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Hidden Role of Anion Exchange Reactions in Nucleation of Colloidal Nanocrystals

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Abstract

We investigate the processes involved in nucleation of colloidal lead selenide nanoparticles. Our studies show that an unusual pathway – an anion exchange reaction, causes the nucleation of lead selenide nanocrystals. In this process, one quantum dot is transformed into another due to a substitution of its constituent anions. The existence of this pathway was never anticipated perhaps due to its unusually rapid kinetics. The nucleation and growth kinetics of colloidal lead selenide quantum dots are found to fit well to a two-step process. The rate constant associated with the anion exchange process is found to be four orders of magnitude greater than nanocrystal growth. The complete consumption of the initial oxide nanoparticle thus provides a sharp, temporally well-defined nucleation event.

Introduction

Quantum dots (QDs) prepared from narrow band gap semiconductors have received considerable attention over the past decade. While organic chromophores successfully compete with QDs over visible wavelengths, QDs exhibit significantly higher quantum yields in the infrared (IR) region.[1, 2] Besides being excellent phosphors, these materials have also shown potential as light absorbers in photovoltaics[3, 4] as well as in detectors.[5] Among IR QDs, lead chalcogenide QDs have been a particular curiosity because of their unusual band structure as well as a slew of odd physical properties.[6-13] The interest in these materials from a purely chemical viewpoint has been of a commensurate intensity.[6, 14, 15] In particular, synthetic schemes for preparation of lead chalcogenides have advanced tremendously over the years, allowing for the preparation of QDs with near unity quantum yields,[1, 2, 16] even though the emission lifetimes are several microseconds long.[16-18] Despite great progress in the physical chemistry of lead chalcogenides, several problems still remain. Most proposed applications of IR QDs require copious amounts of material. Scaling up of a reaction requires considerable optimization of conditions as well as an in depth knowledge of various steps that occur during the course of a synthesis. In this regard, the mechanistic steps[19, 20] involved in lead chalcogenide formation remain somewhat obscure. This work addresses the reaction pathways involved in the case of lead selenide QD synthesis, although the mechanism proposed is general enough to have other, far reaching consequences. We find that lead selenide nucleation occurs through the initial formation of PbO nanoparticles. These are directly converted to PbSe via an anion exchange reaction. The proposed mechanism also opens up the possibility of synthesis of novel classes of symmetry broken and heterostructured materials.

Colloidal lead selenide QDs were reported by Murray et. al..[21]

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Despite considerable research, the process employed in current literature is essentially similar to the original. Briefly, a typical synthesis consists of the preparation of lead oleate as the first step, followed by the injection of selenium in trioctylphosphine (TOP) into the reaction mixture. While a growth temperature as high as 180°C leads to the formation of lead selenide QDs, Evans et. al.[22] reported the formation of small, highly luminescent magic sized nanocrystals (MSNCs) if the reaction is performed at room temperature (RT). These synthetic steps are summarized in figure 1a.[23-25]

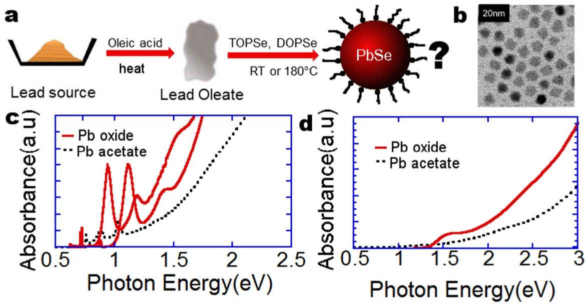

Figure 1a. Schematic of the conventional picture of PbSe synthesis. **b**. TEM image of PbSe NCs. The scale bar is 20 nm. **c**. Absorption spectra of PbSe QDs prepared using lead oxide (red, solid line) and lead acetate (black, dotted line) as lead sources. **d.** Absorption spectra of PbSe MSNCs from lead oxide (red) and lead acetate (black dotted line) as lead source.

Lead selenide QDs synthesized in this manner are most typically spherical, however relatively minor modifications to reaction conditions are found to give rise to unusual anisotropic morphologies.[26-28] The great sensitivity of this reaction to slight changes in the synthetic conditions makes it atypical among colloidal syntheses. This naturally drew attention towards steps involved in PbSe QD formation. Streckel et. al.[29] proposed the role of a nucleophilic attack by TOPSe on Pb^{+2} ions as the primary reaction step. The discovery of a reductive step in PbSe formation by these authors represents a major conceptual leap in the understanding of PbSe chemistry. The role of impurities in commercial TOP was recognized independently by several workers.[30, 31] Bae et. al. studied the effects of surface chemistry[21] on PbSe synthesis. It was further observed that impurities such as dialkyl phosphines (e.g. dioctylphosphine(DOP)) had a deleterious effect on PbSe QD surface[32] and quantum yield.[33] Instead, the addition of an alternative reducing agent, viz, 1, 2-hexadecanediol (HDD) led to significantly improved emission quantum yields.

