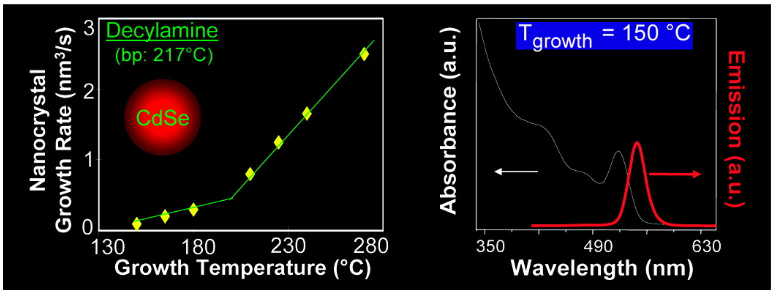
JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

Surface Ligand Dynamics in Growth of Nanocrystals

Narayan Pradhan, Danielle Reifsnyder, Renguo Xie, Jose Aldana, and Xiaogang Peng

J. Am. Chem. Soc., **2007**, 129 (30), 9500-9509• DOI: 10.1021/ja0725089 • Publication Date (Web): 10 July 2007



ACS Publications
High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
ARTICLES
Published on Web 07/10/2007

Surface Ligand Dynamics in Growth of Nanocrystals

Narayan Pradhan, Danielle Reifsnyder, Renguo Xie, Jose Aldana, and
Xiaogang Peng*

Contribution from the Department of Chemistry and Biochemistry, University of Arkansas,
Fayetteville, Arkansas 72701

Received April 10, 2007; E-mail: xpeng@uark.edu

Abstract: Amine ligands were identified to bond on the surface of CdSe nanocrystals in a dynamic fashion under elevated temperatures in the reproducible growth domain of the specific designed growth reactions. The surface ligand dynamics was found to strongly depend on the growth temperature, the ligand concentration, and the ligand chain length. The strong chain-length dependence was originated from the interligand interactions in the ligand monolayer of a nanocrystal, provided fatty amines being weak ligands for CdSe nanocrystals. When the growth reaction was above the boiling point of an amine ligand, the surface ligand dynamics was violent, a quasi-gas-phase state, indicated by strong temperature-dependent and fast growth rates of the nanocrystals. Approximately below its boiling point, a significantly weak temperature dependence of the growth rate of the nanocrystals associated with the quasi-liquid state of the surface ligands was observed. A direct result of studying the surface ligand dynamics of this well-established nanocrystal system was the formation of high-quality CdSe nanocrystals under much reduced temperature, 150 °C, in comparison to the standard 250−350 °C temperature range. This was achieved by using fatty amines with a short hydrocarbon chain at a low ligand concentration in the solution. Preliminary results indicate that a similar temperature (160 °C) also worked for the growth of InP nanocrystals.

Introduction

Synthesis of high-quality nanocrystals has been advanced dramatically in recent years. This progress has been largely inspired by the successful growth of high-quality CdSe nanocrystals under elevated temperatures through either the original organometallic approaches[1,2] or their alternative routes (also known as greener methods).[3−6] Today, a variety of high-quality nanocrystals have been grown under high temperatures, typically between 250 and 350 °C. One hypothesis[7,8] assumes that such high temperatures are needed because this is the only way to maintain a dynamic bonding of the surface ligands of nanocrystals, "on" and "off" the surface periodically. Another hypothesis[7,9] assumes that high temperature is necessary for the growth of single-crystalline nanoparticles with desired surface structures. These two assumptions, the first one being more fundamental and the other being more practical, are widely accepted in the field and have been considered as basic rules for design and optimization of synthetic chemistry of a new type of nanocrystals. Unfortunately, there are no solid data to support these assumptions although it is a known fact that II−VI and III−V semiconductor nanocrystals synthesized at relatively low temperatures do not show the same optical quality as those grown under high temperatures (roughly 250−350 °C).[7,9]

The surface ligands used in the high-temperature synthesis of high-quality nanocrystals are usually quite bulky, with a small anchoring group for bonding onto the surface of nanocrystals and a long/large hydrocarbon chain.[7,9] Without a rapid dynamics of these bulky surface ligands,[8] it would be difficult to understand the coexistence of a decent growth rate and the well-passivated surface of the resulting high-quality nanocrystals. It is also known that ligands with strong anchoring group(s) to the surface atoms of nanocrystals are often not good choices for synthesizing the nanocrystals.[7] This fact is again consistent with the dynamic bonding of the surface ligands. This is so because ligands with strong anchoring groups would not allow them to be dynamic through a medium-level thermal excitation in the temperature range between roughly 250 and 350 °C.

The fundamental importance for studying ligand dynamics can also be visualized by considering the shape control of nanocrystals.[7] It has been frequently observed in the traditional crystallization field that bonding of ligands on the surface of a crystal dominates crystal habits.[10] Some data in the field of nanocrystal growth[11,12] also supports such a growth model. Certainly, this model is quite different from the mechanism proposed for shape control of high-quality nanocrystals grown

---

(1) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115* (19), 8706−8715.
(2) Peng, X.; Wickham, J.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1998**, *120* (21), 5343−5344.
(3) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123* (1), 183−184.
(4) Qu, L.; Peng, Z. A.; Peng, X. *Nano Lett.* **2001**, *1* (6), 333−337.
(5) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124* (13), 3343−3353.
(6) Qu, L.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124* (9), 2049−2055.
(7) Peng, X.; Thessing, J. *Struct. Bonding (Berlin)* **2005**, *118*, 79−119.
(8) Yin, Y.; Alivisatos, A. P. *Nature* **2005**, *437* (7059), 664−670.
(9) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545−610.
(10) Mullin, J. W. *Crystallization*, 3rd ed.; Linacre House, Jordan Hill: Oxford, UK, 1997.
(11) Li, F.; Ding, Y.; Gao, P.; Xin, X.; Wang, Z. L. *Angew. Chem.* **2004**, *43* (39), 5238−5242.
(12) Chen, J.; Herricks, T.; Xia, Y. *Angew. Chem.* **2005**, *44* (17), 2589−2592.

10.1021/ja0725089 CCC: $37.00

by the common high-temperature routes, which implies that the growth of elongated nanocrystals would be mostly controlled by manipulating the activity of the monomers.[13] This means that the growth of elongated nanocrystals could only occur with a high monomer activity in the growth solution, and the resulting elongated nanocrystals would become dot-shaped when the monomer activity decreased.[5,13,14] The difference on growth of shape-controlled nanocrystals between the room-temperature and high-temperature approaches might also be a result of the different surface ligand dynamics in different temperature ranges. It is reasonable to consider that, at low temperatures, ligands or additives in a crystallization system will more likely stay on the surface of the nanocrystals and, thus, strongly affect the growth habits of the crystals. On the contrary, thermal agitation allows the surface ligands to be dynamic, which limits their influence on the growth habits of the crystals. As a result, the bonding of surface ligands could not hold the unstable shapes of the nanocrystals at high temperature, and the elongated shapes would be converted into stable dot-shaped ones upon the decrease of the monomer activity.[14,15]

In practice, it is desirable to reduce the reaction temperature for synthesis of high-quality nanocrystals for safety, energy efficiency, simplicity, and cost. In the recent years, greener methods[7] were introduced, which have substantially simplified synthetic chemistry of high-quality nanocrystals. For instance, high-quality CdS nanocrystals were grown in octadecene (ODE) with CdO and elemental S as the precursors and fatty acids as the ligands.[16] However, such a simple reaction would only work at elevated temperatures, between 250 and 310 °C, which required careful air-free operation. This is so because the flash point and autoignition point of the solvent, ODE, are in the range of approximately between 150 and 250 °C. Therefore, a low reaction temperature, preferably below 150 °C, will not only save energy, but also greatly simplify the operation. However, if high temperature is necessary for achieving high crystallinity, it would be impossible to reduce the growth temperature. It is thus much needed to distinguish which one of these two concerns, i.e., the surface ligand dynamic concern and crystallinity concern, provides the low-temperature limit for formation of high-quality nanocrystals.

