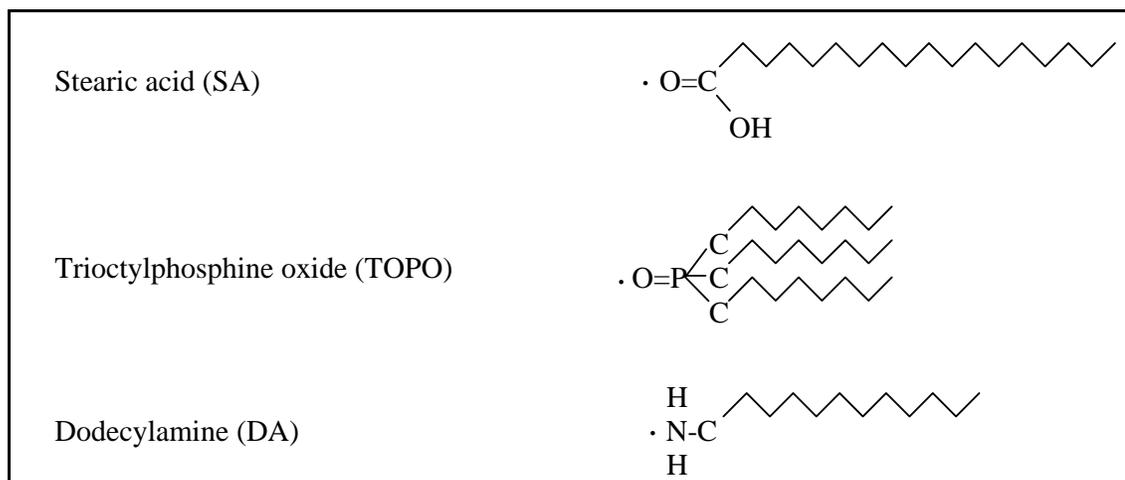


Figure 7-2. Molecular structures of organometallic solvents. The “.” indicates where the solvent may form a metal chelate complex with Cd. Zigzagged lines indicate the length of carbon chains.

A more careful study could keep the functional group constant while varying the chain length. If Q increased linearly with chain length, then the chelate interaction energy might be estimated from the y-intercept of Q versus chain length. Alternatively, solvents with the same chain length but different terminal functionalities could be compared. Then changes in Q for synthesis in different solvents could provide estimates of differences in the chelate interaction energy for different functional groups.

If chelate interaction energy is later shown to affect Q in a logical way, this would support the idea of reaction-limited growth. However, diffusion must also control quantum dot growth, because all synthesis in this work exhibited self-focusing PL emission until Cd was exhausted. Furthermore, self-focusing of particle size distributions is only predicted for diffusion-limited growth, not reaction-limited growth.³⁷ It seems safest to assume that organometallic synthesis is governed by mixed control modes, where the growth rate is affected both by the rate of chelate diffusion through the ligand barrier and by the reaction rate of chelate decomposition to form CdSe.

Conditions that Improve PLQY

For optimum quantum dot performance, including both high brightness and narrow line width, extraction should be timed to obtain the highest PLQY, since the emission width generally remained near the minimum value for a range of emission wavelengths from $\lambda_c - 40$ nm to $\lambda_c + 5$ nm. Bright emission occurred within the window of conditions for narrow emission. In all three solvents tested, local maxima in PLQY were observed at reaction times earlier than those producing the narrowest emission. Why were PLQY and emission width optimized under different synthesis conditions?

The detailed study of CdSe nanocrystal growth in TOPO at 285 °C with the standard molar ratio, Cd:Se = 1:1.3, helped to interpret PLQY evolution at other temperatures. In Figure 7-3 (c), PLQY is shown versus the absorbance peak wavelength for synthesis in TOPO under a wide range of synthesis temperatures. Regardless of synthesis temperature, the brightest emission generally occurred when the absorbance peak wavelength was between 505 nm and 530 nm. This wavelength range was bracketed by several transitions in the growth conditions. As the absorbance peak wavelength became longer than 505 nm, Figure 7-3 (a) shows that the average growth rate dropped below its maximum value. Also in Figure 7-3 (b), the Cd and Se concentrations dropped sharply after the absorbance wavelength exceeded 530 nm. Consistent with observations by Qu & Peng,¹ moderate growth rates and high selenium levels seem to produce good surface quality for high photoluminescence quantum yields.