Results and Discussion

Despite the proven role of the reduction pathway in PbSe formation, certain oddities of PbSe remain difficult to reconcile within this framework. Rather, there are indications of the existence of other, critical reaction steps that have a significant bearing on material quality. Most surprising is the peculiar dependence of the reaction on the history of the lead oleate precursor. Conventionally, lead oleate is prepared by heating lead oxide at 180°C in the presence of oleic acid. Lead oleate that is thus prepared causes the formation of high quality PbSe QDs as exemplified by TEM image in figure 1b as well as the spectra shown by solid lines in figure 1c. Injection of selenium precursor at room temperature gives rise to high quality magic sized nanocrystals[34] (Figure 1d, solid lines). However, the QD quality is markedly poorer if lead oleate is prepared differently.

In particular, if lead oleate is prepared from lead acetate, the PbSe QDs are found to have a poor size dispersion. Polydispersity is observed in the case of both PbSe QDs as well as MSNCs even though all other parameters during the synthesis are maintained the same. This observation is exemplified by the dashed lines in figures 1c and 1d, where such samples are seen to lack clear excitonic features as well as exhibit a long tail in the absorption spectrum. The peculiar dependence of PbSe QD quality on the history of the cationic precursor certainly cannot be explained within the existing framework of known reaction steps, and consequently, alternate possibilities need to be considered.

The presence of impurities within various starting lead compounds could provide one possible explanation of the above observations. Since all lead compounds used in our synthesis were of a high purity (99.99%, metals basis or higher), we discounted this possibility. It is also important to note that the presence of impurities cannot explain observations that we describe later in this work. Yet another alternative was the possibility of incomplete conversion of

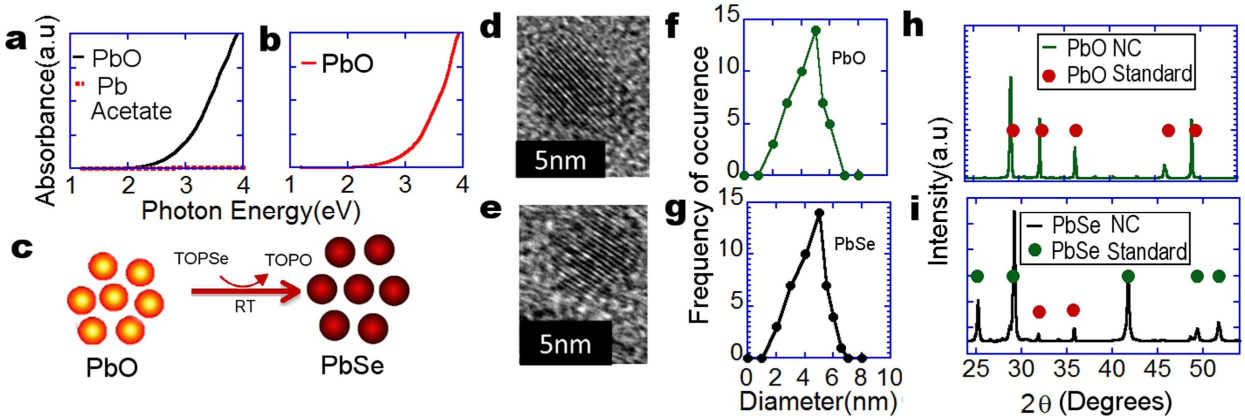

Figure 2a. Absorption spectra of lead oleate prepared from lead oxide (solid line) and lead acetate (dashed line) respectively. **b.** Absorption spectra of PbO Nanoparticles. **c.** Schematic of the anion exchange reaction. **d.** High Resolution TEM (HRTEM) image of PbO QDs. **e.** HRTEM image of PbSe QDs **f.** Size histogram of PbO QDs. **g.** Size histogram of PbSe QDs. **h.** XRD pattern of PbO **i.** XRD pattern of PbSe QDs prepared from the PbO QDs using anion exchange. Note the residual PbO lines. The symbols in **h** and **i** indicate the standard positions of the corresponding reflections in bulk material.