We have developed various techniques to quantitatively evaluate the ligand dynamics on the surface of inorganic nanocrystals in a wide temperature range, from room temperature to about 300 °C. The results at room temperature on ligand dynamics of presynthesized and purified nanocrystals will be reported separately. This report will concentrate on ligand dynamics under elevated temperatures for the most studied model system, CdSe nanocrystals with fatty amines as the ligands. The results suggest that the surface ligand dynamics is not only a function of the reaction temperature but also strongly depends on the interligand interactions. For fatty amine ligands bonded onto the surface of CdSe nanocrystals under elevated temperatures, the boiling/melting points of the free ligands provide reasonable reference points to manipulate the surface ligand dynamics. The active surface ligand dynamics was found to play a critical role for determining the size, size distribution, growth rate, and even Ostwald ripening of a synthetic system. The results further indicate that, without sacrificing the quality of the nanocrystals, the growth temperature of high-quality CdSe nanocrystals can be significantly reduced (∼150 °C) than what are considered as today's standards (about 250−350 °C).

Results

The model system for studying surface ligand dynamics is chosen to be the CdSe nanocrystals grown under elevated temperatures using fatty amines as the ligands. This most studied system possesses a vast amount of data as references, and the resulting nanocrystals have been considered as standards for high-quality nanocrystals.[7,9] In addition, their excellent size-dependent optical properties provide convenient probes for studying the surface ligand dynamics.[17] Furthermore, these optical properties shall also offer some insight about the surface perfection of the nanocrystals as it was reported that CdSe nanocrystals with single-crystalline internal structure will not show excellent emission and absorption properties if the surface structure is not at an optimal state.[6]

Amines are known to be relatively weak ligands to a variety of compositions, including semiconductor, metal, and metal oxides, and thus they are widely used for synthesis of high-quality nanocrystals. For CdSe nanocrystals, it was observed that the photoluminescence (PL) brightness and solubility in nonpolar solvents decreased as the surface ligand coverage of amine ligands decreased during the purification step.[6] Interestingly, a reversible bonding of amines onto bulk CdSe crystals was also observed for reversibly enhancing the PL brightness of the bulk crystal.[18] This relationship, PL brightness versus the coverage of the surface ligands, has been exploited for studying the ligand dynamics of the CdSe nanocrystals as to be demonstrated below and the room-temperature results to be published separately. Furthermore, there are numerous types of fatty amines commercially available with low cost (see examples in Figure 1). As to be shown below, the structural diversity offers an important handle for probing the surface ligand dynamics.

Synthesis of high-quality CdSe nanocrystals was mostly developed before the introduction of noncoordinating solvent approaches.[1−6] However, a synthetic system based on coordinating solvents is not ideal for probing the surface ligand dynamics. This is so because a strong coordinating environment offered by a coordinating solvent system might force the surface ligands preferably to stay on the surface of the nanocrystals, i.e., an always saturated coverage of the surface ligand. For this reason, all results to be discussed below were obtained in a noncoordinating solvent, 1-octadecene (ODE). ODE is inexpensive (less expensive than toluene), not toxic (much less toxic than toluene), and more importantly, has a wide temperature window as a stable liquid for studying surface ligand dynamics, about from 20 to 315 °C.

Surface ligand dynamics of presynthesized CdSe nanocrystals at elevated temperatures was studied using their PL properties as the probe. Different from the related research conducted at room temperature (to be published separately), these high-temperature studies were designed to reveal

---

(13) Peng, X. *Adv. Mater.* **2003**, *15* (5), 459−463.
(14) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123* (7), 1389−1395.
(15) Yu, W. W.; Wang, Y. A.; Peng, X. *Chem. Mater.* **2003**, *15* (22), 4300−4308.
(16) Yu, W. W.; Peng, X. *Angew. Chem.* **2002**, *41* (13), 2368−2371.
(17) Brus, L. E. *Nanostruct. Mater.* **1992**, *1* (1), 71−75.
(18) Lisensky, G. C.; Penn, R. L.; Murphy, C. J.; Ellis, A. B. *Science* **1990**, *248* (4957), 840−843.

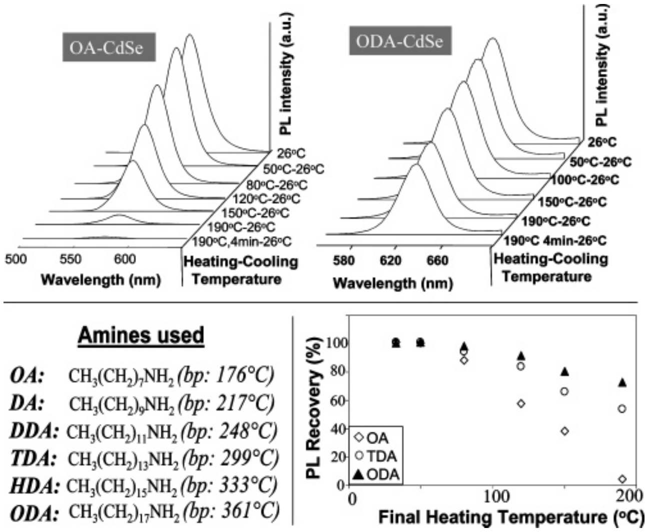


Figure 1. Top: PL spectra of CdSe nanocrystals coated with OA (left) and ODA (right) after the hot aliquots were cooled down to room temperature (26 °C). Bottom left: molecular formula and boiling point (bp) of all fatty amines used in this study. Bottom right: PL peak intensity for the aliquots taken at different temperatures and measured at 26 °C.

relevant information for growth of the nanocrystals. Thus, the studies were performed in a similar solvent/ligand system, with ODE as the solvent and amine as the ligand. The fundamental rational behind these tests is that, as mentioned above, the PL intensity of the nanocrystals will diminish (enhance) if the surface ligand coverage of the nanocrystals decreases (increases).[6]

Although the focus of this work was on the surface ligand dynamics in growth of the nanocrystals, results on presynthesized nanocrystals actually offered us some significant insights for designing the experiments with growth reactions.

The first set of data were collected by taking aliquots from a given hot ODE solution with the presynthesized CdSe nanocrystals dissolved in it. The aliquot taken at a given temperature was immediately diluted to a given concentration with room-temperature hexanes. PL spectra for all diluted solutions were recorded under the same conditions. Two such sets of PL spectra are shown in Figure 1 (top). As expected, CdSe nanocrystals lost their PL intensity upon heating them to elevated temperatures. The lower the boiling point of the amine ligand was, the easier the nanocrystals lost their PL brightness (Figure 1, bottom right). For instance, after heating up to about 190 °C, the PL intensities of the CdSe nanocrystals coated with octylamine (OA), tetradecylamine (TDA), and octadecylamine (ODA) recovered about 5%, 55%, and 72%, respectively. Furthermore, a prolonged heating at a given temperature impacted the CdSe nanocrystals coated with different amines in a substantially different way. As shown in Figure 1 (top), by heating at 190 °C for 4 min, the PL recovery dropped to almost zero for the OA-coated nanocrystals and hardly changed for the ODA-coated ones.