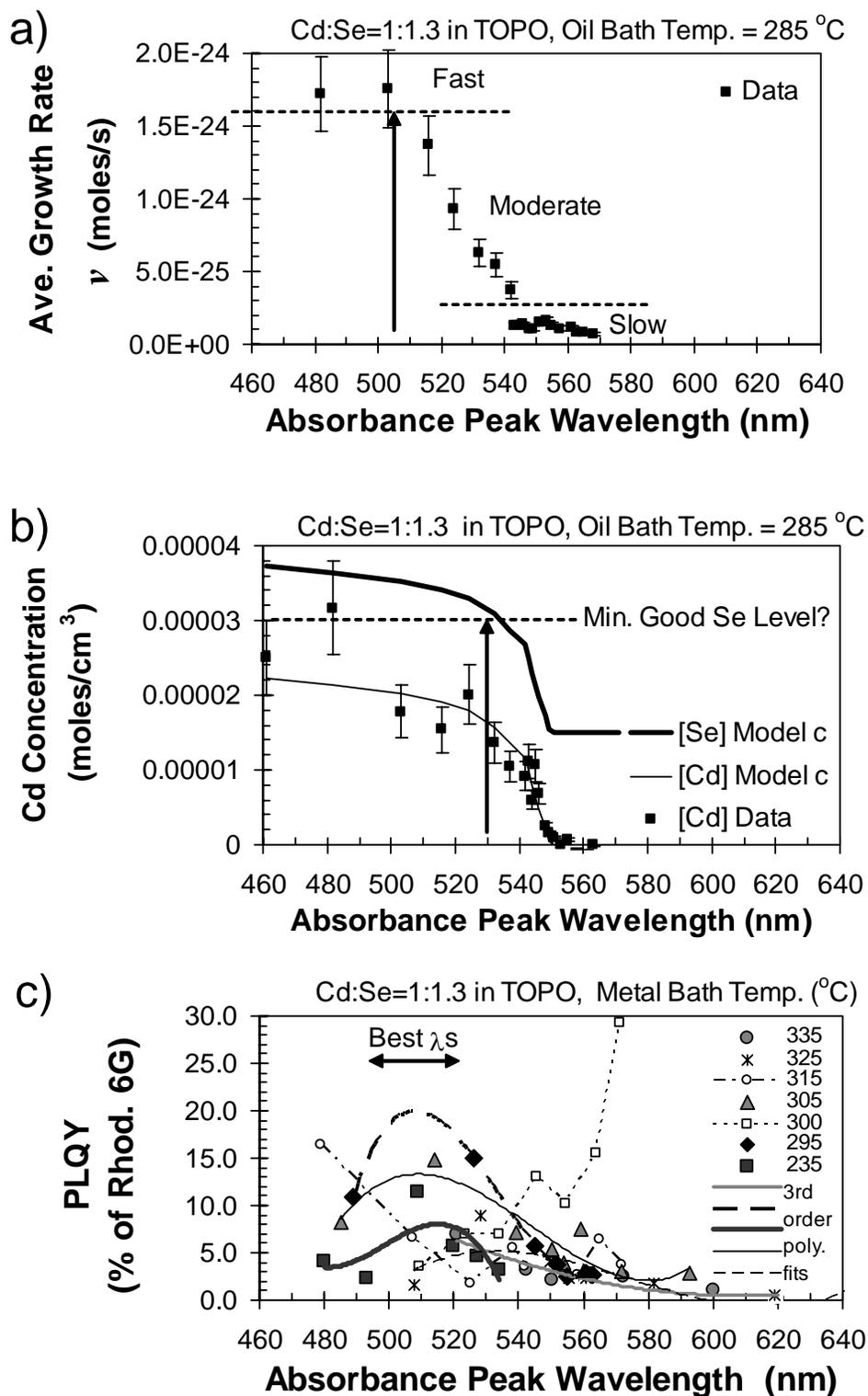


Figure 7-3. PLQY may be affected by growth rate and Se level. PLQYs for CdSe quantum dots grown in TOPO c) were highest when the peak absorbance was between 505 and 530 nm. Perhaps a) the growth rate was too fast for λ_{abs} below 505 nm, and b) the Se concentration may have been too low for λ_{abs} longer than 530 nm.

