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In-Situ Observation of Nucleation and Growth of PbSe Magic-Sized Nanoclusters and Regular Nanocrystals

Kui Yu, * Jianying Ouyang, and Donald M. Leek

*In-situ observation of the temporal evolution of the absorption of PbSe nanocrystals (NCs) via a low-temperature noninjection approach is presented. Based on a model reaction of lead oleate ($\text{Pb}(\text{OA})_2$) and *n*-trioctylphosphine selenide (TOPSe) in 1-octadecene at 35–80 °C, the use of commercially available TOP (90 or 97%) in affecting the formation of the NCs is explored. TOPSe solutions made from TOP 90% exhibited higher reactivity than those made from TOP 97%. ^{31}P NMR spectroscopy detected no dioctylphosphine selenide (DOPSe) but some DOP in ≈ 1.0 M TOPSe/TOP solution (made from TOP 90%), as well as no diphenylphosphine selenide (DPPSe) when DPP was added to the ≈ 1.0 M solution. Hence, it is proposed that, for the formation of PbSe monomers, an indirect pathway dominates with the formation of a Pb–P complex/intermediate, which results from the activation of $\text{Pb}(\text{OA})_2$ by a phosphine compound (such as DPP, DOP, or TOP) and in turn reacts with TOPSe. With the use of TOP 90% and the addition of secondary phosphine DPP, the formation of PbSe magic-sized nanoclusters (MSNCs) and regular NCs (RNCs) is investigated. With proper tuning of the synthesis conditions, the formation of various PbSe MSNCs versus RNCs is monitored in situ with versus without the addition of DPP, or at different reaction temperatures but otherwise identical synthetic formulation and reaction parameters. Accordingly, the degree of supersaturation (DS) of the PbSe monomer affecting the development of these PbSe MSNCs versus RNCs is proposed; the higher the DS, the more the MSNCs are favored. Also, surface-determined cluster–cluster aggregation is proposed to be the growth mechanism for both the RNCs and MSNCs. For the former, quantized growth is followed by continuous growth. For the latter, the sizes of the magic-sized families are calculated.*

1. Introduction

Current efforts in the synthesis of colloidal semiconductor nanocrystals (NCs) have opened up several new directions to advance various applications such as biolabeling/imaging,^[1–3] photovoltaics (PVs),^[4–7] and light-emitting diodes (LEDs).^[8,9]

PbSe NCs have generated significant attention due to their potential in these applications. The synthesis of colloidal PbSe NCs was first reported in 2001 by Murray and co-workers via a hot-injection approach.^[10] Immediately, the optical properties of the PbSe NCs were documented in 2002 by Guyot-Sionnest and co-workers as well as by Krauss and co-workers.^[11,12] Basically,^[10–15] lead oleate ($\text{Pb}(\text{OA})_2$) was used as a Pb precursor and *n*-trioctylphosphine selenide (TOPSe) as a Se precursor. The latter was prepared with a 1Se-to-2.2TOP feed molar ratio; thus, the concentration of the resulting TOPSe/TOP solution was ≈ 1.0 M. The TOPSe/TOP solution was injected swiftly into a $\text{Pb}(\text{OA})_2$ solution in 1-octadecene (ODE). The injection and growth temperature

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was in the range of 250–80 °C, with the growth periods varying from a few seconds to a few minutes to achieve desired sizes. To synthesize small-sized PbSe NCs, this approach suffers from low particle yield (in terms of NC concentration or the number of particles formed) and low chemical/reaction/conversion yield.^[13,16–19] The former seemed to be more suitable than the latter to compare reactions.^[19]

Since the first report on the synthesis of the PbSe NCs, there has been a limited body of literature exploring fundamental issues on the progression of the NCs, which involve the formation of monomers and their combination leading to nucleation and growth.^[16–19] The comprehension of the formation of the monomer and crystallization plays a crucial role in the design and synthesis of desired NCs with high quality, high synthetic reproducibility, and high reaction yield. In 2006, Bawendi and co-workers proposed the formation mechanism of the PbSe monomer (as described by Equations (a) and (b)) and its combination in nucleation and growth of the PbSe NCs (as depicted by Scheme S1 in the Supporting Information).^[16] For the formation of the monomer, two reaction routes/pathways were proposed to occur simultaneously. Equation (a) shows Route (a); Equation (b) shows Route (b), the reduction of Pb²⁺ to Pb⁰, which was proposed to react with Se⁰ from TOPSe. Route (b) was proposed based on ³¹P NMR spectroscopy probing a reaction carried out at 170 °C between Pb(OA)₂ and TOPSe in the presence of diphenylphosphine (DPP). The observation of solid Pb⁰ was at 180 °C with DPP and at 250–320 °C without. The authors pointed out that TOP, dialkyl phosphines (which might be the impurities in TOP), or DPP added could reduce Pb(OA)₂ to Pb⁰, and DPP was a strong reducing agent. Also, the presence of DPP led to the growth of larger PbSe NCs with an increase of reaction yield. For instance, with the feed molar ratio of (0, 0.08, 0.15)DPP-1Pb-5TOPSe and the injection/growth at 135 °C, the first absorption peaks of the resulting PbSe NCs redshifted from 1358 nm to 1736 and 1716 nm, while the reaction yields increased from 2.3% to 11.6 and 16.2%, respectively.