The above results imply that the response of the surface ligands to the temperature change is associated with the chain length of the amine ligands of the free ligand. This result is actually reasonable. Amine ligands are weak ligands for CdSe nanocrystals as pointed out above, and thus the ligand−ligand interaction on the surface of a nanocrystal will dominate the ligand−nanocrystal interaction. Therefore, the dynamics of the surface ligands at a given temperature should resemble that of free ligands, which is reflected by their melting point and boiling point. As the chain length of the amines increases, the boiling/melting points increase quite significantly (see the boiling point listed in Figure 1) as their interchain interaction increases. Similarly, the chain-length dependence of the interligand interaction on the surface of a nanocrystal should strongly impact the surface ligand dynamics in the ligand monolayer of the nanocrystal. Consequently, as the chain length of an amine ligand increases, the tendency of the ligand leaving the surface of a nanocrystal decreases at a given temperature.

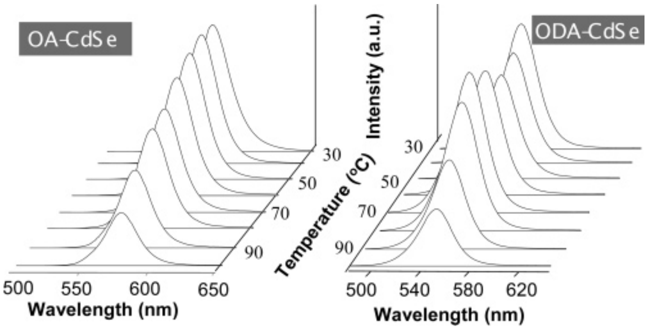


Figure 2. In situ PL spectra of CdSe nanocrystals at different temperatures.

Figure 2 illustrates the in situ PL spectra of CdSe nanocrystals in ODE at different temperatures. To make the results reproducible, it was necessary to add about 5% of free amine in the solution. Without free amines added, the experimental results were generally irreproducible and precipitation of nanocrystals could occur, indicating dramatic loss of the surface ligands. Again, the nanocrystals behaved quite differently in this set of experiments as the chain length of their amine ligands varied. The OA-coated CdSe nanocrystals (Figure 2, left) had a monotonic and gradual decrease in intensity as the temperature increased, which is consistent with the thermal excitation of the lattice phonons of CdSe nanocrystals as reported in the literature.[19] However, the response of the PL spectrum of the ODA-coated CdSe nanocrystals against temperature change (Figure 2, right) had a rather complex pattern. A relatively quick decrease in intensity was observed as the temperature increased from 30 to about 50 °C. After that, the PL was enhanced and followed by a decrease. As to be illustrated in the next paragraph, this complex pattern can be well explained by considering the chain-length dependence of the surface ligand dynamics.

The melting points (mp) of free OA and ODA are −4 and 51 °C, respectively. When OA was used as the ligands, all temperatures tested were higher than the mp of OA (Figure 2, left), and the phonon-induced PL quenching[19] was playing a dominating role in determining the PL spectrum evolution upon changing the temperature. This should result in a monotonic decrease (Figure 2, left). However, for the case of ODA (Figure 2, right), this monotonic decrease was interrupted by the melting of the surface ligands. When the temperature was above 50 °C (roughly the mp of the surface ligand in the bulk form), ODA molecules should become much more mobile/dynamic on the surface of a nanocrystal. Consequently, this quasi-melting event offered the surface ligands some freedom to optimize their

---

(19) Empedocles, S. A.; Norris, D. J.; Bawendi, M. G. *Phys. Rev. Lett.* **1996**, *77* (18), 3873−3876.

bonding situation on the surface of the CdSe nanocrystals, which resulted in a local maximum in the PL intensity evolution by changing the solution temperature. When the temperature was above about 70 °C, the universal phonon-induced PL quenching took control of the system again.

The melting-induced reversible PL brightening (Figure 2) is somewhat similar to the photoinduced PL brightening observed previously.[20] When the temperature is higher than the mp of the ligands, the gained freedom of the hydrocarbon chain during a phase transition shall enable the amine group of a ligand to achieve an optimal bonding geometry with the surface metal ions. For similar reasons, to be discussed below, the ligand dynamics shall also be related to the boiling point of the ligands. Generally speaking, the mobility of relatively weak ligands either within the ligand monolayer or away from the ligand shell is not solely determined by the bonding between the weak bonding group and the surface atoms on the nanocrystals. Instead, the molecular interactions between the organic chains shall also play a visible role.

It should be pointed out that PL antiquenching in heating up amine-coated CdSe nanocrystals by exciting the rotational motion of the surface ligands associated with a solid−solid phase transition was reported in the literature.[21] Usually, the influence on molecular dynamics caused by a solid−liquid phase transition should be much more pronounced than that in a solid−solid phase transition. Therefore, the observation of a local maximum of PL brightness around the mp of the ligands (Figure 2, right) should be reasonable. As to be discussed below, an even more dramatic effect on surface ligand dynamics would be encountered when the molecules underwent a liquid−gas phase transition.

There are two important pieces of information that need to be mentioned for supporting the analysis of the in situ experiments in Figure 2. One, the temperature-dependent patterns in Figure 2 was repeatedly recorded as long as the maximum heating temperature was significantly below the boiling point of the corresponding free ligands. The process was quite reproducible as long as the heating temperature was not too high (see more discussion in the next paragraph). Two, it is reasonably safe to claim that the universal PL quenching observed in Figure 2 was mostly due to the phonon-induced quenching.[19] For instance, comparing the data in Figure 1 and Figure 2, one can conclude that the PL quenching in the temperature range in Figure 2 could be mostly recovered upon cooling down the system, especially for the ODA−CdSe case.

The dynamic nature of the surface ligands actually made the data shown in Figures 1 and 2 be less quantitative as they seemed to be. The surface ligand coverage of the presynthesized and purified CdSe nanocrystals might vary from sample to sample. For the same sake, the free ligand concentration in a given sample was also difficult to control. Furthermore, it was not possible to study the ligand dynamics of the presynthesized nanocrystals under these conditions to even higher temperatures. This is so because CdSe nanocrystals would go for Ostwald ripening at temperatures higher than approximately 200 °C under the given conditions.

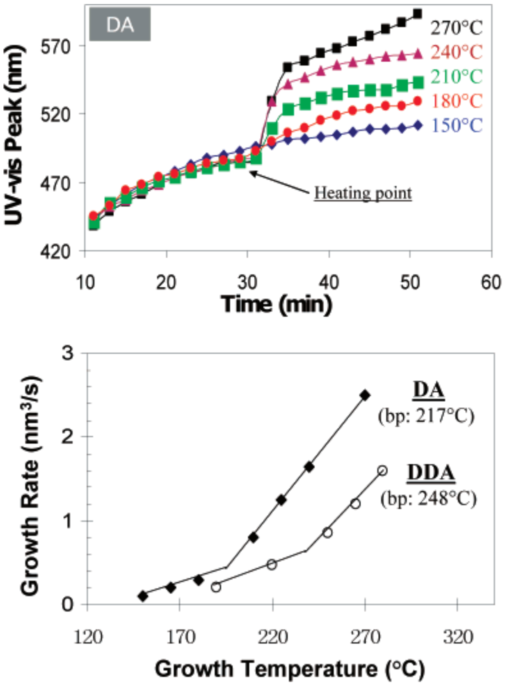


Figure 3. Temperature-dependent growth rates of CdSe nanocrystals. Top: raw data for DA−CdSe system. Bottom: calculated volume growth rates for DA− and DDA−CdSe systems at different temperatures.