The diagrams in Figure 7-4 illustrate how surface quality may be affected by different growth conditions. During Oswald ripening (a), some nano-crystals are shrinking. As material leaves, the surface may be etched, and some passivating ligands may be removed. Therefore, low PLQY is expected from quantum dots after cadmium has been exhausted. Early in synthesis, the growth rate may be so rapid (b) that adatoms attach at the first available surface site. If radial growth surpasses lateral mobility, there might not be time for atoms to find positions with lower Gibbs free energy (c), before being locked in place by subsequent deposition. Slower growth would allow surface reconstruction to produce smoother surfaces. If ligands only attach to cadmium atoms,³⁶ there may be a tendency for the surface to become cadmium rich (d), so that even an atomically smooth surface could represent a series of stoichiometric surface defects. Qu and Peng observed substantial improvements in PLQY by growing CdSe quantum dots in solutions containing up to 900 % molar excess of selenium,¹ perhaps because high selenium concentrations helped restore ideal surface stoichiometry (e).

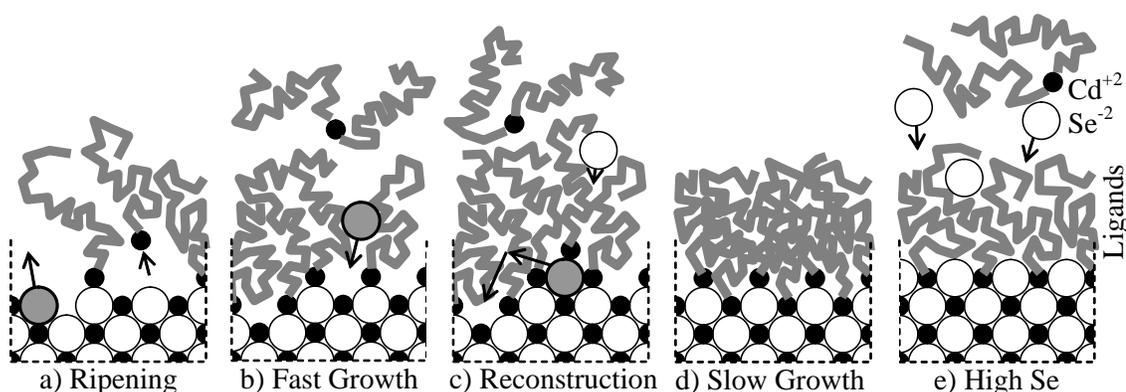


Figure 7-4. Atomistic CdSe surface defects. The text explains how a) ripening, b) fast growth, c) reconstruction, d) slow growth, and e) high Se levels might affect the surface quality and thereby the PLQY. Some Se atoms are shaded to highlight their role.

Defects are expected to reduce the PLQY by increasing the probability of undesired nonradiative recombination, as discussed in Chapter 3. Even in a perfect nanocrystal, the entire surface represents a deviation from a continuing periodic crystal lattice, due to missing neighbors and unsatisfied bonds. It is well known that ligands can passivate quantum dot surfaces to improve the PLQY. All three solvents tested produced comparable maximum PLQY, indicating a similar ability to passivate the surface under ideal growth conditions. If ligands were damaged or broken off at higher temperatures, this may explain the decrease in PLQY observed above optimum growth temperatures, which varied with the choice of solvent.

Based on annealing during synthesis, one would expect progressively higher maximum PLQY from synthesis at higher temperatures, and this is true for growth in TOPO. However, for synthesis in dodecylamine, temperatures above 195 °C actually reduced PLQY, and in stearic acid the maximum PLQY decreased with synthesis temperatures above 255 °C. Higher temperatures produced faster growth rates, as indicated by higher redshift rates. The decrease in PLQY at higher temperatures for DA and SA suggests that the growth rate may have exceeded the surface reconstruction rate, so that annealing during growth became less effective. When the initial precursor concentrations are held constant, one might expect the growth rates and the reconstruction rates to follow the same temperature dependence, but only if both processes were characterized by the same activation energy.

In addition to moderate growth rates, perhaps optimum reconstruction requires the availability of both cadmium and selenium precursors. This would explain why the highest values of PLQY were generally observed for synthesis times significantly before

the exhaustion of cadmium precursors. Later during Ostwald ripening, the growth rates were slow, but reconstruction seemed to be hampered by the lack of cadmium, since PLQYs were very low for wavelengths longer than λ_c .

