

# A Simple, Open Air Method to Synthesize Monodisperse and Size Selective PbSe Quantum Dots

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## ABSTRACT

A simple, open air method to synthesize monodisperse and size selective PbSe quantum dots is reported here. PbCl<sub>2</sub> complexed with oleylamine was used as the Pb precursor. Se powder dissolved in 1-octadecene was used as the Se precursor. The size and shape of the PbSe quantum dots were controlled by changing injection temperature, precursor concentrations, reaction temperature, and reaction time. The sizes of the PbSe quantum dots ranged from 6.5 nm to 15.0 nm with a standard deviation of ~1.9-6.9%. The shapes of the PbSe quantum dots were either spherical (< ~9-10 nm) or cubic (> ~9-10 nm). The as-synthesized PbSe quantum dots were characterized by transmission electron microscopy, high resolution transmission electron microscopy, selected area X-ray diffraction, energy-dispersive X-ray spectroscopy, and powder X-ray diffraction.

**Keywords:** PbSe semiconductor quantum dots, PbCl<sub>2</sub>, monodisperse colloidal synthesis, oleylamine, 1-octadecene

## 1 INTRODUCTION

Semiconductor lead selenide (PbSe) nanoparticles have attracted great attention due to their strong quantum confinement properties. The quantum confinement to its nanostructures stems from their unique properties of small band gap (0.27 eV at 300K) [1], large exciton Bohr radius of 46 nm [2], and large static dielectric constant of 280 [3].

Since Murray's group [4] reported the first colloidal synthesis of PbSe quantum dots (QDs) in 2001, several modified synthesis methods have been reported [5], [6], [7], [8]. PbSe QDs are usually synthesized (Figure 1) by rapidly injecting of Se precursor—Se powder dissolved in tri-n-octylphosphine (TOP) or in tri-n-butylphosphine (TBP) solution, into a heated solution of Pb precursor, typically lead acetate or lead oleate in a non-coordinating solvent 1-octadecene (ODE) solution. Both oleic acid (OA) and TOP or TBP were used as capping ligands. Either

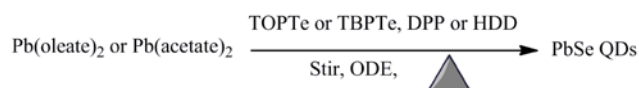


Figure 1. Synthesis Scheme I

diphenylphosphine (DPP) or 1,2-hexadecanediol (HDD) was used to increase the yield and quality of the PbSe QDs. The main problems of the current synthesis methods are complicated reaction conditions with multiple reagents, reagent impurities of TOP, difficulty of changing capping ligands completely due to the strongly bound phosphines from TOP or TBP and oxygens from OA to Pb, ligand effects of the syntheses [9], and low yield. Furthermore, TOP and TBP need special handling. They are very toxic, air sensitive and expensive reagents.

Our group has developed a simple, open air method (Figure 2) to solve these problems. First, we select stable phosphine-free solutions [10] to replace both TOPSe and TBPSe as Se precursor. SeODE is the choice we used in this report. Raston's group [11] found that the SeODE precursor was about twice reactive than that of TOPSe. Besides, SeODE is easy to prepare, inexpensive, and air-stable. Second, we use PbCl<sub>2</sub> as Pb metal source. Last, we choose oleylamine as the only capping ligand because it can not only form complex with PbCl<sub>2</sub> but also a weak capping ligand and relative easy to be substituted [12], [13]. The synthesis results are reproducible with relatively high yield. The synthesis can be a potential candidate for industrial scale production due to less reagents usage and reduced cost via simplified reaction and post reaction processes.