In 2009, Klimov and co-workers employed a relatively mild reducing agent compared to DPP, 1,2-hexadecanediol (HDD), to synthesize PbSe NCs (with the feed molar ratio of 1Pb-to-2TOPSe and injection/growth at 160/120, 200/150, or 240/180 °C).^[17] Similarly, the presence of HDD led to an increase of chemical yield and the number of PbSe NCs. Also, the occurrence of Pb⁰ from a reaction of HDD and Pb(OA)₂ at 200 °C for 1 h confirmed that HDD reduced Pb²⁺ to Pb⁰. Both DPP and HDD were believed to efficiently reduce Pb(OA)₂ to Pb⁰, thereby leading to a substantial increase of the supersaturation rate of the monomer and thus the nucleation rate.^[16,17] Clearly, the degree of supersaturation (DS) was promoted via Route (b) with the use of DPP and HDD.

In 2010, Krauss and co-workers proposed a different reaction mechanism on the formation of PbSe monomers.^[18] The authors made a clear statement that pure tertiary phosphine selenides such as TOPSe did not react with Pb(OA)₂, but secondary phosphine selenides Se=PH(R_a)₂ did (such as dioctylphosphine selenide, DOPSe). At the same time, the authors commented that the control of quantum dot (QD) sizes with pure secondary phosphine selenide was not well understood. Meanwhile, the authors declared that Route (b) was negligible and Pb⁰ was not likely to be involved in the formation of the PbSe monomer. Such a dispute about Route (b) was based on the observation on the occurrence of Pb⁰ from a reaction of DPP and Pb(OA)₂ at 140 °C taking hours, much longer than needed for a typical PbSe synthesis in their study. Also, Pb⁰ was affirmed to be inert to common Se sources used, such as TOPSe.

For the formation mechanisms proposed by the three studies with the different opinions expressed,^[16–18] we tried to associate meticulously their reported experimental conditions. The formation of the PbSe QDs from Pb(OA)₂ and pure TOPSe (obtained from purified TOP and thus free of secondary phosphine selenide) was reported with injection/growth at 200/150 °C via a hot-injection approach.^[17] The formation of regular CdSe nanocrystals from pure TOPSe at temperatures higher than 120 °C was also documented.^[20] The little reaction between Pb(OA)₂ and pure TOPSe reported may be due to the low reaction temperature (40 °C).^[18] It is reasonable that the reactivity of secondary phosphine selenide (such as DOPSe) was higher than that of tertiary phosphine selenide (such as TOPSe).^[18] Meanwhile, the observation of Pb⁰ in the three studies was in the absence of a Se compound but from the reactions between Pb(OA)₂ and DPP or HDD at temperature such as 140 °C or higher.^[16–18]

The present study focuses on the *in situ* observation of the nucleation and evolution of PbSe NCs via a noninjection-based low-temperature approach, which can be represented by Equation (1):

This model reaction system consisted of Pb(OA)₂ and TOPSe in ODE, with/without the addition of DPP. All the chemicals were used as received without purification and were loaded at room temperature; reactions were carried out at 35–80 °C. This study reports on our experimental data collected from batches with the use of commercially available TOP 90% and TOP 97% and without the addition of DPP, followed by our experimental data from batches with the use of TOP 90% and with the addition of DPP. Systematic tuning of the synthesis conditions was performed to monitor *in situ* the evolution of various PbSe magic-sized nanoclusters (MSNCs) versus regular nanocrystals (RNCs), under identical synthetic formulation and reaction parameters except, for example, the presence of DPP or reaction temperature. Based on our experimental data and previous studies reported,^[16–19] we propose a modified mechanism on the formation of the PbSe monomer. For our low-temperature approach under our experimental conditions, we propose

that Route (b) dominates while involving a Pb–P complex reacting with TOPSe. Also, we discuss the formation of the PbSe MSNCs versus RNCs from the viewpoint of the DS of the PbSe monomer. It seems that the DS plays a major role in nucleation to initiate the development of magic-sized nuclei and/or regular nuclei for the formation of the MSNCs and/or RNCs, respectively. Furthermore, we discuss the fact that the growth of the MSNCs is quantized via cluster–cluster aggregation and reorganization; the size of the MSNCs could be calculated accordingly. Meanwhile, the growth of the RNCs is also characterized by cluster–cluster aggregation but only in the very early growth stage; such a quantized pattern is followed in a continuous manner. The coexistence of the RNCs and MSNCs suggests that the cluster–cluster aggregation is surface-determined. The discussions on the DS of the PbSe monomer and on the surface-determined aggregation share similarity to the study on surface-induced crystallization in supercooled liquids.^[21]

2. Results and Discussion

Herein, we present our experimental data for three fundamental subjects in the synthesis of colloidal semiconductor QDs: 1) the formation mechanism of monomers, 2) the evolution of MSNCs versus RNCs, and 3) the growth patterns of MSNCs and RNCs. The identification of reactive species for the formation of PbSe NCs with commercially available TOP 90% and TOP 97% is presented in Section 2.1. The formation of the PbSe RNCs versus MSNCs with commercially available TOP 90% and the addition of DPP is dealt with in Sections 2.2 and 2.3, with the feed molar ratios of 1Pb-to-2.5Se and 8Pb-to-1Se, respectively. Section 2.4 offers possible mechanisms for the formation of the PbSe monomer, the evolution of the RNCs versus MSNCs (from the viewpoint of monomer saturation), and quantized-growth patterns of the RNCs and MSNCs. For the former, it is their early-growth stage. For the latter, it is possible to identify the sizes of various MSNC families based on the cluster–cluster aggregation mechanism proposed. For each batch presented, see Table S1 in the Supporting Information for details on its synthetic formulation and in situ collection of absorption.