Even significantly after Cd was exhausted, CdSe quantum dots made by Qu and Peng in a mixture of hexadecylamine, SA, and TOPO exhibited PLQYs higher than 40%; their secret was to boost the Se level to 10 times the Cd molar concentration.¹ Having a high concentration of Se even when Cd is scarce might give surface atoms more options during reconstruction. Consider the analogy of Cd bricks and Se mortar in a nanocrystal wall. If there is plenty of mortar available, bricks from a higher part of the wall can be easily laid to fill holes in a lower part of the wall. In this way, a more even wall could be achieved even if new bricks were in short supply. High Se levels may facilitate surface reconstruction.

Effects of Selenium on Nucleation

The diffusion model outlined in Chapter 4 assumed that the growth rate was limited by the Cd concentration, not the Se concentration, since there was always at least a 30% molar excess of Se. This treatment also assumed that Se precursor species could migrate faster than the Cd complexes, so that Se would not be involved in any rate-limiting steps. To test some of these assumptions, one of the objectives of the second set of synthesis runs in TOPO using the oil bath was to see if quantum dot growth kinetics was affected by the selenium concentration. Parameters which describe the individual quantum dots, such as emission wavelength, individual growth rates, and redshift rates, were only slightly altered by doubling the selenium concentration. However collective

characteristics of the reaction solution, such as the Cd precursor concentration, the rates of Cd depletion, and the peak absorbance of the solutions, changed dramatically in response to higher Se concentrations.

These changes in reaction solution can be explained through the effect that selenium concentration had on the evolution of the number of particles. Ten times higher initial particle counts with higher Se concentrations resulted in higher absorbance values (*i.e.* lower optical transmission) because the absorbance has been shown to be proportional to the total volume of CdSe quantum dots.⁷¹ Even when individual quantum dots grew at the same rate, higher particle counts in the presence of higher Se concentrations resulted in more rapid reduction of the Cd precursors, resulting in Cd exhaustion within a shorter period of time.

A changing particle count is undesirable for several reasons. With a Cd:Se ratio of 1:1.3, the number of particles increased with time, suggesting that nucleation continued during growth, and that smaller nanocrystals appeared while larger crystals grew. Without continued nucleation, size distribution could have been even narrower. On the opposite extreme, with a Cd:Se ratio of 1:2.6, the particle count decreased with time, suggesting that either 1) smaller nuclei were dissolving and making the size distribution wider than it could have been, or 2) particles were fusing together and forming irregular shapes, with poorly defined emission wavelengths and potentially higher defect densities. For these reasons it is desirable to find synthesis conditions, such as Cd:Se ratios, that produce stable particle counts.

Potential Improvements to the Diffusion Model

Overall, the diffusion model reasonably describes the experimental evolution of PL emission or absorbance peak wavelength with synthesis time, as shown by the master curve in Figure 7-5.

