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On the Mechanism of Lead Chalcogenide Nanocrystal Formation

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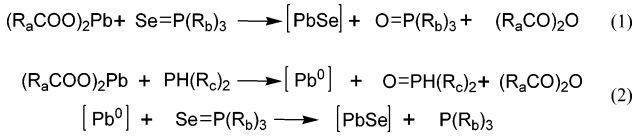
Significant advances in the synthesis of semiconductor nanocrystals (NCs) have made possible the preparation of samples with narrow size distributions and high quantum yields. Most procedures involve the rapid injection of precursors into a heated mixture of solvents and ligands; organo-phosphines, organo-phosphine oxides, and carboxylic acids are often used during the preparation of II−VI, III−V, and IV−VI NCs.[1] The formation of NCs in solution is driven by the supersaturation of "monomers" which undergo a nucleation and growth process. Despite the large number of recipes developed that produce high quality particles, progress toward understanding nucleation and growth has been limited to measurement of the size, particle number, and yield.[2] Very little specific information is known regarding the mechanism by which monomers are generated in solution. In this study, we used ^{31}P NMR spectroscopy to monitor key compounds (alkylphosphines and alkylphosphine oxides) involved in the formation of PbSe NCs. On the basis of the NMR data, we propose that two competing mechanisms occur simultaneously to generate monomers in the preparation of PbSe NCs.

Lead selenide NCs are typically synthesized by rapidly injecting TOPSe into a heated solution of lead precursor, Pb(oleate)$_2$.[3] Because of relatively low injection temperatures, the PbSe system is ideal for mechanistic studies aimed at gaining insight into NC chemistries. We propose that the following two mechanisms occur during the formation of PbSe NCs.



It is possible that analogous mechanisms occur in other NC syntheses using metal salts and phosphine chalcogenides. Because of the weak P−X (X = Se, Te) bond,[4] R$_3$P═X can be regarded either as a source of X^0 or X^{2-}. In the first mechanism (1), tri-*n*-octylphosphine selenide (TOP═Se) delivers selenium as a Se^{2-} species, resulting in the production of monomer, tri-*n*-octylphosphine oxide (TOP═O), and an anhydride. In the second mechanism (2), TOP═Se can be regarded as delivering Se^0 to a reduced Pb^0 species, resulting in the formation of monomer, an anhydride, and free TOP. Once the monomer concentration increases above the solubility limit (supersaturation), the monomers combine by a nucleation and growth process to form NCs. The monomer is a transient species that is likely a PbSe unit stabilized by a number of ligands present in solution, and we label it as [PbSe] in our mechanisms.

The basic model system we used to study the formation of PbSe NCs consisted of Pb(oleate)$_2$ and TOPSe (pure TOPSe, with no free TOP) in 1-octadecene.[5] Concentrations and reaction times in our experiments were optimized for ^{31}P NMR signal and not size distribution. Figure 1 shows the results of an experiment designed

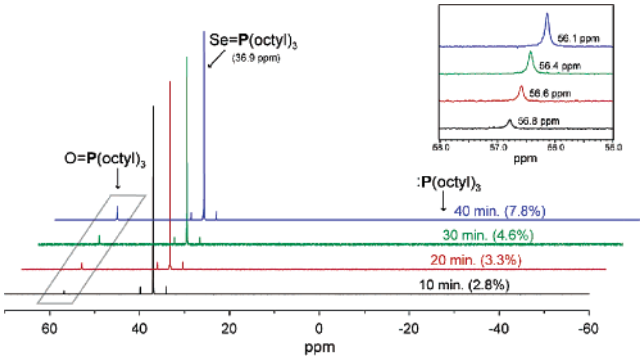
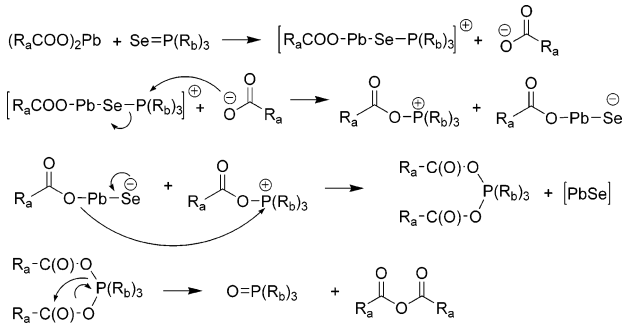