2.1. Formation of PbSe NCs with a 1Pb-to-2.5Se Feed Molar Ratio, with Commercially Available TOP 90% and TOP 97%

The combination of the PbSe monomer leads to nucleation and growth of the PbSe NCs (as depicted by Scheme S1, Supporting Information).^[16] Different opinions on the formation mechanism of the PbSe monomer have been expressed,^[16–19] which involve the two Routes a and b affected by DOPSe/TOPSe and DOP/TOP, respectively.^[16–19] Thus, the identification of reactive species to understand the formation mechanism of the monomer is very much fundamental, while its appreciation becomes extraordinarily critical to designing experimental methods for the achievement of reproducible syntheses of high-quality QDs with high reaction yield and desired sizes for various applications.

Thus, to explore the formation mechanism of the monomer (see Section 2.4.1), we investigated the in situ observation of the formation of PbSe NCs via our low-temperature noninjection approach; several experiments at 50 °C were designed with commercially available TOP. TOP 90% and TOP 97% were used as received without purification. Without the addition of DPP, there were six batches designed, with **Figure 1** showing the in situ observation of the temporal evolution of the PbSe NCs. For the six batches with the 1Pb-to-2.5Se feed molar ratio and $[\text{Pb}] \approx 178 \text{ mmol kg}^{-1}$, see Table S1 for the preparation of the Se precursor. The temporal evolution of absorption from Batches 1 to 5 is presented in Figure 1; due to the little reaction monitored (less than Batch 5), the temporal evolution of absorption from Batch 6 is not shown but a comparison of the six batches at 30 min growth is presented in the bottom-right part of Figure 1. Figure S1 in the Supporting Information shows the absorbance from the six batches at 400 nm, for which the absorption coefficient was proposed to be independent of PbSe sizes.^[22a] The absorbance at 400 nm was argued to provide information on precursor reaction kinetics and the formation of the PbSe pair;^[22a] for CdSe NCs, it is the absorbance at 350 nm.^[20,22b]

Both Figure 1 and Figure S1 suggest a decrease in the precursor reaction kinetics from Batches 1 to 6. Consequently, it seems reasonable to conclude that TOP 90% is more reactive than TOP 97% under our experimental conditions at 50 °C: the reactivity of TOPSe made from TOP 90% was higher than that from TOP 97%, and the reactivity of TOP 90% added was higher than that of TOP 97% added. Hence, the nature and amount of TOP used in the preparation of a TOPSe stock solution is an important parameter affecting synthetic reproducibility, due to the presence of DOP or DOPSe, which may be the active agent for Route (b) or Route (a), respectively.

As mentioned before, for Route (a) it is DOPSe and/or TOPSe that react with $\text{Pb}(\text{OA})_2$, while DOPSe is much more reactive.^[16–19] For Route (b), it is DOP and/or TOP that react with $\text{Pb}(\text{OA})_2$ leading to the formation a Pb–P complex which in turn reacts with TOPSe, while DOP is much more robust.^[16–19] Accordingly, for the six batches, TOP used for the preparation of TOPSe solutions could assist the explanation of the role of DOPSe/TOPSe for Route (a), while TOP added for Batches 2, 3, and 5 could assist the inspection of the role of DOP/TOP for Route (b). Commercially available TOP 90% is used from now on.

2.2. Formation of PbSe MSNCs with 1Pb-to-2.5SeTOP and DPP Addition versus RNCs without DPP Addition

Figure 1 shows the presence of PbSe RNCs at 50 °C, without the addition of DPP. As mentioned above, the presence of DPP could lead to an increase of the supersaturation rate of the monomer and thus the nucleation rate.^[16,17] Accordingly, the addition of DPP was performed at 50 °C, and the temporal evolution of absorption which was monitored in situ is presented in **Figure 2**. Meanwhile, a comparison of the in-situ-monitored nucleation and growth of the PbSe RNCs (Figure 1, Batch 4) versus MSNCs (with DPP added) is shown in Figure S2A in the Supporting Information.

Figure 1. Investigation on the use of TOP 90% and TOP 97% in affecting the progression of PbSe NCs, via in situ observation of the nucleation and growth of the PbSe NCs from five synthetic batches at 50 °C. The growth periods examined are designated for each of the five batches, with the red lines signifying the growth periods of 100 and 200 min. The preparation of the TOPSe solution is indicated, together with the presence or absence of additional TOP.

Also, the formation of the PbSe RNCs (without DPP added) versus MSNCs (with DPP added) was examined at 55 °C (Figure S2C) and at 65 °C (Figure S2D). As indicated by the optical density at 400 nm of the batches shown in Figure 1, 2, S1, S2,^[22a] the presence of DPP promoted significantly the formation of the PbSe pair.

Meanwhile, when the reaction temperature is lower than 50 °C, there is a large window for in situ observation of the nucleation and growth of the PbSe MSNCs, as demonstrated by **Figure 3**. Note that the amount of DPP added was the same (5 μ L) for the two batches shown in the left and right parts of Figure 3. The Pb and Se precursors used were the same as those for Batch 1, Figure 1, and for the rest of the

batches shown in **Figure 4** and **Figure 5**. Thus, the formulation of Figure 3 Batch 45 °C is very much similar to that of Figure S2C–bottom (55 °C). The growth period examined was 430 min (top); the corresponding figures for an unambiguous observation of nucleation in the early reaction stage as well as the growth of the MSNCs in the later stage are presented in the middle and bottom panels of Figure 3, respectively.