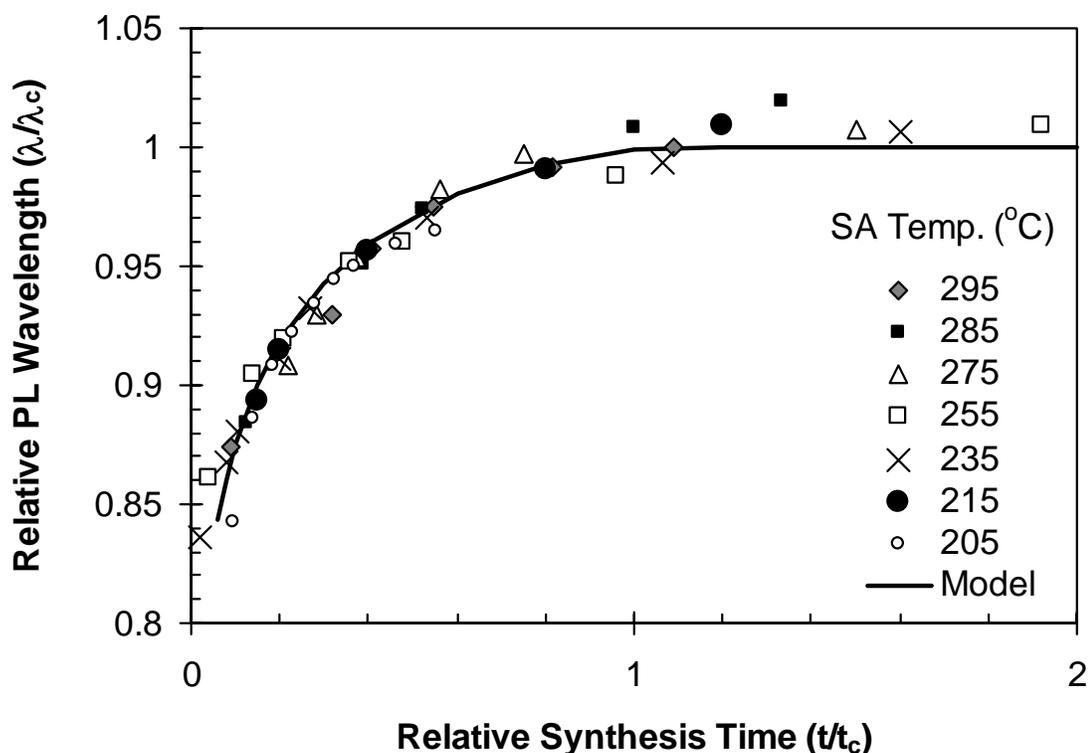


Figure 7-5. Universal PL evolution curve. When the relative emission wavelength, λ/λ_c , is plotted versus the relative synthesis time, t/t_c , the PL emission of CdSe quantum dots grown in 95% stearic acid follows the same master curve regardless of temperature. At higher temperatures, shorter completion times, t_c , brought the observed PL evolution curves into agreement with each other at $0.9 \lambda_c$. In stearic acid, λ_c was 590 nm. The diffusion model followed experimental data best when f_i was 0.9 and t_i was 25 s. The model is defined on Chapter 4, in Equations (4-11) through (4-13).

In its present form, the diffusion model expressions are manageable and easy to manipulate, in order to simulate quantum dot growth. This first approximation was based on several assumptions described in Chapter 4, including that the values of N , L , and Q would not depend on R . Experimental evidence presented in Chapter 6 suggests that these assumptions only hold under some conditions. It might be possible to correct the model so it can describe more complex behavior. However, if the model becomes too sophisticated, it may be more difficult to use, especially if it leads to differential equations that can not be solved analytically. Therefore, science seeks a good compromise between elegance and accuracy.

Since the number of nuclei, N , was not constant during the early stages of growth, the diffusion model could include a function for $N_{(t)}$ in order to improve accuracy. Such a function would need to be based on independent experimental observations, such as those made in Chapter 6, Figure 6-38. The function's form may depend on the initial Cd:Se ratio. If more accurate measurements of Cd depletion show a significant discrepancy between N_{eff} and N (discussed on pages 113-116), then a more accurate governing differential equation could also include a reaction yield term, $y < 1$, describing the fraction of Cd products that are in the form of suspended CdSe quantum dots.

Careful inspection of Figure 7-5 reveals that the diffusion model often overestimated λ just before t_c , which implies that the growth rate slowed down a little faster than predicted by the model. The simple diffusion model assumed that the diffusion distance, L , was a constant. However, if L was replaced with a function that increased with R , this might account for any buildup of ligand byproducts, possibly

imbedded in the ligand layer, which might physically increase the diffusion barrier and slow down growth later in the growth stage, before Ostwald ripening.

Estimates of Q from redshift rates generally increased with the test wavelength, for synthesis in TOPO and in stearic acid. Several possible reasons for this systematic variation are proposed. An increase in L with R (discussed above) might have this effect. Alternatively, the increase in Q with λ or R might reflect an increase in the average Cd-ligand chelate interaction energy in the ligand barrier around each quantum dot surface. Perhaps ligands of TOPO or stearic acid are gradually replaced by TDPA, which has stronger “bonds” to Cd. Such ligand replacement behavior has been observed by others.³⁸ Based on Talapin’s treatment, Equation (3-41) predicts that the synthesis activation energy would increase with nanocrystal radius, and hence with λ , due to changes in surface energy. Evaluating these possible explanations for the increase in Q with R is a good area for future research.

Sources of Error

The chief sources of uncertainty in activation energy estimates came from uncertainty in the synthesis temperature, because Q was estimated from the temperature dependence of growth rates. The growth rate is expected to be proportional to the redshift rate at a fixed test wavelength if the particle count stays constant. If nucleation changes systematically with temperature, this could alter the consumption of Cd and could skew the slope of Arrhenius plots. Concerns have also been raised that even with constant particle counts, systematic variation in [Cd] with temperature could have a secondary affect on estimates of Q from redshift rates at a common test wavelength.⁶⁹

However, continued analysis of the diffusion model and Figure 7-5 shows that regardless of temperature, fixing the ratio λ_{test}/λ_c also fixes the ratio t/t_c , which determines the ratio $[Cd_{(t)}]/[Cd_0]$, so the increase in Q with longer test wavelengths is probably real, and not just an artifact of using redshift rates to get Q .