The temperature-dependent surface ligand dynamics during nanocrystal growth was studied using the CdSe/amine nanocrystal/ligand system in ODE. The results in Figure 2 indicated that the dynamics of surface ligands changed at around the mp of the corresponding bulk crystals of the fatty amines. The data in Figure 1 suggested that the surface ligand dynamics may be also a function of the boiling point of the ligands. As boiling usually changes the molecular dynamics of a molecule more dramatically than melting does, it would be reasonable to hypothesize that the surface ligand dynamics should change dramatically around the boiling point of the corresponding free ligands. However, the experiments with presynthesized nanocrystals discussed above could not reach the desired high temperature due to Ostwald ripening. In this subsection, we will illustrate some clear evidence observed in the growth of the nanocrystals to support this hypothesis.

Formation of high-quality nanocrystals has two distinguishable stages, nucleation and growth.[10] To study the surface ligand dynamics, it is important to confine the system in one single stage. The growth stage was chosen in this work since the nucleation stage of nanocrystals is much less studied and more difficult to control. As shown in Figure 3, a reaction system was allowed to pass the nucleation stage and reach a stable growth pattern before the growth temperature was suddenly varied. In this way, it was possible to study the temperature factor during the growth of nanocrystals by fixing the other reaction parameters.

The size-dependent absorption spectrum of CdSe nanocrystals[22] is used as a convenient probe for monitoring the growth of the nanocrystals. As shown in Figure 3 (top), the red-shift of the UV−vis peak of the nanocrystals indicated the increase of their size over time. By adopting a relatively inactive

---

(20) Nazzal, A. Y.; Qu, L.; Peng, X.; Xiao, M. *Nano Lett.* **2003**, *3* (6), 819−822.

(21) Wuister, S. F.; van Houselt, A.; de Mello Donega, C.; Vanmaekelbergh, D.; Meijerink, A. *Angew. Chem.* **2004**, *43* (23), 3029−3033.

(22) Yu, W. W.; Qu, L.; Guo, W.; Peng, X. *Chem. Mater.* **2003**, *15* (14), 2854−2860 with a correction published in **2004**, *16*, 560.

cadmium precursor, cadmium TDPA (cadmium tetradecylphosphonate salt), the nucleation of the nanocrystals was controlled to occur in a slow rate, taking about a few minutes to show any detectable formation of nanocrystals. This allowed repeating each growth reaction reliably as indicated by the reproducible temporal evolution traces of the UV−vis peak position for five repeated reactions (before the heating point in Figure 3 (top)).

When the reaction temperature was suddenly increased from the base temperature, 150 °C for the case using DA and 180 °C for the case using DDA shown in Figure 3, the growth rate of the nanocrystals increased, and the degree of rate increase depended strongly on the new growth temperature. Following this rapid growth period, the growth always ended in a plateau as repeatedly observed previously under constant reaction temperatures.[7]

The initial growth rate of the nanocrystals upon increasing the reaction temperature was calculated for each reaction in the rapid growth period upon varying the reaction temperature. This calculation was based on the sizing curve of CdSe nanocrystals reported in the literature.[22] These initial growth rates for the cases using decylamine (DA) and dodecylamine (DDA) are shown in Figure 3 (bottom). The same trend also observed for other amines (data not shown).

Because all reactions in each reaction series shown in Figure 3 were designed to be the same before increasing the reaction temperature (see above), the monomer concentration, particle concentration, and the solution composition for each reaction before the temperature increase should be similar to each other in each reaction series; it should thus be justifiable to compare the growth temperature effect using the initial reaction rates. After the initial stage, the monomer concentration depleted rapidly by the growth of the nanocrystals. The faster the nanocrystals grew, the faster the depletion of the monomers was. This means that the rapid drop of monomer concentration depended on the final temperature. Therefore, the reaction rate in late stage (the plateau part in each reaction (Figure 3, top)) could not be directly related to the change of reaction temperature. For the purpose in the current study, we would concentrate on the initial rates only.

The results in Figure 3 (bottom) revealed that the temperature dependence of the volume growth rate of the CdSe nanocrystals with a given type of amine had two different linear regimes (see the Discussion section below for justification), a sharper increase in the relatively high-temperature window and a smaller slope in the low-temperature range. The transition point for these two regimes was about 10−20 °C below the boiling point of the free ligands in this specific system (Figure 3, bottom).

A similar transition point, always close to the boiling point of the amine ligands, was also observed using other types of amine ligands, such as OA, DDA, and TDA, and/or with a different cadmium precursor. For example, when the cadmium TDPA was replaced by cadmium stearate (a relatively reactive cadmium precursor) and DA was used as the ligands, a transition point of the surface ligand dynamics was identified to be between 200 and 210 °C (Figure S1, Supporting Information).

A plausible explanation for the two growth regimes with a transition point close to the boiling point of the ligands is that there were two different types of surface ligand dynamics under elevated temperatures, which is the hypothesis given in the beginning of this subsection. As pointed out above, amines are relatively weak ligands for CdSe nanocrystals;[6,18] the interchain interaction would play a key role in determining the surface ligand dynamics. When the temperature was higher than the mp but lower than the boiling point, the surface ligands would be reasonably mobile on the surface of nanocrystals, similar to a quasi-liquid state, which allow them to switch between “on” and “off” states relative to the surface atoms of a nanocrystal. When the temperature was close to or higher than the boiling point, the surface ligands on a nanocrystal become completely dynamic, similar to a quasi-gas phase. As a result, the surface ligands would be mostly at their “off” state, which substantially enhanced the growth rate of the nanocrystals. Some further and quantitative discussion on this matter will be given in the Discussion section.

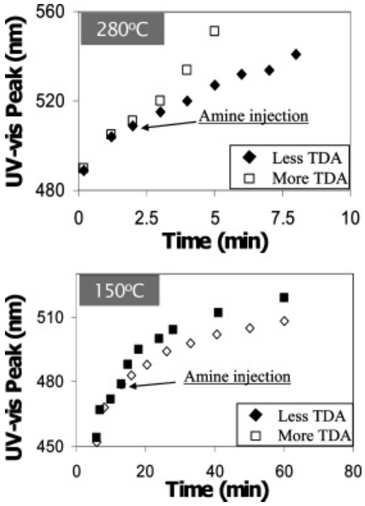


Figure 4. Impact of amine (TDA) concentration on the growth of nanocrystals at 280 °C (above the bp for TDA) (top plot) and 150 °C (below the bp of TDA) (bottom plot).

The concentration-dependent surface ligand dynamics was studied in the growth stage. As the ligands were dynamically bonded onto the surface of nanocrystals at elevated temperatures, the surface ligand coverage should depend on the total concentration of the free ligands in the solution, which should in turn affect the growth rate of nanocrystals.

The experiments for this subsection were carried out in a similar fashion with those in the above subsection. Instead of a sudden increase of the reaction temperature, extra ligands were injected into the reaction system at a give moment (Figure 4). In order to eliminate the dilution factor and temperature difference, the amines were dissolved in ODE to maintain the same total mass for each injection. These amine solutions were heated to about 100 °C prior to the injection into the reaction system to minimize the temperature impact to the reaction system caused by the injection of the amine solution.

Ideally, if the ligands are dynamically bonded onto the surface of the nanocrystals, increase of the total ligand concentration in the solution should increase the number of ligands on the surface of each nanocrystal. This should consequently decrease the growth rate of the nanocrystals. The results shown in Figure 4 (bottom) indicate that the growth rate of the nanocrystals did decrease after the amine concentration in the solution increased when the reactions were performed at 150 °C. Furthermore, the same results in Figure 4 (bottom) also indicate that the response time of the surface ligands to the change of the total concentration of the ligands was within a minute, a very fast process.