It is noteworthy that fascinating PbSe MSNCs were obtained from the large synthetic window, as demonstrated by the experimental conditions such as shown in Figure 2 (50 °C) and Figure 3 (45 and 35 °C). It has been acknowledged that,^[23–27] basically, there are two types of colloidal semiconductor NCs, namely MSNCs and RNCs. The former

Figure 2. Investigation on the addition of DPP promoting the growth of PbSe MSNCs, via in situ observation of the nucleation and growth of the PbSe MSNCs from two synthetic batches (with 0.5 and 5 μ L DPP added) at 50 $^{\circ}$ C. The red absorption spectra stand for the growth periods of 100 and 200 min. For the 5 μ L batch, the light path was 10 mm for the first 30 min and then 4 mm for the rest of the growth. Each arrow represents one MSNC family (F) observed. They are F625, F695, F755, F825, F885, F955, F1015, F1070, and F1130.

are single-sized and the latter have size distribution.^[23–27] Usually, the MSNCs exhibit relatively sharp and persistent absorption peaks; consequently, we have been trying to identify them according to their well-developed persistent absorption peak positions. For example, one MSNC ensemble is described as Family 625, or F625, in accordance with its absorption position peaking at 625 nm.

The arrow lines in Figure 2,3,S2 specify the ten PbSe MSNCs generated, the absorptions of which were resolved

to peaks at 625, 695, 755, 825, 885, 955, 1015, 1070, 1130, and >1170 nm (due to not being fully developed in Figure S2B). The formation of the PbSe MSNCs peaking at 625 nm (shown in the middle panels of Figure 3) was suggested to start at 5–10 min for Batch 45 $^{\circ}$ C ([Pb] = 5 mmol kg^{−1}) and at 15–20 min for Batch 35 $^{\circ}$ C ([Pb] = 102 mmol kg^{−1}). The occurrence of this ensemble may be indicative of nucleation for the two batches, while Batch 45 $^{\circ}$ C exhibited relatively faster nucleation kinetics than Batch 35 $^{\circ}$ C. Thus, the reaction temperature played an important role for the evolution of the PbSe MSNCs from reactions with the presence of DPP, as described by Equation (1). The importance of temperature in nucleation could be found elsewhere.^[28,29]

As shown in Figure 2,3,S2, several MSNC families could coexist with RNCs. Therefore, it is important to comprehend various synthetic parameters and the interplay between them that control the evolution of the MSNCs versus RNCs. It is reasonable that the use of DPP promoted the DS via Route (b), the indirect route (see Section 2.4.1) and thus the PbSe MSNCs were favored instead of RNCs. Note that the perception of the formation mechanism of the PbSe monomer via this indirect route brought us insights into the exploration of a suitable experimental window for in situ observation of nucleation/growth of the PbSe MSNCs versus RNCs. Significant efforts focused on finding the experimental window including the amount of DPP and feed [Se], with which the formation of various PbSe MSNCs versus RNCs could be monitored in situ without detector saturation; also, various families of MSNCs could be formed, particularly large families.

2.3. Formation of PbSe MSNCs versus RNCs with 8Pb-to-1SeTOP and Addition of DPP

In addition to batches with the low Pb-to-Se feed molar ratio (as shown by Figure 2,3,S2), interestingly, batches with high Pb-to-Se feed molar ratios could also engineer various PbSe MSNCs and/or RNCs. Figure 4 shows in situ observation of the temporal evolution of absorption of the PbSe NCs from six identical batches, but with different growth temperatures ranging from 40 to 80 $^{\circ}$ C. For these batches, the Pb-to-Se feed molar ratio was 8:1 and [Se] $\approx$ 20 mmol kg^{−1}. Meanwhile, 5 μ L DPP was added to each of the six Figure 4 batches, which corresponds to a feed molar ratio of 0.6DPP-to-8Pb-to-1Se. The growth periods examined are designated for each of the six batches. The ready observation of the PbSe MSNCs was by Batches 40 $^{\circ}$ C and 50 $^{\circ}$ C, while that of the PbSe RNCs was by Batch 80 $^{\circ}$ C.

In addition to the growth temperature, the effect of the Se feed concentration was explored at 50 $^{\circ}$ C via batches with the 0.6DPP-to-8Pb-to-1Se feed molar ratio (see Supporting Information, Figure S3). It is clear that the occurrence of the ensemble peaking at 625 nm, which might be indicative of nucleation, was monitored at 30–35, 10–20, 10–15, and 5–10 min for the batches with [Se] of 10, 20, 36, and 45 mmol kg^{−1}, respectively.

Furthermore, the effect of the DPP amount was investigated at 50 $^{\circ}$ C via batches with the 8Pb-to-1Se feed molar

Figure 3. Investigation on the addition of 5 μL DPP affecting the development of PbSe MSNCs, via in situ observation of the nucleation and growth of the MSNCs from two synthetic batches, the experimental conditions for which are indicated including the Pb-to-SeTOP feed molar ratios, [Pb] in ODE, and growth temperatures. The red absorption spectra are symptomatic of growth periods of 130, 230, 330, and 430 min.

ratio and $[\text{Se}] \approx 20 \text{ mmol kg}^{-1}$ (see Supporting Information, Figure S4). The nucleation, the presence of F625, was monitored at 90, 40–45, 20–30, 10–20, and 10–15 min for the five batches with DPP of 0.01, 0.12, 0.31, 0.62, and 1.24, respectively. The ready in situ observation of nucleation is presented in Figure 5. Clearly, the optimization of the experimental conditions to examine in situ nucleation leading to the formation

of the PbSe MSNCs and/or RNCs was achieved, based on our comprehension of the formation mechanism of the monomer (see Section 2.4.1 and Equations (Direct) and (Indirect) and their combination leading to nucleation/growth (Scheme S1).

