

# OPEN AIR SYNTHESIS AND STABILITY ANALYSIS OF AIR-STABLE PBSE QUANTOM DOTS

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**Abstract** - Air-stable lead selenide quantum dots were synthesized with a simple PbCl<sub>2</sub>-oleylamine system in open air, using selenium dissolved in 1-octadecene as Se precursor. The as-synthesized PbSe quantum dots were air-stable and their air stability was confirmed by a systematic study with transmission electron microscopy. The protection shields formed by chloride anions, oleylamine, and organic and inorganic hybrid were discussed.

**Keywords** - Air-stable quantum dots, Lead chalcogenide, Lead selenide, Lead chloride-oleylamine system, Open air synthesis.

## I. INTRODUCTION

Colloidal PbSe quantum dots (QDs) have been widely investigated as promising nanomaterials for optoelectronic devices,<sup>1</sup> especially for solar cells.<sup>2-6</sup> Beard et al discovered in 2011 that PbSe QDs films used as the active layer of solar cells can produce very large currents by the process of multiple exciton generation (MEG).<sup>7</sup> Since then, studies for PbSe QDs as the preferred nanomaterials for the next generation QD-based solar cells have been intensified.<sup>7-9</sup> However, few discussions of the design and the synthesis of air-stable PbSe QDs were reported until recently.<sup>8, 10-12</sup> The inadequate investigations of the synthesis of air-stable PbSe QDs hindered the applications of PbSe QDs in QD-based solar cells.

Articles published by Alivisatos<sup>13</sup> et al and recently by Sargent<sup>9</sup> et al indicated that halide anions play an important role for the air-stability of the QD-based photovoltaic devices. The Sargent group also revealed that oleylamine (OLA) processed devices had excellent air- and light-stability.<sup>14</sup> These suggest that incorporating either halides or OLA on the surface of PbSe QDs may lead to air-stable PbSe QDs. Indeed, by including only halides on the surface of PbSe QDs, Klimov<sup>10</sup> et al reported chlorine processed PbSe QDs were air-stable for 24 days with improved photoluminescence efficiency and photocharging. Our group not only obtained PbSe QDs<sup>11</sup> with long-term air-stability of at least 24 months but also synthesized other air-stable lead chalcogenide QDs—PbTe<sup>15</sup> and PbS QDs<sup>16</sup> by using the same PbCl<sub>2</sub>-OLA system that provided both OLA and chloride anions, which can keep QDs synthesized air-stable.<sup>14</sup> Although our synthetic protocol is a simple, practical, and may be one of the most favorable solution-based methods to fabricate air-stable PbSe QDs so far, we find that several procedures still need to be improved to further reduce the cost and to simplify the overall reaction process, such as carrying on the reaction in open air, using less toxic and room temperature stable Se precursor, and

finding high concentration Se precursor to achieve easy fabrication of the air-stable PbSe QDs either with a hot-injection or a noninjection method. Towards this end, we report a simple, facile and open air hot-injection method to further streamline the reaction process that could enable a cost-effective way for industrial scale production of fabricating air-stable PbSe QDs for solar cell applications. We have obtained nearly monodispersed PbSe QDs ranging from 6.5 nm to 5.5 nm with relative standard deviations of 1.9%-6.9%. The as-synthesized PbSe QDs were air-stable for at least 22 months when stored as thin film. The highlight of the simple approach includes: (1) Contrary to the routine synthetic approach for air-stable QDs, all procedures involving synthesis and separation were carried on in an open air environment. (2) The simple PbCl<sub>2</sub>-OLA system was used as the lead precursor and the capping ligand provider, while low cost, less toxic, room temperature stable SeODE (Se powder dissolved in 1-octadecene) was selected as the Se precursor to substitute SeOLA (Se powder dissolved in OLA) which generates precipitations at room temperature. (3) The upper limit of the size of the PbSe QDs synthesized was extended from 13.9 nm (SeOLA as Se precursor) to 15.5 nm (SeODE as Se precursor).