different lead sources into lead oleate during the first step. While the presence of acetate has previously been observed to give rise to non-spherical PbSe QDs, there is no reason to expect trace amounts of acetate to have a major impact on the size distribution. We further observed no improvement in the quality of PbSe even if lead acetate was heated with oleic acid at 100°C for longer periods of time (e.g. as long as 8 hours). The independence of PbSe quality on the time devoted to prepare lead oleate implies that incomplete transformation of the cationic precursor is not primary cause of the poor size dispersion. We further note that a timescale as long as 1 hour is generally considered adequate to remove residual acetate from lead oleate.[26] Lead oleate prepared from PbO (black, solid line) is associated with an intense absorption at blue wavelengths, that is entirely absent in the lead oleate that is prepared from lead acetate(red, dashed line). The optical absorption of high temperature lead oleate was found to be similar to the optical absorption of PbO (Figure 2a and 2b). Fatty acid salts of lead are known to undergo decarboxylation upon heating.[35, 36] In particular, Pb(II) salts are known to give rise to a ketone as well as PbO. Continued heating at 180°C therefore makes PbO QDs the most likely outcome. The presence of lead oxide in lead oleate prepared at high temperature encouraged us to further consider possible roles that it could play in PbSe QD formation.

The enthalpy of formation of lead selenide (-100 kJ/mol)[37] is lower than the enthalpy of formation of PbO (-219 kJ/mol).[38] Thermodynamics thus suggests that the direct reaction of PbO with selenium to produce PbSe is infeasible. Hard-soft acid-base theory however dictates that an exchange reaction $PbO + TOPSe \rightarrow PbSe + TOPO$, shown in figure 2c is certainly expected. In terms of the hard-soft interaction picture, TOPO and PbSe formation through an exchange reaction represents the pairing up of relatively harder (P, O) and softer (Pb, Se) acids and bases.

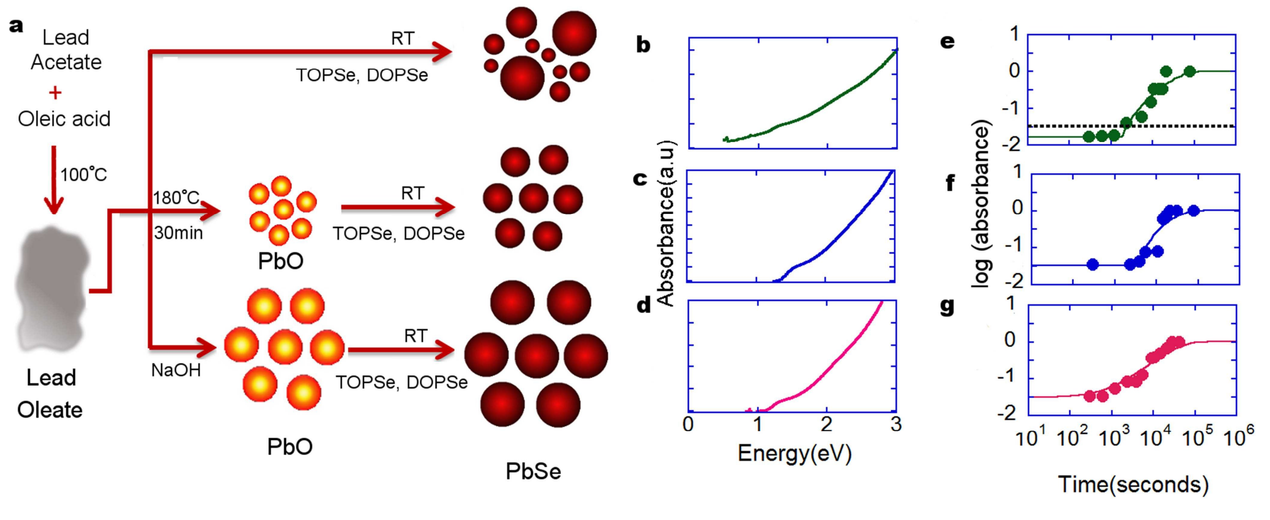

Figure 3a. Schematic of reactions done with a single batch of lead oleate. The three reactions and their outcomes correspond to three different post-preparative treatments done to the lead oleate. **b., c. , d.** absorption spectra of the resultant PbSe QDs. **e. f. g.** reaction kinetics plotted on a double logarithmic scale. The reaction kinetics has been inferred by monitoring absorbance at 400 nm. Reaction conditions are mentioned in panel a in each case.