Our experimental results suggest that, with the presence of DPP, the development of the PbSe MSNCs versus

Figure 4. Investigation on the effect of growth temperature affecting the evolution of PbSe NCs, via in situ observation of the nucleation and growth of the PbSe NCs from six identical synthetic batches with the 0.6DPP-to-8Pb-to-1SeTOP feed molar ratio and $[\text{Se}] \approx 20 \text{ mmol kg}^{-1}$. The red absorption spectra stand for the growth periods of 200, 400, 600, and 800 min for Batches 40 °C and 50 °C, 100 and 200 min for Batch 60 °C, 100 min for Batch 65 °C, and 50 min for Batches 70 °C and 80 °C.

RNCs could be in situ monitored under different reaction temperatures but otherwise identical synthetic formulation and reaction parameters. The formation of the PbSe MSNCs is favored at temperatures lower than 50 °C, while the PbSe RNCs are favored at 80 °C. Figure S5 summarizes the absorbance at 400 nm of these batches studied for in situ observation of the nucleation/growth of the PbSe MSNCs and RNCs.

2.4. Possible Mechanisms

2.4.1. Formation of PbSe Monomers

The $\approx 1.0 \text{ M}$ TOPSe solution made from TOP 90% was used for Batch 1, Figure 1, and the batches shown in Figure 3,4,5. Interestingly, for our $\approx 1.0 \text{ M}$ TOPSe/TOP stock solution made

Figure 5. In situ observation of the nucleation of the four batches with the DPP-to-8Pb-to-1SeTOP feed molar ratio, a feed [Se] of 20 mmol kg⁻¹, and a reaction temperature of 50 °C. The growth periods are indicated. The DPP amounts are expressed as the feed DPP-to-8Pb molar ratios; see Supporting Information Figure S4C for Batch 0.01DPP.

from TOP 90% with a 1Se-to-2.2TOP feed molar ratio, ³¹P NMR spectroscopy detected no DOPSe ($\delta = 4.7$ ppm)^[18] but some DOP ($\delta = -68.9$ ppm).^[18] Our NMR data, presented in **Figure 6** (top), suggest the presence of DOP instead of DOPSe. Accordingly, Route (b) should be dominant even without the addition of DPP in our low-temperature approach;^[16–19] such rationalization is in agreement, partially, with the three studies documented.^[16–18] Furthermore, ³¹P NMR spectroscopy detected no DPPSe ($\delta = 7.5$ ppm)^[18] with the addition of DPP to the ≈ 1.0 M TOPSe/TOP solution.^[19] The NMR study presented in Figure 6 (bottom) suggests the presence of DPP instead of DPPSe. Subsequently, it is Route (b) that dominates in our low-temperature approach with the addition of DPP.

Hence, for our low-temperature approach under our experimental conditions (Equation (1), Figure 3,4,5 and Figure S1–S5), we propose modified mechanisms for the formation of the monomer by Equations Direct and Indirect:^[16–19]

For the Route Direct, it could be DOPSe that reacts with Pb(OA)₂ forming a Pb-Se complex; however, there was

little DOPSe detected by the ³¹P NMR spectra (Figure 6, top). For the Route Indirect, it is DPP mainly that reacts with Pb(OA)₂ forming a Pb-P complex, which then reacts with TOPSe. For those HDD-involved reactions,^[17] Route Indirect might be engaged with a Pb-O complex formed. For those amine-involved reactions to CdSe MSNCs,^[23] a Cd-N complex might be involved for Route Indirect. The formation of a Cd-P complex was proposed for the growth of CdSe MSNC Family 408 in TOP.^[24d] Also, a Zn-N complex was proposed for the growth of ZnSe NCs in amines;^[27a] a reaction path was suggested.^[27b] Thus, Route Indirect might be correlated with different complexes, such as Pb-O, Pb-N, and Pb-P complexes, when different compounds are used, such as HDD,^[17] amine, and DPP,^[16–19] respectively. Note that the episode of Pb⁰ from the Pb-P and Pb-O complexes during the formation of the PbSe NCs could be questionable, particularly at low temperature. Route Indirect proposed here involves the Pb-P complex but not Pb⁰.^[16–19] Thus, our modified mechanism proposed, shown by Equations Direct and Indirect, is based on the three studies^[16–18] and on our in situ experimental observations presented in Figure 1,2,3,4,5 together with our ³¹P NMR study shown in Figure 6, which reveals the presence of little DOPSe but a trace amount of DOP in our ≈ 1.0 M TOPSe/TOP stock solution, and little DPPSe when DPP was added to the TOPSe/TOP stock solution even at 80 °C.^[19] Accordingly, without and with the addition of DPP, Route Indirect dominates in our low-temperature approach.

Figure 6. Top: ^{31}P NMR spectroscopy detected no DOPSe ($\delta = 4.7 \text{ ppm}^{[18]}$) but some DOP ($\delta = -68.9 \text{ ppm}$), together with TOPSe ($\delta = 36.9 \text{ ppm}$) and TOP ($\delta = -31.7 \text{ ppm}$) from the $\approx 1.0 \text{ M}$ TOPSe/TOP solution. Bottom: ^{31}P NMR spectroscopy detected no DPPSe ($\delta = 7.5 \text{ ppm}^{[18]}$) with the addition of DPP ($\delta = -39.5 \text{ ppm}$) to the $\approx 1.0 \text{ M}$ TOPSe/TOP solution. The magnifications of the insets are indicated. For larger views, see the Supporting Information Figure S6.