Figure 1. ^{31}P NMR spectra of four PbSe NC samples grown over 40 min at 170 °C with the corresponding reaction yields (from flame atomic-absorption spectroscopy) shown in parentheses. No free TOP was observed in the injection solution or throughout the run. The inset shows the detail view of the TOPO region.

Scheme 1. Proposed Mechanism for Reaction 1[a]



[a] R$_3$P═Se (TOPSe) and metal carboxylates (Pb(oleate)$_2$) react to form monomer ([PbSe]). The [PbSe] species is likely stabilized by the presence of free ligands in solution (R$_3$P═O and R$_3$P═Se). R$_a$ = (CH$_2$)$_7$CH═CH(CH$_2$)$_7$CH$_3$, R$_b$ = octyl

to elucidate reaction 1 in which our model system was held at an elevated temperature for four lengths of time (10, 20, 30, and 40 min). The growth solution for each time span was then quenched thermally and by dilution. The ^{31}P NMR spectra reveal that the TOPO concentration increased over time (figure inset). We attribute the slight shift in TOPO chemical shift to a change in the local environment as NCs are being formed in large amounts. Flame atomic absorption spectroscopy was also performed on these same samples, and PbSe reaction yield was found to increase correspondingly with the TOPO concentration.

Scheme 1 shows in more detail our proposed mechanism for reaction 1 in which TOPSe reacts directly with the Pb^{2+} center to produce TOPO, an oleate anhydride, and PbSe monomer. The Pb center remains Pb^{2+}, while the Se is delivered formally as a Se^{2-} species. It is important to note that only TOPO and the anhydride are formed in Scheme 1, consistent with the observation that no free TOP is generated (Figure 1).

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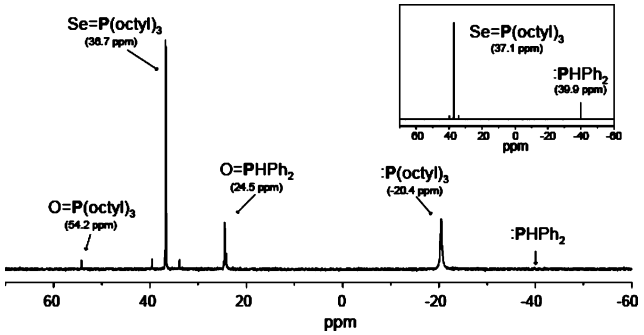
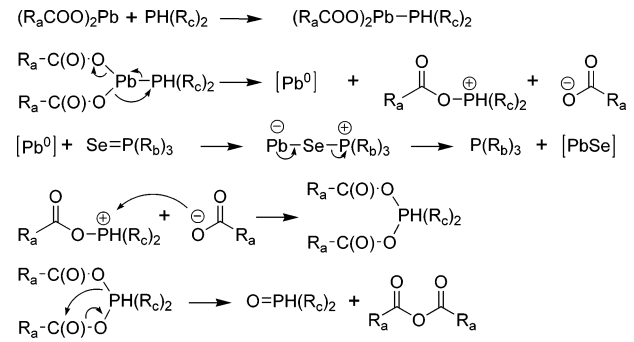


Figure 2. ^{31}P NMR spectrum of the growth solution of PbSe NCs synthesized using TOPSe doped with diphenylphosphine. The inset shows the ^{31}P NMR spectrum of the TOPSe/DPP solution before combining and reacting with the $Pb(oleate)_2$ solution. Reaction performed at 170 °C for 10 min.