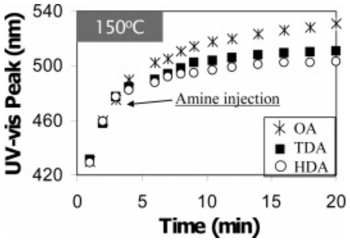


Figure 5. Impact of ligand chain length on the growth rate of the nanocrystals.

However, when the same experiments were performed at 280 °C for TDA, the activation of the precursors took control over the fast surface ligand dynamics in the quasi-gas dynamics. It was known that amines are both ligands and activation reagents for synthesis of oxide and chalcogenide nanocrystals when fatty acid salts and phosphonic acid salts were used as the precursors (see Figure S2, Supporting Information). Therefore, addition of amines in the growth stage will initiate two competitive processes, accelerating the growth by activating the precursors and decelerating the growth by providing an increased ligand coverage for the nanocrystal surface. At 280 °C, the molecular dynamics of this specific ligand system should be in its quasi-gas window, and the ligands would spend most of their time apart from the surface of nanocrystals. However, a high reaction temperature would greatly enhance the activation capability of the amines toward the reactivity of the precursors. Thus, the overall result was an increased growth rate of the nanocrystals at this high-temperature case.

It should be pointed out that 150 °C was within the activation temperature range for amines (Figure S2, Supporting Information), which means the activation process should also have occurred at this temperature. Therefore, the decrease of growth rate revealed in Figure 4 (bottom) caused by a high concentration of amine was actually underestimated. It should also be pointed out that the suppressed growth rate at relatively low reaction temperature was found to be independent of the type of amine and/or the cadmium precursor (Figure S3, Supporting Information).

The surface ligand dynamics of amines with different chain lengths was directly compared. The results illustrated in Figures 1−3 indicate that the surface ligand dynamics of amine ligands in the current system was highly dependent on the reaction temperature relative to the boiling/melting points of the bulk amines. This conclusion would be better supported by the results obtained by only varying the structure of the amines. This is so because the nucleation of the nanocrystals using different types of amines discussed above was substantially different from each other. Consequently, the concentration of the particles, remaining monomer concentration, and the size of the nanocrystals were all noticed to be different from one type of amine to another.

The results for the three reactions in Figure 5 were obtained by initiating all reactions using an identical system including the initial amine ligands (OA). After the system passed the initial nucleation and the fast growth period, the same molar amount of amines with different chain lengths, OA, TDA, and HDA, were separately dissolved in a given amount of ODE and injected into a given reaction. The reaction temperature, 150 °C, was selected to confine all three amines in their quasi-liquid state on the surface of nanocrystals.

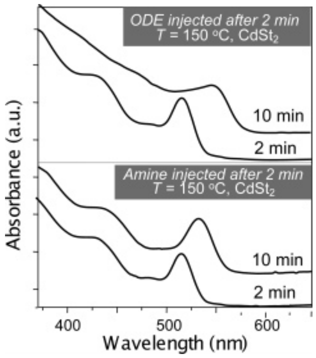


Figure 6. Effects of surface ligand dynamics in Ostwald ripening. Note: cadmium stearate ($CdSt_2$) was used as the cadmium precursor.

The results in Figure 5 clearly reveal that, in the growth stage under a given temperature, the growth rate of the nanocrystals decreased by the increase of the chain length of the amines. This observation is consistent with the other results discussed above. As the chain length of fatty amines increases, their boiling point increases, and thus the surface ligands becomes less dynamic on the surface of nanocrystals.

Ligand dynamics in Ostwald ripening was also observed in the experiments. Ostwald ripening[10] refers to the process in which the small particles dissolve and the monomers grow back onto the relatively large particles in the solution. Ostwald ripening usually broadens the size distribution of the nanocrystals, also known as “defocusing of size distribution”.[2] This is driven by the fact that the solubility of nanocrystals increases sharply as the particle size decreases. After a nanocrystal ensemble goes through Ostwald ripening, the total surface free energy decreases and the system becomes more thermodynamically stable.

Similar to the growth of nanocrystals, Ostwald ripening should also require that the surface ligands not completely coat the nanocrystals, at least not all the time. If the surface ligands are dynamic in a reaction system, the surface ligand coverage at a given moment shall depend on the total ligand concentration in the solution. Consequently, the rate of Ostwald ripening should slow down as the total ligand concentration increases. This was actually observable in the current reaction system. As shown in Figure 6, the size distribution of the CdSe nanocrystals in the reaction with amine added (Figure 6, bottom) was more or less retained from 2 to 10 min, revealed by the similar sharpness of the absorption features in the corresponding absorption spectra. Conversely, the absorption spectrum at 10 min became more or less structureless for the control experiment with pure ODE injected, implying a significant broadening of the size distribution of the nanocrystals. It should be pointed out that cadmium steareate (or other types of cadmium fatty acid salts, such as cadmium oleate) was used as the cadmium precursor, instead of cadmium TDPA, in order to observe significant Ostwald ripening at a relatively low reaction temperature. When cadmium TDPA was used, the reaction was too slow to show dramatic effects for Ostwald ripening.

In practice, a major goal for synthesis of nanocrystals is to obtain nearly monodisperse nanocrystals. The results in Figure 6 imply that manipulation of ligand dynamics might also be exploited in certain cases to achieve this goal.

Formation of high-quality CdSe nanocrystals at 150 °C, a temperature substantially lower than the standard protocols

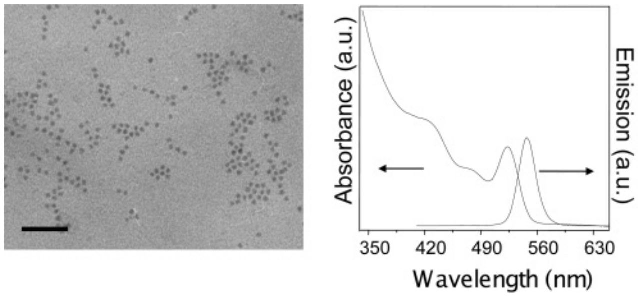


Figure 7. TEM image (left) and PL (right) properties of the CdSe nanocrystals grown at 150 °C. Scale bar = 50 nm.

(250−350 °C),[7,9] became evident during this study although the main goal of this work was to understand the surface ligand dynamics. The general understanding on formation of high-quality semiconductor nanocrystals is that a synthetic system should maintain a balanced rate of nucleation and growth.[7,9] To maintain this balance, a successful synthetic scheme at a substantially reduced reaction temperature was to apply amine ligands with a significantly decreased hydrocarbon chain in comparison to the typical ones in the literature, such as ODA, hexadecylamine (HDA), and oleylamine.

As pointed out above, amines were acting as both activation reagents and the ligands in the current system. Without the addition of amine, the nucleation of CdSe nanocrystals took more than 10 min at 150 °C if cadmium TDPA was used as the precursor (Figure S2, left, Supporting Information), indicated by the color change of the solution from colorless to yellow/orange. In addition, the growth of the slowly formed CdSe nuclei in the case without amine was quite fast because of the relatively high remaining monomer concentration in the solution. As a result, a balanced nucleation and growth was not reached, indicated by the broad features in their absorption spectra.