2.4.2. Degree of Supersaturation of the Monomer Affecting the Formation of PbSe MSNCs and/or RNCs

The concept of the DS was addressed before in classical nucleation theory (CNT).^[28,29] When nucleation takes place, the change in Gibbs free energy ΔG can be described by Equation (2). Usually, nucleation means the very first evolution of a solid phase, with a phase transformation from solution to solid. For the occurrence of a spherical nucleus with a radius r , the overall change in free energy is

$$\Delta G = (4/3)\pi r^3 \Delta G_v + \pi r^2 \gamma \quad (2)$$

Here, ΔG_v means the bulk free energy difference per unit volume between the new/solid and old/liquid phase, while γ is the surface free energy per unit area. When ΔG is negative, nucleation is favored. For nucleation to proceed, the nucleus size should be reaching a critical value, r^* , as described by Equation (3).

$$r^* = 2\gamma / \Delta G_v = 2\gamma V_m / [RT \ln(1 + \text{DS})] \quad (3)$$

Here, R is the gas constant, T absolute temperature (K), V_m molar volume, and $\text{DS} = (C - C_0)/C_0$, where C is the

concentration of the monomer and C_0 the solubility of the monomer.

Figure 3 and 4 demonstrate that the same PbSe MSNC families were obtained from the batches with the 1Pb-to-2.5Se feed molar ratio and with the 8Pb-to-1Se feed molar ratio, respectively. Such a difference in the Pb-to-Se feed molar ratios between these experiments is worthy of notice. Careful observation suggests the presence of a certain amount of RNCs in Figure 4 Batches 40 °C and 50 °C and few in Figure 3 Batches 45 °C and 35 °C. Due to the fact that the Pb precursor was $\text{Pb}(\text{OA})_2$ prepared with a 2.2OA-to-1PbO feed molar ratio in ODE, there was more free oleic acid present in the Figure 4 batches (with the 8Pb-to-1Se feed molar ratio and $[\text{Se}] \approx 20 \text{ mmol kg}^{-1}$) than in the Figure 3 batches (with the 1Pb-to-2.5Se feed molar ratio and $[\text{Pb}] \approx 51$ and 102 mmol kg^{-1}). Such a difference in the amount of the free oleic acid might lead to a distinction in the DS of the PbSe monomer. The DS might be relatively low for the Figure 4 batches (40 °C–80 °C) as compared to that for the Figure 3 batches (35 and 45 °C); few RNCs were present in the Figure 3 batches.

The three batches shown in Figure 2, S1 (with the feed molar ratio of 1Pb-to-2.5SeTOP at 50 °C) demonstrate that the presence of DPP promoted the DS and favored the formation PbSe MSNCs. The six batches shown in Figure 4 (with the feed molar ratio of 8Pb-to-1SeTOP) reveal clearly that various PbSe MSNCs and/or RNCs could be synthesized with an identical synthetic formulation but different reaction temperatures. The effect of the reaction temperature on the presence of the PbSe MSNCs versus RNCs is worthy of notice. From Batches 40 °C to 80 °C, it seems sensible to argue that the precursor reaction kinetics increases (as demonstrated by Figure S5, top), thus leading to an enhancement of the concentration of the PbSe monomer. Meanwhile, the solubility of the PbSe monomer increases. Subsequently, the DS of the PbSe monomer (at the early stage of the reactions) decreases: the relatively high DS (of Batches 40 °C and 50 °C) favored the growth of the PbSe MSNCs, while the relatively low DS (of Batches 70 °C and 80 °C) favored the growth of the PbSe RNCs.

It might be of help to mention briefly that a high chemical potential environment was argued to be responsible for the formation of CdSe MSNCs observed with a hot-injection approach.^[26] A high chemical potential environment seems to be linked with a high monomer concentration in a reaction. Accordingly, for our noninjection-based low-temperature approach shown by Equation (1), the DS of the PbSe monomer seemed to play a major role in the formation of the PbSe MSNCs versus RNCs. Basically, for the in situ observation of the formation of the PbSe MSNCs versus RNCs, our blueprint of experimental conditions of Figure 4 batches could be explained by the control of the DS of the monomer at different temperatures, while Figure S1 batches have the addition of DPP.

Thus, our experimental data shown in Figure 2, 3, 4, S2–S4 suggest the existence of a synthetic window for the tuning of the presence of the PbSe MSNCs versus RNCs. It seems reasonable that the DS plays an important role. Moderate DS could lead to the coexistence of the MSNCs and RNCs (as

Scheme 1. A plausible mechanism proposed for the formation of the PbSe MSNCs and RNCs from the low-temperature reactions shown by Equation (1). Based on the in situ observation of the progression of the PbSe NCs, the DS of the PbSe monomer plays a critical role. When the DS is high, the formation of the MSNCs is favored. When the DS is low, the formation of the RNCs is favored. This paper does not address the dashed arrows including the transformation between the MSNCs and RNCs; such information can be found elsewhere.^[35]

shown in Figure 4, Batches 40 °C to 70 °C), while high DS leads to the MSNCs (as shown in Figure 3, Batches 45 °C and 35 °C) and low DS to the RNCs (as shown in Figure 4 Batch 80 °C, and those batches without the addition of DPP shown in Figure 1,S2). Based on our experimental observation, we propose that the DS plays an important role in the formation of PbSe MSNCs versus RNCs; such a concept of the DS affecting the formation of the PbSe NCs is described by **Scheme 1**. It seems that our in situ observation represents one step forward to understanding nucleation/growth in colloidal semiconductor NC systems.

As shown by Equation (3), the size of a critical nucleus depends on the DS. The higher the DS, the smaller the critical nucleus size; as shown by Scheme 1, the more the MSNCs are favored. Also, the smaller the DS, the larger the critical nucleus size; as shown by Scheme 1, the more the RNCs are favored. Such statements seem to be well supported by our experimental data shown in Figure 3 and 4, where the MSNCs were favored at low growth temperature (such as 35–50 °C) and the RNCs at high growth temperature (such as 70 and 80 °C).