## II. DETAILS EXPERIMENTAL

### 2.1. Materials and Procedures

PbCl<sub>2</sub> (99-100%) was from J.T. Baker. Methanol (absolute reagent, 99.8%, A.C.S.) was purchased from Spectrum Chemical. Oleylamine (OLA, 80-90%), selenium (Se, 99.5%, powder, 200 mesh), tetrachloroethylene (TCE, 99+%), and 1-octadecene (ODE, 90%) were purchased from ACROS Organic. Open Air Synthesis And Stability Analysis Of Air-stable PbSe Quantum Dots

A general procedure to synthesize a 9.5 nm cubic PbSe sample (QD-3) is described below. Se precursor stock solution (SeODE) of 0.2 M was prepared by dissolving 0.300 g of Se powder in 15.00 g of ODE

under refluxing for about 2-3 h. Then, the temperature of the SeODE stock solution was maintained at around 140°C. The Pb precursor was prepared by introducing 0.093 g (0.33 mmol) PbCl<sub>2</sub> and 3.35 g (10.17 mmol, 4.14 mL) OLA to a threeneck round-bottom flask. The mixture was magnetically stirred and heated to 120° C for 15 min. Then, the temperature of the Pb precursor solution was further raised to 200° C. 2.5 mL (0.50 mmol) of 0.2 M SeODE precursor (the feed mole ratio of Pb to Se was 1:1.5) from 0.2 M SeODE stock solution maintained at 140° C was quickly injected into the Pb precursor solution. The temperature of the reaction mixture dropped to 180° C and was maintained at that level for 5 min. Then, 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, and the crude was centrifuged again and the supernatant was removed. 5 mL of TCE was added into the crude to extract PbSe nanoparticles. The solution was centrifuged and the residues were removed. And the as-synthesized PbSe nanoparticles were stored in TCE. A temperature-based synthetic method was used to obtain various sizes of PbSe samples (QD-1 to QD-7) by carrying different batches of the synthesis under the same conditions (with the same recipe): the same amounts of chemical reagents were used, Pb to OLA feed mole ratio of 1:30, Pb to Se feed mole ratio of 1:1.5, the growth time of 5 min., but at a variety of growth temperature of 130° C, 165° C, 180° C, 200° C, 215° C, 230° C, and 215° C (under nitrogen protection) respectively. The reaction conditions and results are listed in Table 1. All processes were carried on in open air except QD-7 (synthesized under nitrogen protection).

### 2.2 Sample characterization

The size, shape, crystal structure, composition, and surface ligand of the air-stable PbSe nanoparticles were characterized by transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), selected area X-ray diffraction (SAED), FT-IR (Fourier transform infrared spectroscopy) spectrometer, energy-dispersive X-ray spectroscopy (EDS), and powder X-ray diffraction (XRD) diffractometer.

TEM images of PbSe nanoparticles were taken by a Zeiss EM 920 instrument operated at 80 kV. High resolution TEM images of PbSe nanoparticles 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 nanoparticles in TCE on a 300 mesh carboncoated, copper grid from Electron Microscope Sciences. The grid was dried by evaporating the solvent in air. The sizes and size distributions (relative standard deviation) of the PbSe nanoparticles were measured from TEM images using iTEM 5.1 of Olympus Soft Imaging Solutions GmbH.

A minimum of 120 nanoparticles were counted on each image to obtain the average diameter of the PbSe QDs. SAED patterns were obtained using JEM-2100F. The EDS spectra were recorded using EDS attached to JEM-2100F.

**Table 1: Reaction Condition and PbSe Nanoparticles Synthesized**

Sample #	Size (nm)	$\sigma$	Growth temp. (°C)	SeODE (°C)	Injection temp. (°C)
QD-1	6.5 ± 0.4	6.2%	130	128	140
QD-2	8.3 ± 0.2	1.9%	165	130	180
QD-3	9.5 ± 0.5	5.7%	180	140	200
QD-4	12.1 ± 0.8	6.9%	200	160	220
QD-5	15.0 ± 0.9	6.1%	215	160	235
QD-6	15.5 ± 0.7	5.9%	230	160	245
QD-7	15.0 ± 0.7	4.9%	215	160	235

### 2.3 Stability test

For each size of PbSe nanoparticles to be tested (refer to Table 2), two types of TEM samples were used: (1) TEM sample made immediately after synthesis. (2) The same TEM sample stored on TEM copper grid in ambient environment for twenty-two months and measured again.