When amines were added into the noncoordinating reaction solvent (ODE), the nucleation process was shortened to about a couple of minutes (Figure S2, right and middle, Supporting Information), and a significant "focusing of size distribution"[2] was observed, evidenced by the sharp features in the absorption spectra for the samples after the reactions proceeded more than 10 min. The results in Figure S2 further indicate that, by using an amine with a short chain length (DA instead of DDA), the growth rate of the high-quality nanocrystals was significantly increased. According to the results discussed above, this was likely due to the fast surface ligand dynamics of DA in comparison to that of DDA. Furthermore, the size range and reaction rate can also be adjusted by using a more reactive cadmium precursor, such as cadmium stearate, in place of cadmium TDPA. A few examples of absorption spectra of high-quality CdSe nanocrystals formed using cadmium stearate as the precursor can be found in Figure 6.

Some of the nanocrystals formed at 150 °C were examined under transmission electron microscope (TEM). The samples with sharp UV spectra were found to possess a similar tight size distribution with the standard samples obtained through the traditional high-temperature approaches[6] (See Figure 7, left, for an example), and the nanocrystals were found to possess cubic structure by using electron diffraction.

It has been a general concern that the emission properties of semiconductor nanocrystals grown at relatively low temperatures would be poor. In addition, existing data in the literature also imply that CdSe nanocrystals synthesized using short amine ligands in the classic temperature range did not show desirable emissive properties.[6] However, the CdSe nanocrystals synthesized at 150 °C using fatty amines with a relatively short hydrocarbon chain as the ligands did show excellent PL properties. It was possible to have pure band gap emission with a PL line width comparable to the best values reported in the literature. For instance, the PL spectrum shown in Figure 7 (right) did not have any deep trap emission and the full width at half-maximum (fwhm) was about 25 nm (about 90 meV). The PL quantum yield of these nanocrystals was estimated to be between 20% and 50%, similar to those reported for standard samples synthesized under high temperatures using those amines with a long hydrocarbon chain (ODA and HDA),[6] although the reaction schemes discussed here were not particularly optimized for obtaining a high PL quantum yield.

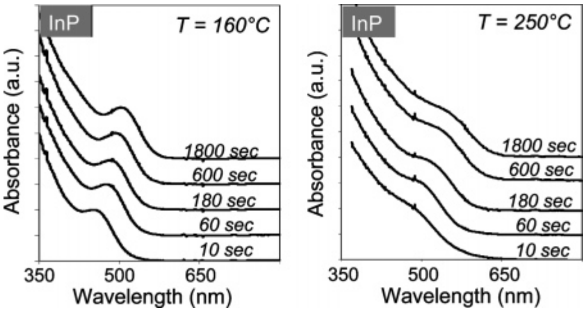


Figure 8. Temporal evolution of absorption spectra of InP nanocrystals grown at 160 °C (left) and 250 °C (right), with TDA as the ligand.

Formation of high-quality CdSe nanocrystals at around 150 °C implies a much extended temperature range for consideration while developing synthetic chemistry for new nanocrystal systems. InP nanocrystals[23−29] are one of the most studied systems for III−V semiconductor nanocrystals, and their quality, however, has been significantly lower than that of CdSe ones. Preliminary results indicate that growth of InP nanocrystals with quality comparable to that of the InP nanocrystals reported in the literature[23−29] was possible at 160 °C without size sorting (Figure 8, left). As comparison, the quality of the resulting InP nanocrystals (Figure 8, right) grown under standard temperatures (250 °C), judged by the sharpness of the absorption spectra, was substantially worse than that of the ones grown under 160 °C with the other conditions being the same. These preliminary results are strong encouragements for us to develop an economic and reliable synthetic chemistry for InP and other types of III−V semiconductor nanocrystals with their quality being comparable to that of the standard CdSe ones.

The results in Figures 7 and 8 indicate that effects of ligand dynamics should be taken into account while developing a high-performance synthetic scheme for a nanocrystal system. One

---

(23) Micic, O. I.; Sprague, J. R.; Curtis, C. J.; Jones, K. M.; Machol, J. L.; Nozik, A. J.; Giessen, H.; Fluegel, B.; Mohs, G.; Peyghambarian, N. *J. Phys. Chem.* **1995**, *99* (19), 7754−7759.

(24) Guzelian, A. A.; Katari, J. E. B.; Kadavanich, A. V.; Banin, U.; Hamad, K.; Juban, E.; Alivisatos, A. P.; Wolters, R. H.; Arnold, C. C.; Heath, J. R. *J. Phys. Chem.* **1996**, *100* (17), 7212−7219.

(25) Battaglia, D.; Peng, X. *Nano Lett.* **2002**, *2* (9), 1027−1030.

(26) Talapin, D. V.; Gaponik, N.; Borchert, H.; Rogach, A. L.; Haase, M.; Weller, H. *J. Phys. Chem. B* **2002**, *106* (49), 12659−12663.

(27) Lucey, D. W.; MacRae, D. J.; Furis, M.; Sahoo, Y.; Cartwright, A. N.; Prasad, P. N. *Chem. Mater.* **2005**, *17* (14), 3754−3762.

(28) Gerbec, J. A.; Magana, D.; Washington, A.; Strouse, G. F. *J. Am. Chem. Soc.* **2005**, *127* (45), 15791−15800.

(29) Xu, S.; Kumar, S.; Nann, T. *J. Am. Chem. Soc.* **2006**, *128* (4), 1054−1055.

Table 1

	temperature above ligand bp	temperature below ligand bp
growth rate	Generally fast. Difficult to reduce by decreasing ligand concentration, but feasible by increasing chain length of ligands at a fixed temperature.	Generally slow. Accelerated by using a high ligand concentration and a ligand with less steric hindering.
size of the nanocrystals	High growth rates makes reactions under these conditions are more suited for synthesizing nanocrystals with large sizes.	Mild growth rates render better control of the size of the nanocrystals. A low ligand concentration benefits growth of large nanocrystals.
size distribution	Defocusing of size distribution occurs readily. May be controlled by reducing the nuclei concentration to have more monomers in the solution.	Defocusing of size distribution may be avoided by using a high ligand concentration to better passivate the surface of the nanocrystals.
surface coverage of ligands	A high ligand concentration can offer a decent surface ligand coverage of the nanocrystals.	Ligand concentration can be increased after the size of the nanocrystals reaches the desired value.

of the reviewers suggested that the authors offer a summarizing table for such effects. Table 1 is a direct result of this suggestion. It should be noticed that the surface ligands may play multiple roles in a synthesis, such as stabilizing reagents for the monomers, activation/prohibiting reagents for the monomers, and reducing/oxidation reagents, etc. These additional effects are not discussed in Table 1. For instance, amines are certainly an activation reagent for the monomers in the current system, in addition to their role as the surface ligands to the nanocrystals in the current system.

Discussion

The results illustrated above reveal that the bonding of amine ligands to the surface of CdSe nanocrystals at elevated temperatures is dynamic in nature. The response time to the change of solution environment, such as temperature (Figures 1−3), concentration (Figures 4 and 6), and chain length of the amine ligands (Figure 5), was beyond the resolution of the experiments (less than 1 min). Such fast response of the surface ligands was consistent with the decent growth rate of high-quality nanocrystals in similar reaction systems. The dynamic nature ensured that there should be a sufficient ligand coverage on a nanocrystal at a given moment, which resulted in a good solution stability.

The temperature dependence of the surface ligand dynamics was not completely surprising as thermal agitation should always excite the molecular random motion in general. The relationship between the surface ligand dynamics and the boiling/melting points of the corresponding ligands in bulk, however, was interesting. Because the boiling/melting points of fatty amines are mostly determined by the chain length of the molecules (see Figure 1 for the data of boiling points), the surface ligand dynamics should thus be closely related to their chain length. This means that the reaction temperature, if only determined by the surface ligand dynamics, should be considered as a relative parameter which should be measured using the ligand boiling/melting points as the references. The results reported here reveal that, at least for CdSe nanocrystal system, the surface ligand dynamics did play a key role for determining the reaction temperature.