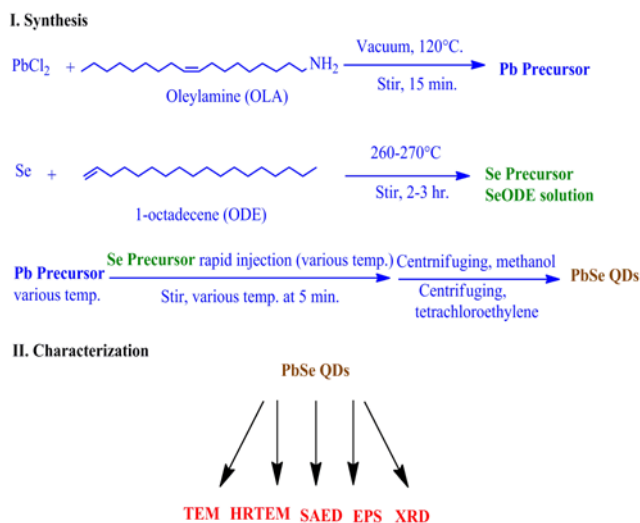


Figure 2. Synthesis and Characterization Scheme II

## 2 EXPERIMENTAL SECTION

### 2.1 Chemicals

PbCl<sub>2</sub> (99-100%) was obtained from J.T. Baker Chemical Company. Methanol (absolute reagent, A.C.S.) was purchased from Spectrum Chemical. Tetrachloroethylene (TCE), selenium (Se, 99.5%, powder, 200 mesh), oleylamine (OLA, 80-90%), and 1-octadecene (ODE, 90%) were purchased from ACROS Organic. All chemicals were used as received without further purification. The reference synthesis experiments under inert environment were carried out using standard Schlenk line techniques with dry nitrogen. 0.2 M SeODE stock solution was prepared by dissolving 0.441 g (8.5 mmol) of Se powder in 22.000 g ODE and heated with vigorous stirring at 260-270°C for 2-3 hr.

### 2.2 Synthesis and Separation of PbSe QDs

The synthesis was performed in a three-neck round-bottom flask with a condenser and a temperature controller. The Pb precursor was prepared by adding OLA into a three-neck, round-bottom flask loaded with PbCl<sub>2</sub>. The feed mole ratio of OLA to Pb was varied from 30:1 to 38:1. The Pb concentration was from 0.037 to 0.05 M. The mixture was then stirred vigorously while being pre-heated under vacuum at 120°C for about 15 min. Then, it was heated to the injection temperature. A portion of the SeODE stock solution (corresponding to various Pb to Se feed mole ratio) was injected into the Pb precursor (Table 1) rapidly at various temperature. After the injection, the temperature of the mixture dropped to its lowest point swiftly, the reaction was maintained at that point for QDs growth for various times. After reaction, the crude solution was cooled immediately in a water bath to 50-60°C. Then, the crude was centrifuged. A minimum amount of methanol was added. The crude was centrifuged again to remove OLA and other starting materials by dumping the supernatant. Finally, about equal amount of TCE was added into the crude to extract PbSe QDs. The crude was centrifuged again to precipitate solid impurities and starting materials. The as-synthesized PbSe QDs were kept in TCE for storage. The PbSe QDs can further be converted to solid to run XRD measurements.

### 2.3 Open Air, Temperature Controlled Size Selective Synthesis of PbSe QDs

A typical synthesis of cubic 15.0 nm PbSe QDs is described below. Pb precursor was prepared by introducing 0.093 g (0.33 mmol) PbCl<sub>2</sub> and 3.35 g (12.5 mmol, 4.14 mL) OLA to a three-neck round-bottom flask. The mixture was magnetically stirred and heated to 120°C under vacuum for 15 min. Then, the Pb precursor solution temperature was further raised to 235°C. 2.5 mL (0.50 mmol) of SeODE precursor (the feed mole ratio of Pb to Se was

1:1.5) from 0.2 M SeODE stock solution maintained at 160°C was quickly injected into the Pb precursor solution. The temperature of the reaction mixture dropped to 215°C and was maintained at that temperature for 5 min. At the sixth minute, the crude solution was cooled immediately in a water bath to about 50-60°C. The crude was centrifuged. 5 mL of methanol was added. The crude was centrifuged again and the supernatant was removed. 5 mL of TCE was added into the crude to extract PbSe QDs. The solution was centrifuged and separated. The as-synthesized PbSe QDs were stored in TCE. The synthesis conditions and results are listed in Table 1. The reaction time was 5 min. each. The actual yield is around 20%-70%.

### 2.4 Synthesis of PbSe QDs Under Nitrogen

All other conditions for the reference synthesis of PbSe QDs under nitrogen are same as the open air synthesis, except using standard Schlenk line techniques with dry nitrogen.