To test the viability of this process, we started with a sample of PbO QDs. These were prepared using a standard procedure that involves heating lead acetate, oleic acid and octadecene in presence of controlled quantities of atmospheric oxygen. While heating lead oleate at 180°C is sufficient to produce PbO QDs, the presence of trace amounts of oxygen increases their size.[39] These PbO QDs (5 nm diameter) were purified, and separated from starting lead salts. The absorption spectrum of these PbO QDs is shown in figure 2b while the transmission electron microscopy (TEM) image is shown in figure 2d. Treatment of PbO QDs with TOPSe even at room temperature gives rise to a dark coloration that is identified to be PbSe based on the interplanar spacing observed in TEM (Figure 2e). TEM images further suggest that the PbSe QDs are highly crystalline. A comparison between the initial PbO QDs and the final PbSe QDs reveals that both are have an identical size. In fact an examination of the size dispersions of the PbSe and PbO QDs (Figure 2f, 2g) reveals the final product entirely retains the size dispersion of the starting PbO QDs. Given that this reaction has been carried out in complete absence of any lead source other than the PbO QDs themselves, the direct transformation of PbO to PbSe becomes the only possible pathway. To test the generality of this transformation, we synthesized larger (>20 nm) PbO QDs and subsequently converted them to PbSe through a room temperature treatment of the QD film with TOPSe. A comparison of the patterns of the starting and final products shows that even at room temperature, the anion exchange process goes to completion, leading to the formation of pure PbSe. Typically, the complete conversion of PbO to PbSe occurs over 30 to 45 min. The progress of this reaction may also be monitored either optically or through NMR spectroscopy. ^{31}P NMR reveals that appearance of PbSe in XRD is correlated with the disappearance of TOPSe signatures in the NMR as well as the appearance of peaks corresponding to TOPO (See Figures S1, S2 in the supplementary section). We thus infer that the anion exchange pathway in figure 2c can convert a wide size range of PbO QDs into PbSe QDs in a single step.

While the above structural, chemical and spectroscopic evidences support the existence of an anion exchange reaction of the sort conjectured in figure 2c, its relevance to PbSe synthesis becomes apparent from a study of the kinetics of PbSe formation.[40] In this experiment we prepared lead oleate by heating lead acetate, octadecene and oleic acid at 100°C for 90 min under vacuum. The lead oleate that is formed by this procedure is colourless, and does not exhibit PbO-like optical absorption. This precursor was split into three parts. In each case the final addition of TOPSe was performed at room temperature, however the precursor was subjected to slightly different treatments prior to the final TOPSe addition (Figure 3a).

To the first part of the lead oleate, TOPSe was added at room temperature without any intermediate steps. As commented in the introductory discussion, this leads to a sample of PbSe QDs with poor size dispersion and no well-defined excitonic features (Figure 3b).

The second part of the lead oleate was heated to 180°C and annealed for 30 min under an argon atmosphere. This treatment leads to the appearance of a yellowish color and optical absorption associated with PbO formation. This substance is subsequently cooled to room temperature and then treated with TOPSe. This leads to the formation of high quality PbSe MSNCs (Figure 3c).

A 0.2 M solution of sodium hydroxide in isopropanol is swiftly injected at room temperature to the third part of lead oleate. The addition of a strong alkali again leads to the partial conversion of lead oleate into PbO. The resultant solution is then treated with TOPSe. Once again this solution is observed to lead to high quality PbSe MSNCs (figure 3d).

The vastly different outcomes of the three reactions confirm the role of anion exchange in PbSe formation. Lead oleate prepared at 100°C does not show any detectable evidence of decomposition to PbO. Annealing at 180°C as well as treatment with NaOH encourage the formation of PbO QDs. The presence of PbO QDs is thus entirely correlated to the quality of lead selenide that results from a reaction.

The reasons behind the existence of this correlation can be inferred from the reaction kinetics shown in figures 3e, f and g. Here the lead oleate stock solution has been treated with equal quantities of TOPSe at room temperature. Subsequently, the amount of PbSe formed is monitored by measuring the optical absorbance at 400 nm. This wavelength is chosen because it is sufficiently high in energy to be relatively unperturbed by quantum confinement and size distribution effects.[41] Figures 3e, f and g plot the logarithm of absorbance as a function of the elapsed time. After sufficient time has elapsed (105 s), all three solutions have roughly equal absorbances, suggesting equal quantities of PbSe formation in each flask. This is regardless of the fact that two of the flasks have good size dispersion while one of the flasks contains an extremely poor size distribution of PbSe QDs. This suggests that PbO does not control the total amount of PbSe produced in the reaction, but rather plays a key role in controlling monodispersity.