Since growth rate has a nearly exponential dependence on temperature, it is not surprising that control of temperature was a significant issue during the comparison of reaction kinetics in different solvents. Although the metal bath temperature was stable and accurately measured using an immersed thermocouple, the reaction solvents were probably at least 10 °C cooler than the metal bath, based on measurements plotted in Figure 6-41. Despite constant stirring, temperature gradients were likely inside the reaction solution. The stainless-steel stirring rod could act as a significant heat sink. Heat was also carried away by purging with argon at room temperature. The initial reaction temperature could also vary significantly depending on the temperature of the Se-TOP solution that was injected to start the reaction. These factors taken together may explain the scatter in growth rates observed as a function of temperature.

The experimental apparatus was redesigned in set II to help reduce and monitor any fluctuations in temperature. Even so, Figure 6-40 showed that even with these improvements, the reaction solvent temperature stabilized to about 10 °C cooler than the oil bath temperature. Since significant nucleation occurs immediately following injection, the temperature during nucleation could significantly alter the number of particles, which in turn significantly affects the rate of depletion of cadmium precursors. Therefore it is recommended that the Se-TOP solution be heated to the reaction

temperature immediately prior to injection, in order to minimize temperature fluctuations during the first minutes of synthesis.

In general, optical measurements of photoluminescence were found to be less susceptible to internal noise than optical measurements of absorbance, using spectrometers of a similar caliber from the same manufacturer, Hitachi. The accuracy of PLQY estimates at wavelengths other than 555 nm was limited because comparisons of PL intensity were used without corrections for variation in absorbance at the excitation wavelength of 370 nm. A more accurate approach would have used multiple standards at different wavelengths. The following systematic errors arose from the samples themselves. During photoluminescence measurements, the peak emission wavelength could be redshifted significantly due to reabsorption of emitted light, if the concentration was too high. During absorbance measurements designed to track cadmium precursor levels, the background absorbance decreased with handling time, probably due to coagulation and settling of precursor material in toluene solutions.

Several optical methods of estimating particle count were compared, as shown in Figures 6-36, 6-37, and 6-38 of Chapter 6. Dividing the solution absorbance by the absorbance per nanocrystal volume proved to be the most precise method, since the average quantum dot radius was unambiguously estimated from the wavelength of the first absorbance peak, using the empirical Equation (2-6) discussed in Chapter 2. Scatter in measurements of residual Cd concentration was the largest source of uncertainty in estimates of N_{eff} .

Conclusions

Growth of CdSe quantum dots during the early stages of organometallic synthesis was reasonably described by an analytical model of the diffusion and depletion of Cd complexes. Nanocrystal growth was much more sensitive to Cd concentration than to Se concentration. Initial nucleation and final surface reconstruction were facilitated by high Se levels.

Photoluminescence and absorbance spectra were a convenient way to track the Arrhenius behavior of QD synthesis rates, using either redshift rates or reaction completion rates. Comparing growth in different coordinating solvents revealed that the activation energy could be tailored by the choice of solvent, to focus growth towards a desired nanocrystal size for a desired emission wavelength. Compared to growth in TOPO or in DA, CdSe nanocrystals grew more rapidly in SA, and produced narrow PL emission peaks at longer wavelengths, before the onset of unwanted Ostwald ripening.

Optimum quantum dot performance (in terms of high brightness and narrow spectral emission) was obtained by stopping growth significantly before Cd precursors were exhausted at the reaction completion time. The PLQY of quantum dots was highest at emission wavelengths about 30 nm shorter than λ_c , the wavelength for narrowest PL emission before the onset of Ostwald ripening. PLQY was more sensitive to growth conditions than emission width. Surface reconstruction of nanocrystals may be most effective when the growth rate is moderate (to give time for lateral mobility) and when the Se concentration is high (to restore surface stoichiometry).

For organometallic synthesis using TOPO, SA, or DA, the growth rate of CdSe quantum dots is probably controlled by the rate of diffusion and the rate of decomposition

of Cd-ligand complexes in the ligand barrier region. Both the physical structure and the chemical chelate interaction energy of the Cd-ligand complexes may contribute to the synthesis activation energy. Further experiments would be needed to separately estimate the magnitudes of the reaction rate and the diffusion rate in each solvent. Since all solvents narrowed the PL emission width as long as Cd was available, a slow diffusion rate must help control the growth rate.