Thus, it was possible to synthesize high-quality nanocrystals with a much reduced temperature by applying a weak ligand with a relatively low boiling point. For the model system used here, CdSe nanocrystals with fatty amines as the ligands, the reaction temperature could be reduced from 250 to 350 °C[1−6] to at least as low as 150 °C without sacrificing the quality of the nanocrystals. Further reduction of the reaction temperature might need to take the viscosity of the solution, the reactivity of the precursors, and the monomer dynamics on the surface of nanocrystals into account. The latter parameter is directly associated with the crystallinity and surface optimization of the resulting nanocrystals,[6] which will in turn determine the optical quality of the nanocrystals.

The optimal reaction temperature for a given amine is usually in the range slightly below its boiling and much higher than its mp, i.e., in the high-temperature section of its quasi-liquid state on the surface of nanocrystals. Not surprisingly, this has been true for the successful traditional organometallic approaches and greener approaches as well.[1−6] When a coordinating solvent was applied, the upper limit of the temperature must be the boiling point of the ligands. As high reaction temperature (250−350 °C) was used, ligands with a long hydrocarbon chain would be natural choices. For the synthesis using noncoordinating solvent, the growth reaction can be performed under a temperature significantly below the boiling point of the ligands (Figure 3). This actually illustrates one advantage of noncoordinating solvent approaches.[16] If one prefers a low reaction temperature, significantly below the boiling point of a ligand, the slow growth rate of the nanocrystals at such a temperature could be accelerated by reducing the total ligand concentration in the solution (Figure 4).

Shape-controlled synthesis of nanocrystals has attracted significant attention in recent years. Many experimental results for the formation of elongated semiconductor nanocrystals at high temperatures indicate that the chemical potential of the monomers, i.e., the activity of the monomers, has played a decisive role.[7] For instance, elongated nanocrystals were often formed when the monomer activity was high. When the monomer activity decreased to below a certain threshold, the formed nanocrystals with an elongated shape actually became unstable and were readily converted into dot-shaped nanocrystals.[7] However, growth of shape-controlled nanocrystals at room temperatures was often observed to be solely determined by the existence of ligands/adsorbents, and thus they are stable in the reaction system.[11,12]

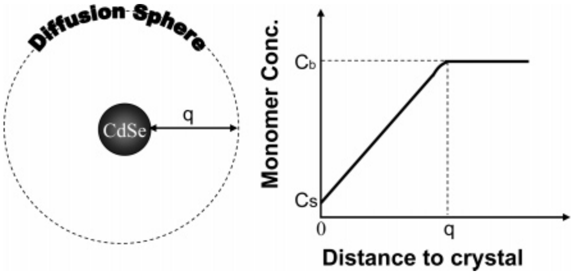


Figure 9. Schematic diagram of the diffusion-controlled growth model. C_b and C_s are the monomer concentration in the bulk and at the nanocrystal surface, respectively.

From surface ligand dynamic point of view, the difference for shape-controlled growth of nanocrystals at room temperature and under elevated temperature seems to be quite reasonable. At room temperature, the ligands on the surface of a crystal should pack well and behave as a condensed phase monolayer, either quasi-solid state or the low-temperature limit of quasi-liquid state, instead of a highly dynamic state, i.e., close to quasi-gas phase under elevated temperatures. Consequently, template effect of ligands might only be observed at room temperature. This explanation is actually consistent with the results about the self-assembly of surfactants, for which organized structures would be completely destroyed in solution when the temperature is sufficiently high.

The temperature-dependent growth rates shown in Figure 3 (bottom) are very interesting. At this moment, most experimental data for the growth of high-quality nanocrystals under elevated temperatures have been considered to be consistent with diffusion-controlled growth.[7] A diffusion-controlled model (Figure 9) for the growth of crystals assumes that every nanocrystal is surrounded by a diffusion sphere. The concentration gradient for diffusion is built up by the monomer concentration difference between the bulk solution (C_b)—outside the diffusion sphere—and at the nanocrystal–ligand interface (C_s).[7]

The diffusion flux (f) passing through the diffusion sphere of a crystal can be calculated by Fick's first law:

$$f = -(4\pi q^2)D(\mathrm{d}C/\mathrm{d}r) \tag{1}$$

Here, D is the diffusion coefficient of the monomers. C is the monomer concentration and r is the distance from the surface of a nanocrystal (Figure 9). q is the radius of the diffusion sphere, and the corresponding surface area of the diffusion sphere is $4\pi q^2$, assuming that the size of the nanocrystal is negligible in comparison to q. In the fast growth period shown in Figure 3 (top), the monomer concentration in the solution was sufficiently high in comparison to the monomer concentration at the surface of the nanocrystal. Therefore, it is reasonable to assume that the concentration gradient (dC/dr) crossing the diffusion sphere can be simplified as $-C_b/q$.

The volume growth rate (dV/dt) for a diffusion-controlled crystal growth process is solely determined by the diffusion flex going into the diffusion sphere.

$$\begin{aligned}\mathrm{d}V/\mathrm{d}t &= -(4\pi q^2)D\,\mathrm{d}C/\mathrm{d}r\\ &= (4\pi qD)C_b\\ &= ((2qRT)/(3\eta a))C_b\end{aligned} \tag{2}$$

The last step was performed by replacing D by $(RT)/(6\pi\eta a)$, which is the Stokes–Einstein equation.[30] R, T, η, and a are the gas constant, absolute temperature, viscosity in the diffusion sphere, and the hydrodynamic radius of the monomers, respectively. The monomer concentration in the bulk solution, C_b, in the rapid growth period was about the same when temperature was suddenly varied in Figure 3 for a given amine system. Therefore, the volume growth rate of nanocrystals should be linearly proportional to the reaction temperature, assuming that q, η, and a are constants. That is,

$$\begin{aligned}\mathrm{d}V/\mathrm{d}t &= ((2qRC_b)/(3\eta a))T\\ &= \alpha T\end{aligned} \tag{3}$$

Equation 3 was the quantitative justification for the linear trend lines used in Figure 3 (bottom) and Figure S1 in the Supporting Information. Evidently, experimental results in Figure 3 (bottom) and Figure S1 indicate that there were two different α values, a small value for the temperatures approximately below the boiling point of the free amines and the other for the relatively high temperatures. The difference between two α values was quite significant. For example, the high-temperature α was about 4.2 times larger than that for the low temperature for the DA system in Figure 3. In this simple model, the significant difference of α values in different temperature windows could be considered as a result of a sudden change of the viscosity *within the diffusion sphere* as the surface ligand dynamics underwent a phase transition from a quasi-solution state to a quasi-gas state as discussed above. This is so because the phase transition from a quasi-solution state to a quasi-gas state should reduce the temporal average ligand coverage on the surface of each nanocrystal, which in turn should decrease the barrier for the diffusion.

Conclusion

Ligand dynamics on the surface of CdSe nanocrystals under elevated temperatures was found to depend on the solution temperature, the concentration of the ligands, and the chain length of the ligands. The latter was due to the fact that the fatty amines used in this study were weak ligands to CdSe nanocrystals. Therefore, the ligand–ligand interaction on the surface of a nanocrystal played a determining role for the surface ligand dynamics. For the same reasons, the boiling/melting points were identified as important parameters for determining the growth modes for colloidal nanocrystals in solution. Typically, the growth rate of nanocrystals would be too fast in the quasi-gas-phase temperature regime and too slow when the temperature was significantly below the boiling point of the ligands. The volume growth rates of CdSe nanocrystals were found to be approximately linearly proportional to the reaction temperatures, with a large slope in the quasi-gas regime of the surface ligands and a small slope in the quasi-liquid temperature range. With this understanding, reducing of the growth temperatures for high-quality CdSe nanocrystals from around 250–350 °C to at least as low as 150 °C by using amines with a relatively short hydrocarbon chain at a low total ligand concentration was realized. These results imply that the temperature range for the growth of high-quality semiconductor

---

(30) Atkins, P. W. *Physical Chemistry*, 6th ed.; W. H. Freeman Company: New York, 1998.

nanocrystals in nonpolar solutions, such as the InP ones briefly described here, could be substantially extended.