A second key observation is that even though all three reactions finish over roughly similar timescales, the presence of PbO significantly alters the initial progress of the reaction. Over the time resolution afforded within this experiment, the data shown in figure 3e indicate that there is no PbSe produced within the reaction mixture until 1000 s. Instead, both figure 3f and 3g where PbO QDs are present indicate the formation of PbSe well before 1000 s. The dashed line in figure 3e represents the first recorded absorbance of both panels 3f and 3g. Thus, in both reactions 3f and 3g, PbSe is already produced within the first 100 s of addition of TOPSe. The strong difference in the early time response of the two types of reactions suggests that PbO is directly involved in the nucleation of PbSe QDs. The kinetics also explains the peculiar correlation between monodispersity and the presence of PbO. In absence of PbO QDs, the nucleation process itself is delayed (for example, in figure 3e, PbSe formation is observed as late as 2000 s after the TOPSe addition). In absence of a single, clear nucleation event, the reaction mixture presumably attains supersaturation several times, giving rise to a poor size dispersion.

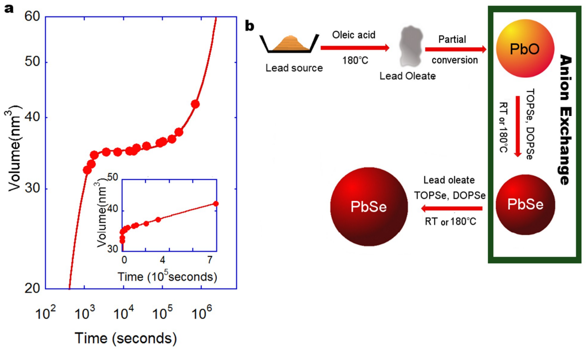

Figure 4a. Plot representing the nucleation and growth kinectics of PbSe synthesis (volume of PbSe dots V/S time in seconds).**b.** Schematic of PbSe synthesis.

The identification of anion exchange as the nucleation step can be made by examining the early time kinetics of PbSe growth. In this experiment, we synthesized lead oleate through the conventional route, i.e. by reacting bulk PbO with oleic acid at 180°C. We monitor the absorption maximum in order to track the PbSe QD reaction progress. Using the PbSe sizing curve reported by Moreels et. al.,[41] it is possible to convert the position of the absorption maximum to the particle size. We find the PbSe QD size increases in two distinct steps. There is an initial burst of rapid growth, followed by an extremely slow increase in particle size that occurs over a timescale of several days. This peculiar growth kinetics may be readily fit to a two-step model, where the initial growth is triggered by anion exchange ($k_1 \sim 2.1 \times 10^{-3}\ s^{-1}$ at room temperature), while the second, slower growth step occurs because of reaction between lead oleate and selenium precursors via the already known reductive pathway ($k_2 \sim 3.06 \times 10^{-7}\ s^{-1}$). The rapid initial step suggests the important role of the anion exchange pathway in PbSe formation. While the kinetics data have been collected at room temperature in all these cases, it is abundantly clear that anion exchange occurs on a significantly shorter timescale than PbSe formation through the reductive pathway. Despite its faster kinetics, this reaction is nevertheless limited by the exhaustion of one of the principal reagents, viz. PbO. Thus, although anion exchange cannot lead to the growth of large sized PbSe QDs, it plays the role of a nucleation center that starts off the reaction. The role of this pathway in PbSe QD formation is summarized in figure 4b.

CONCLUSION

In conclusion, we demonstrate the existence of an anion exchange pathway for PbSe synthesis. While cation exchange reactions[42, 43, 44, 45] have contributed greatly to the development of novel nanocrystalline materials, there have been no reports of the anionic analogs to these reactions. We find that not just do anion exchange reactions exist, but that they also play a surprisingly important role in the formation of PbSe QDs. The nucleation of colloidal lead selenide nanoparticles is found to be completely determined by this pathway, while other previously anticipated routes are found to be involved in QD growth. The rate constants of the two pathways differ by almost four orders of magnitude, allowing for a clear separation of the nucleation and growth events.

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TOC: We show the existence and importance of anion exchange reactions in colloidal chemistry.