Note that, for Scheme 1 in the present study, additional consideration is needed for Equation (3).^[28–30] Firstly, classical nucleation theory assumes that the center of a nucleus is a new bulk-like phase. Secondly, the surface energy of a nucleus is lacking the consideration of curvature, but is the same as that of an infinite planar surface. Thirdly, a critical nucleus size considered is not 1–2 nm, but on the order of a few nanometers.

2.4.3. Surface-Determined Cluster–Cluster Aggregation: Quantized Growth for the RNCs at the Initial Growth Stage and for the MSNCs

For the PbSe RNCs, Figure 4 Batch 80 °C suggests little MSNC absorption feature, with the first ensemble monitored at 0 min peaking at ≈ 660 nm (as demonstrated by the bottom-right part of Figure S7). The in situ absorption spectra collected in the initial 15 min of growth are broad, which suggests the occurrence of regular nuclei with different sizes (also called regular clusters). Meanwhile, they experienced cluster–cluster aggregation to grow in size with significant redshifts of their absorption peak positions; the addition of the PbSe monomer might be active simultaneously. More

study is necessary to address the aggregation with or without chemical interactions involved, as classic cluster chemistry does.^[31] In the later stage, the growth seemed to be more continuous, together with a continuous decrease in the size distribution. Accordingly, we argue that, for the growth of the RNCs, a cluster–cluster aggregation might be involved in the very early growth stage, right after nucleation with the formation of regular nuclei with a certain size distribution; the addition of the monomer might be active at the same time. Along with the reaction, there might be a requirement for a minimum concentration (C^*) of the monomer; when the monomer concentration drops to this critical value (C^*), the smallest NCs may dissolve back into the monomer to feed the further growth of the other NCs, together with the stopping of the cluster–cluster aggregation growth mode. Meanwhile, the relatively small NCs may grow faster than the relatively large ones, thereby resulting in the continuous decrease of the size distribution with the occurrence of a continuous growth mode. The argument on the decrease of the size distribution at such a growth stage could be reasoned with equal-sized diffuse spheres, which can be found elsewhere.^[26b] Herein, we offer the concept that there is cluster–cluster aggregation in the very early growth stage of the PbSe RNCs, while does not address further issues such as whether nucleation is taking place at this stage. A more detailed quantification (such as the change of the NC concentration) would be needed to propose a growth pattern with quantized and continuous stages. The proposed cluster–cluster aggregation growth pattern followed by continuous growth is shown in **Scheme 2** (top).

For the PbSe MSNCs shown in Figure 2,3,4,S2–S4 from our noninjection approach and those PbSe and CdSe MSNCs reported,^[15,23] we argue that their growth manner is quantized via cluster–cluster aggregation and recrystallization. The aggregation results in an absorption redshift with a discontinuous mode. The recrystallization causes a certain degree of absorption redshift to a fixed position with a continuous mode and increase of optical density. Furthermore, F625 MSNCs seem to be the critical nuclei in the present study.

Interestingly, a previous study reported similar PbSe MSNCs with their sizes estimated to be 1.0, 1.2, 1.4, 1.6, and 1.8 nm for F625, F690, F750, F820, and F880, respectively.^[15] Such estimation was based on an extrapolation of the relationship between the energies of the first exciton absorption peak positions and the sizes of spherical NCs.^[12,15] Consequently, the volume of each F695, F755, F825, and F885 is equal to that of two, three, four, and six F625 MSNCs, respectively. Note that in the present study (Figure 2,3,4,5,S2–S4), slightly different absorption peak positions are assigned: they are F625 (purple arrowed lines), F695 (blue arrowed lines), F755 (red arrowed lines), F825 (blue arrowed lines), and F885 (red arrowed lines). Furthermore, larger MSNCs were prepared in our laboratories and reported herein; they are F995 (blue arrowed lines), F1015 (red arrowed lines), F1070 (blue arrowed lines), and F1130 (red arrowed lines).

Importantly, Figure 3 Batch 45 °C suggests that the disappearance of F695 at 90 min is accompanied by the presence of F825 and the disappearance of F755 at 120 min is accompanied by the presence of F885. Figure 3 Batch 35 °C suggests

Scheme 2. A plausible mechanism proposed for the growth of PbSe RNCs and MSNCs. Top: For the small-sized PbSe RNCs monitored (such as from Figure 4, Batch 80 °C), the cluster–cluster aggregation takes place in the initial stage of growth with a broad size distribution. At the same time, the monomer addition might be active. Along with the reaction accompanied by the decrease of the monomer concentration, there is little cluster–cluster aggregation and the growth of NCs becomes continuous instead of quantized. Further growth might be accompanied by an increase of the size distribution, which is not addressed herein. Bottom: Cluster–cluster aggregation with recrystallization leads to the quantized growth of the MSNCs. Two F625 grow into one F695, and three F625 into one F755. Afterwards, two F695 grow into one F825, two F825 into one F955, and two F955 into one F1070, etc. Meanwhile, two F755 grow into one F885, two F885 into one F1015, and two F1015 into one F1130, etc. The cluster–cluster aggregation should be surface-determined.

that the disappearance of F695 at 150 min is accompanied by the presence of F825 and the disappearance of F755 at 240 min is accompanied by the presence of F885. Figure S3B (50 °C) suggests that the disappearance of F695 at 120 min is accompanied by the presence of F825 and the disappearance of F755 at 190 min is accompanied by the presence of F885.