Scheme 2. Proposed Mechanism for Reaction 2[a]



[a] $R_3P{=}Se$ (TOPSe), a metal carboxylate ($Pb(oleate)_2$), and a reducing agent (diphenylphosphine) react to form monomer ([PbSe]). The [PbSe] species is likely stabilized by the presence of free ligands in solution (R_3P, R_2HP, $R_2P{=}O$, and $R_3P{=}Se$). $R_a = (CH_2)_7CH{=}CH(CH_2)_7CH_3$, R_b = octyl, and R_c = phenyl.

Semiconductor NC preparations often involve a significant amount of free organo-phosphine, which has been shown to act as a reducing agent. For example, triphenylphosphine reduces divalent palladium in the complex $Pd(OAc)_2$ through oxidation to triphenylphosphine oxide.[6] In a second experiment, designed to probe proposed mechanism 2, diphenylphosphine (DPP) was added to our model system, and products and reaction yield were studied. When diphenylphosphine was added to the TOPSe solution during the NC synthesis (Pb/Se/DPP mole ratio of 1:1:0.3), we observed the complete oxidation of DPP to $DPP{=}O$ (Figure 2) and a resulting significant increase in the PbSe NC reaction yield (54% compared to 2.8% with no DPP (Figure 1)). The ^{31}P NMR spectra in Figure 2 also show peaks corresponding to TOP and TOPO (small), the latter of which indicates that the reaction in Scheme 1 is proceeding to some extent, as well.

Scheme 2 describes our second proposed mechanism for reaction 2 in more detail. Pb^{2+} is reduced by DPP, giving a Pb^0 species and DPPO. The Pb^0 species then reacts with TOPSe to liberate TOP and form PbSe. In contrast to Scheme 1, the Se can be regarded as being delivered to Pb^0 as a Se^0 species (TOP: $+Se^0$). Though TOP is a weaker reducing agent than DPP, TOP likely plays the role of DPP (Scheme 2) to some extent because it is often present in large excess in NC syntheses. Heating $Pb(oleate)_2$ with either TOP or DPP provided further evidence that organo-phosphines serve as reducing agents in NC synthesis. We found that substantial amounts of solid Pb^0 forms at 250−320 °C in the presence of TOP and at ∼180 °C in the DPP case.

Table 1. Results of Three Batch PbSe NC Preparations Using 0, 0.08, and 0.15 mmols of Diphenylphosphine (DPP) Doped into the 1 M TOPSe Injection Solution

DPP/Pb	reacn yield [%]	no. of NCs	first abs peak [nm]
	2.3	1.81×10^{16}	1358
0.08	11.6	3.09×10^{16}	1736
0.15	16.2	4.53×10^{16}	1716

Dialkyl phosphines can be impurities in TOP, and they can also be generated in situ during the synthesis through a β-hydride elimination mechanism. The mechanism in Scheme 2 can help explain the empirical observation that different lots of TOP or specific heating times sometimes have profound effects on the reaction yield, size, and size distribution of resulting NCs.

With an understanding of the role of each species in the chemistry, we can begin to rationally modify batch NC reactions. For instance, by changing the reducing agent, the rate of reaction 2 can be varied to provide more control over the system. Table 1 shows the results of three batch preparations of PbSe NCs in which DPP was added to TOPSe before injection, increasing markedly the number of NCs formed and the overall reaction yields (see Supporting Information for synthesis details). The presence of DPP increases the supersaturation rate of monomers, thereby increasing the nucleation rate.

In summary, a PbSe NC synthesis was used as a model system to study a mechanism of monomer formation in systems based on lead carboxylates and organo-phosphines. On the basis of our experimental results, we propose that two mechanisms occur simultaneously. One practical example of this understanding is our ability to increase significantly the reaction yield of the PbSe synthesis while maintaining the size distribution.

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Supporting Information Available: Experimental details, characterization of $Pb(oleate)_2$, and PbSe nanocrystal absorption cross section determination. This material is available free of charge via the Internet at http://pubs.acs.org.

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