Experimental Section

1. Materials. Octylamine (OA, Aldrich), dodecylamine (DDA, Alfa), tetradecylamine (TDA, Alfa), hexadecylamine (HDA, Aldrich), octadecylamine (ODA, Fluka), stearic acid (SA, Alfa), cadmium oxide (CdO, Alfa), oleic acid (Alfa), tributylphosphine (TBP, Aldrich), tetradecylphosphonic acid (TDPA, Aldrich), Se powder (Aldrich), technical grade 1-octadecene (Aldrich), hexanes (Aldrich), acetone (Aldrich), and chloroform (Aldrich) were used without further purification. Cadmium TDPA (Cd−TDPA) complex was prepared according to the literature method.[5]

2. Dynamics Study. 2.1. Temperature-Dependent PL Recovery of CdSe Nanocrystals. The CdSe nanocrystals were synthesized according to the literature method.[6] The resulting nanocrystals were repeatedly purified by dissolving in chloroform and precipitating by acetone. The amine ligand exchange procedure for the purified nanocrystals was modified from a report by Weller's group.[31] The nanocrystals were treated with an excess of the desired amine in hexanes (about 5% in mass) under reflex conditions for about 6 h under Ar. The excess amine that remained in solution was removed by the standard extraction procedure using hexanes−methanol system for three times.[16] Subsequently, the nanocrystals were precipitated from the hexanes solution by the addition of acetone. This final product of amine-coated nanocrystals was dissolved in 16 mL of ODE with the absorbance of the nanocrystals to be 2 at 370 nm. An additional 0.05 g of the corresponding free amine was added to the ODE nanocrystals solution for better stabilization of the system as discussed in the text. The solution was purged with argon for 15 min and then heated up. At the desired temperature, 1 mL of the ODE solution was taken out, cooled to room temperature, and diluted with 1 mL of hexanes. UV−vis and PL spectra were recorded, and no change of UV−vis spectrum was ensured for the samples shown in the text.

2.2. In situ PL Measurements of the CdSe Nanocrystals in ODE at Different Temperatures. Amine-capped CdSe nanocrystals prepared according to the procedure described above and 0.01 g of the corresponding free amine were dissolved in 2 mL of ODE (absorbance at 370 nm = 1.2), and the solution was loaded in a cuvette sealed with an airtight septum and degassed using an inlet and an outlet needle through the septum. Then, the cuvette with the solution was heated to the desired temperature (well below the boiling point of ODE, see discussions in the text) and cooled naturally. To adjust the pressure during heating and/or cooling, a 1 mL syringe with an almost friction-free piston was inserted through the septum and placed above the solution. During the cooling process, the PL spectrum at a given temperature was measured.

2.3. Temperature-Dependent Surface Ligand Dynamics during the Growth of Nanocrystals. In a typical experiment (using DA as an example), ODE (3.0 g), Cd−TDPA (0.07 g), and 0.21 g of DA were loaded in a 25 mL three-necked flask. The mixture was heated to about 180 °C under Ar to get a clear solution and cooled to 150 °C. At this temperature, 0.15 mL of the TBP−Se stock solution (1.9 g of Se in 8 g of TBP) was injected. The reaction was maintained at 150 °C, and aliquots were taken to monitor the reaction by UV−vis spectroscopy. After the reaction proceeded for 30 min, the temperature was rapidly increased to a desired temperature (typically around 2 min), which was enabled by using an overpowered heating mantle (100 mL heating mantle for a 25 mL flask) with glass wool to cover the top of the heating mantle and the flask. To monitor the exact temperature in the flask, the thermocouple was poked through the rubber septum and directly immersed in the reaction solution.

2.4. Ligand Concentration-Dependent Surface Ligand Dynamics during the Growth of Nanocrystals. In a typical reaction, Cd−TDPA (0.058 g), TDA (0.05 g), and 4 g of ODE were loaded in a 25 mL three-necked flask and heated up under Ar. Around 180 °C, the solution became clear, and then it was cooled to 150 °C for the injection of the Se stock solution in TBP (TBP/Se = 1.6:1, Se/Cd = 6:1). After the reaction proceeded to the given moment (see main text), injection of either 3.5 g of TDA or an equal amount of ODE (heated to ∼100−120 °C for both cases) was performed. For the high-temperature comparison experiments at 280 °C, the injection of the Se stock solution was performed at 280 °C. Because these reactions occurred at 280 °C, the injection of the amines was performed at a much earlier time (See Figure 4). Similar to what is described above, aliquots were taken at given time intervals for all reactions to monitor the reactions.

2.5. Ligand Dynamics in Ostwald Ripening. In a typical experiment, cadmium stearate (0.064 g), SA (0.05 g), TDA (0.05 g), and 5 g of ODE were loaded in a three-necked flask and heated to 150 °C under Ar. Selenium stock solution was injected (0.6 mmol Se), and the reaction was again monitored by taking aliquots for UV−vis measurements. After 2 min of reaction, the UV−vis peak position shifted to about 510 nm. At this point, an additional 0.12 g of TDA in 0.5 mL of ODE was injected. For the control experiment, an equal volume of ODE without amine was injected.

3. Synthesis of CdSe using Cadmium Stearate ($CdSt_2$) at 150 °C. In a typical reaction, $CdSt_2$ (0.08 g), SA (0.15 g), and 0.3 g of DDA were loaded in a three-necked flask and heated up under Ar to 150 °C. Stearic acid used here, and in the reactions carried out for the Ostwald ripening experiments, was added to suppress the reactivity of the active cadmium precursor.[16] At this temperature, injection of a Se stock solution of TBP−Se was carried out. The color of the solution slowly changed from yellow to orange and then red. Temporal evolution of the UV−vis spectra during the growth of CdSe nanocrystals are shown in the Supporting Information. The comparative results are also provided in the Supporting Information for the control reactions, i.e., without amine and/or without ODE. The quality of the resulting nanocrystals, judged by the UV−vis spectra, was generally better when an amine with a relatively short hydrocarbon chain (DA and DDA instead of ODA and TDA) was used under similar reaction conditions.

4. Measurements. 4.1. Optical Measurements. UV−vis spectra were recorded on an HP 8453 UV−vis spectrophotometer. Photoluminescence spectra were taken using a Spex Fluorolog-3 fluorometer. The excitation wavelength used was 370 nm.

4.2. Transmission Electron Microscopy (TEM). TEM images and electron diffraction were taken on a JEOL CX-100 electron microscope using a 100 kV accelerating voltage at 50k magnification. Specimens were prepared by dipping a Formvar-coated copper grid into a toluene solution of the nanocrystals, and the grid with the nanocrystals was dried in air.

Acknowledgment. Financial support of this work was provided by the National Science Foundation.

Supporting Information Available: Supporting results as mentioned in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0725089

---

(31) Talapin, D. V.; Rogach, A. L.; Kornowski, A.; Haase, M.; Weller, H. *Nano Lett.* **2001**, *1* (4), 207−211.