Furthermore, the growth of the MSNCs seems to begin with F625 followed by F695 coming up as a red-side shoulder. These two families exhibit an increase in their absorbance simultaneously: when the absorbance of F695 becomes larger than that of F625, F625 starts to disappear gradually and F755 comes up as a red-side shoulder of F695. Such a growth pattern seems to repeat for every three adjacent families, namely F625–F695–F755, F695–F755–F825, F755–F825–F885, F825–F885–F955, F885–F955–F1015, F955–F1015–F1070, and F1015–F1070–F1030. Therefore, it seems that the occurrence and disappearance of one MSNC family is closely related to its neighboring families.

Hence, we propose a quantized-growth mechanism for the PbSe MSNCs observed via cluster–cluster aggregation and recrystallization, as illustrated by Scheme 2 (bottom). Our in situ observation of the continuous redshift of absorption together with the absorbance increase during the recrystallization process may be the first, to the best of our knowledge, after some literature reports on the quantized-growth pattern.^[32–34] Such recrystallization may lead to the optimization of geometry/configuration/conformation with the minimization of the surface energy. The formation of the MSNCs

should be thermodynamically driven with a different surface structure from that of the RNCs; usually, a stable electronic structure was argued for the magic of stability.^[32]

Note that these quantized-growth patterns via cluster–cluster aggregation are proposed for the growth of the PbSe RNCs in the very early growth stage and for the growth of the MSNCs. Therefore, it is easy to argue that such cluster–cluster aggregation is surface-determined, with the development of the RNCs from regular nuclei and that of the MSNCs from magic-sized nuclei (F625). Meanwhile, the growth patterns of the RNCs and MSNCs from regular and magic-sized nuclei, respectively, are featured with quantized-growth modes via surface-determined cluster–cluster aggregation. Accordingly, the sizes of the MSNCs can be established (when one family is determined), as shown in **Figure 7**. Finally, we would like to point out that different reaction systems may have different growth mechanisms; for example, the growth mechanism via cluster–cluster aggregation proposed here for the PbSe MSNCs may not be suitable for our reported Cd-based MSNCs,^[24d,25] particularly CdSe MSNC F463.^[24d,25a,b] Hopefully, our fundamental comprehension pre-

sented herein will enable one step forward to rational designs and syntheses of various colloidal semiconductor NCs.

3. Conclusion

We have presented experimental data about the in situ observation of the temporal evolution of absorption of colloidal semiconductor PbSe NCs via a low-temperature non-injection approach, and have probed the formation mechanism of monomers as well as nucleation and growth. The model reaction system involved Pb(OA)₂ and TOPSe in ODE at low temperature (35–80 °C). Without the addition of DPP, we studied the use of commercially available TOP (90% or 97%) in affecting the formation of the PbSe NCs. It seemed that the reactivity of TOPSe made from TOP 90% was higher than that from TOP 97%. Meanwhile, our ³¹P NMR study detected little DOPSe ($\delta = 4.7$ ppm) but DOP ($\delta = -68.9$ ppm^[18]) in our ≈ 1.0 M TOPSe/TOP solution made from TOP 90%. Also, our ³¹P NMR spectra detected little DPPSe ($\delta = 7.5$ ppm^[18]) with the addition of DPP to the ≈ 1.0 M TOPSe/TOP solution. We proposed a modified formation mechanism of the PbSe monomer in our low-temperature approach, namely, a reaction route which involves the formation of a Pb–P complex dominates. Furthermore, we studied the formation of various PbSe MSNCs versus RNCs with the addition of DPP (and the feed molar ratio of 1Pb-to-2.5SeTOP at a constant temperature such as 50 °C), as well as from six identical batches (with the

4. Experimental Section

For a typical synthesis, which starts in a glovebox under N_2 atmosphere, a $Pb(OAc)_2$ stock solution, a TOPSe stock solution, DPP, and ODE were added to a quartz cuvette (optical path 10 mm $\times$ 10 mm, volume 3.5 mL) at room temperature and then sealed with a Teflon stopper. ODE was previously dried, and was degassed (at ≈ 50 mTorr and ≈ 100 $^{\circ}C$) and purged with purified nitrogen three times during a period of 2 h. The total volume of reagents was kept at ≈ 2.9 mL. This cuvette was then transferred out of the glovebox and placed into a Cary 5000 spectrometer for the study of nucleation/growth via in situ observation of the temporal evolution of absorption.

To make TOPSe stock solutions of 1) 1Se-to-2.2TOP (TOP 90%, ≈ 1.0 M), 2) 1Se-to-1TOP (TOP 90%), and 3) 1Se-to-1TOP (TOP 97%), correct amounts of Se powder and TOP (without consideration of the TOP purity) were added to single-necked 25-mL flasks in a glovebox filled with N_2 . For example, Se (1.2256 g, 15.52 mmol) and TOP 90% (12.6569 g, 34.15 mmol) were mixed to make the TOPSe stock solution (1). The mixtures were then stirred overnight at room temperature. The TOPSe solution (1) became clear and was ready. The TOPSe solutions (2) and (3) were heated gently for ≈ 10 min and the solutions became clear.

³¹P NMR Spectroscopy: NMR spectroscopy was performed on a Bruker AV-III 400 spectrometer operating at 161.98 MHz for ³¹P. An external standard comprising 85% H₃PO₄ was used. The NMR samples were prepared, loaded in NMR tubes, and properly sealed in a glovebox. For the NMR study with ≈1.0 M TOPSe/TOP solution, the measurements were carried out between 25 and 80 °C. For the NMR study with the addition of DPP to the ≈1.0 M TOPSe/TOP solution, the stock solution (0.43 mL, 0.44 mmol) was mixed with DPP (0.31 mL, 1.75 mmol) and the NMR measurements were performed between 25 and 80 °C.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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