Sample #	(a)	(b)	(c)	(d)	(e)	(f)
<b>Pb to Se Feed Ratio</b>	1/1.5	1/1.5	1/1.5	1/1.5	1/1.5	1/1.5
<b>OLA to Pb Mole Ratio</b>	37	37	37	37	37	37
<b>SeODE Temp. (°C)</b>	128	130	140	160	160	160
<b>Injection Temp. (°C)</b>	140	180	200	220	235	245
<b>Growth Temp (°C)</b>	<b>130</b>	<b>165</b>	<b>180</b>	<b>200</b>	<b>215</b>	<b>230</b>
<b>TEM Size (nm)</b>	<b>6.5</b>	<b>8.3</b>	<b>9.5</b>	<b>12.1</b>	<b>15.0</b>	<b>15.5</b>
<b>σ</b>	<b>6.2%</b>	<b>1.9%</b>	<b>5.7%</b>	<b>6.9%</b>	<b>6.1%</b>	<b>5.9%</b>

Table 1. Reaction Conditions and Results

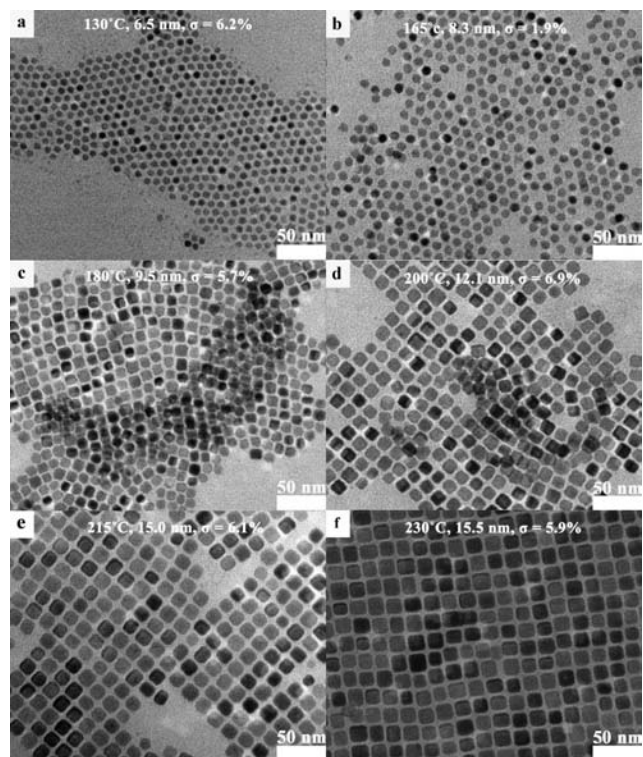
### 2.5 Sample Characterization

Transmission electron microscope (TEM), high resolution transmission electron microscope (HRTEM), selected area x-ray diffraction (SAED), energy-dispersive x-ray spectroscopy (EDS), and powder x-ray diffraction (XRD) diffractometer were used to characterize the size, shape, crystal structure, and composition of PbSe QDs. TEM images of PbSe QDs were taken using a Zeiss EM 920 instrument operated at 80 kV. HRTEM images of PbSe QDs were taken using a JEOL, JEM-2100F

instrument operated at 200 kV. The TEM samples were prepared by drop casting one drop of a dilute solution of PbSe QDs in TCE on a 300 mesh carbon-coated, copper grids from Electron Microscope Sciences. The grids were dried by evaporating the solvent in air. The sizes and size distributions (relative standard deviation) of the PbSe QDs were measured from TEM images using iTEM 5.1 of Olympus Soft Imaging Solutions GmbH. A minimum of 120 QDs were counted on each image to obtain the average diameter and size distribution of the PbSe QDs. SAED images were obtained using JEM-2100F. The EDS spectra were recorded using EDS attached to JEM-2100F. The XRD spectra were recorded on a PanXpert powder X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.1542$  nm).

### 3 RESULTS AND DISCUSSIONS

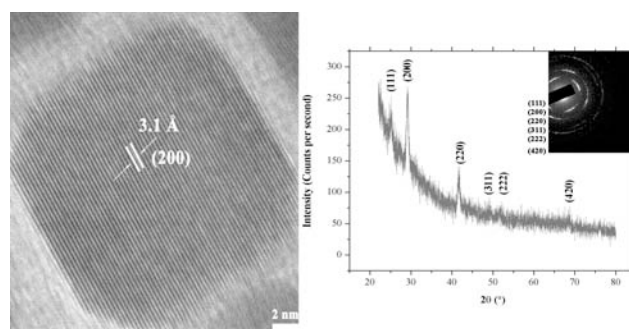
TEM images of the temperature controlled synthesis of PbSe QDs were shown in Figure 3. The sizes were from 6.5 nm to 15.0 nm with a narrow distribution of relative standard deviations  $\sim 1.9$ -6.9%. From TEM image of sample c, we observed that the shape of the PbSe QDs began to transit from spherical to cubic around size of 9 to 10 nm.



**Figure 3.** TEM images of size and size distribution of PbSe QDs. (a)-(f) represent the same sample # as Table 1 shown.

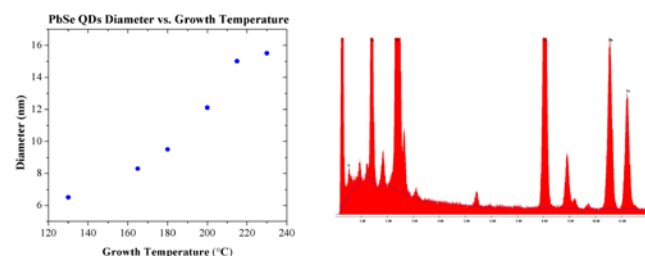
Figure 4 lists sample e's HRTEM image and its XRD and SAED data. The left image of Figure 4 is the HRTEM measurement of lattice fringe of 3.1 Å, which matches the standard card data [14] of 3.07 Å. The right image of

Figure 4, which is sample e's XRD and SAED data, shows that sample e has a fcc structure with the  $Fm\bar{3}m$  space group [14]. The crystalline sizes were calculated by using Scherrer equation for the line broadening of the (200) peak. It was 15.0 nm, which is also consistent with TEM observation of sample e (15.0 nm). The EPS results (Figure 5, right image) reveal that the QDs consist of Pb and Se elements and the atomic ratio of Pb to Se is 1.5/1. The XRD, TEM, HRTEM, SAED, and EPS data prove that sample e is cubic PbSe QDs of 15.0 nm with a size distribution of 6.1%.



**Figure 4.** Sample e's HRTEM image and its combined XRD and SAED data.

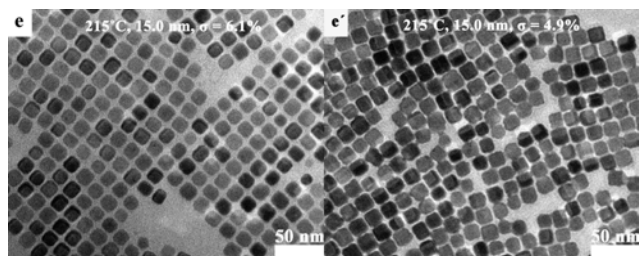
The synthesis curve in Figure 5 is a useful guideline for the synthesis of various sizes of PbSe QDs using the similar synthesis conditions. For example, to obtain PbSe QDs size of 11 nm, we can set the growth temperature at 190°C and growth time for 5 min. To obtain PbSe QDs size smaller than 6.5 nm, we need to set the growth temperature at 130°C and simply reduce growth time to 3 min. or 1 min. or 0.5 min.



**Figure 5.** Temperature Controlled Synthesis Curve and EPS of Sample e.

Comparing the synthesis results of PbSe QDs synthesized with and without nitrogen protection, we found that the element analysis results from EPS of both sample e and sample e' were identical: both had Pb and Se elements with similar ratio; the TEM images also show that the two PbSe QDs have similar shape, size and size distribution (Figure 6). It is well known that PbSe QDs are sensitive in air [9]. However, this is a storage issue. Our synthesis results indicated that there was no significant quality difference between PbSe QDs obtained in air and under

inert condition. Synthesis of PbSe QDs in open air greatly simplified the overall process of making PbSe QDs.



**Figure 6.** PbSe QDs Synthesized without and with Nitrogen Protection (sample e and sample e').

## 4 CONCLUSIONS

We have developed a new, simple method to synthesize monodisperse PbSe QDs. We selected SeODE as Se precursor, PbCl<sub>2</sub> as Pb metal source, and OLA as the only capping ligand. The synthesis does not need to under inert environment. The method used less reagents and reduced cost via simplified reaction and post reaction processes. The sizes of the PbSe quantum dots ranged from 6.5 nm to 15.0 nm with a standard deviation of ~1.9-6.9%. The shapes of the PbSe quantum dots were either spherical (< ~9-10 nm) or cubic (> ~9-10 nm). The synthesis results are reproducible with relatively high yield. The synthesis can be a potential candidate for industrial scale production.

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