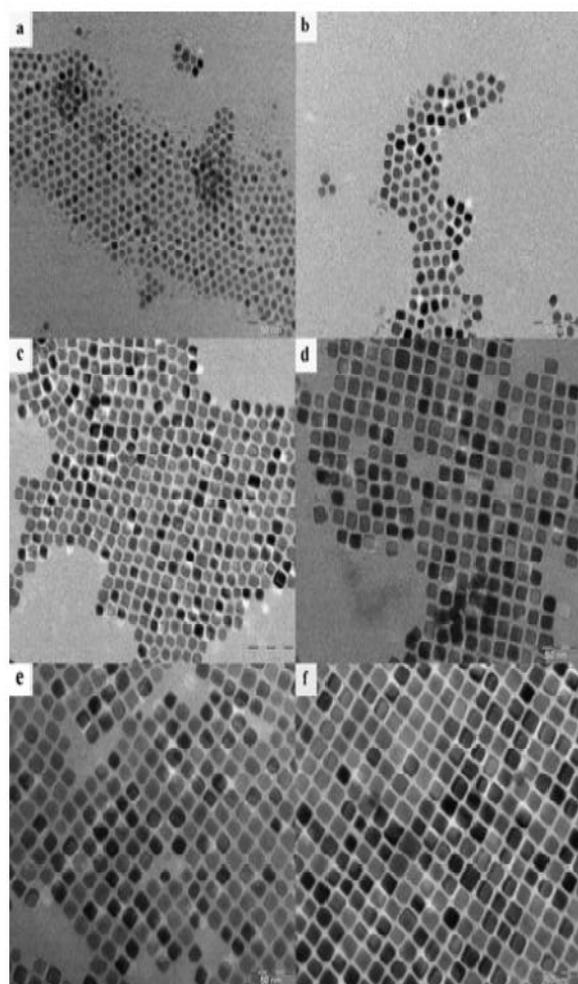
**Table 2: PbSe QDs Stability Test**

Sample #	On TEM after synthesis (nm)	On TEM for 22 months (nm)
QD-3	9.5 ± 0.5	9.7 ± 0.5
QD-6	15.5 ± 0.9	15.0 ± 0.8

## III. RESULTS AND DISCUSSION

TEM images of a series of monodispersed PbSe nanoparticles with sizes of QD-1 (6.5 nm), QD-2 (8.3 nm), QD-3 (9.5 nm), QD-4 (12.1 nm), QD-5 (15.0 nm), and QD-6 (15.5 nm) were shown in Fig. 1 (refer to Table 1). The weak peak at around 3007 cm<sup>-1</sup>, the typical -CH- stretching (attached to the -C=C-double bond) of the FT-IR spectra (Fig. 2) of PbSe nanoparticle QD-3, confirms that OLA is the capping ligand of PbSe nanoparticles. The HRTEM image (top), the SAED diffraction pattern (top right inset from the bottom) as well as the XRD pattern (bottom left) (Fig. 3) of QD-3 confirm that the nanoparticles are single crystals. The lattice fringe of QD-3 was measured at 3.1 ± 0.1 Å, which is in consistent with the (200) lattice plane for bulk PbSe (ICDD, PDF card file no. 01-071-4753, 3.07 Å). The XRD pattern

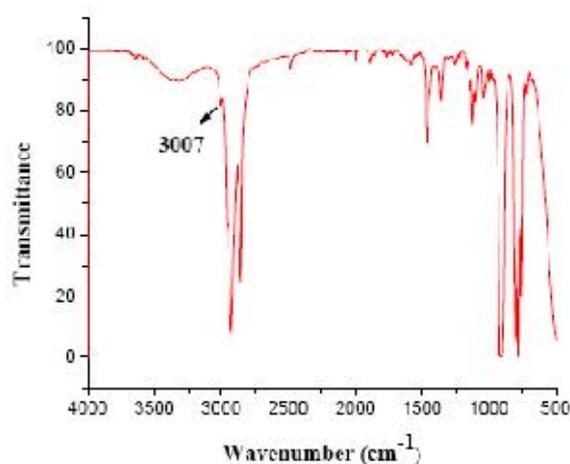
of the resulting PbSe nanoparticles illustrates the values of the major peaks located in the range from  $20^\circ$  to  $80^\circ$  ( $2\theta$ ) corresponding to the characteristic diffraction of PbSe, verifying that only PbSe is present. The crystalline size was calculated by using the Scherrer equation from the line broadening of the (200) peak. It was 9.7 nm, which is also in consistent with TEM observation of the size of QD-3 (9.5 nm). The elemental analysis result (Table 3) of QD-3 from EDS reveals the mole ratio of Pb to Se is around 1.1:1. The non-stoichiometric excess amount of  $Pb^{2+}$  cations measured is in accordance with the results reported by Moreels et al.<sup>17</sup> They play an important role in the air-stability of PbSe QDs. The HRTEM, SAED, XRD, FT-IR, and EDS data all pointed out that the as-synthesized nanoparticles' crystal structure, composition, and surface ligand were PbSe core capped with OLA.



**Fig.1.** TEM images of a series of monodispersed PbSe nanoparticles synthesized. The scale bar from a to e is 50 nm. a to f corresponding to samples QD-1 of 6.5 nm with size distribution  $\sigma = 6.2\%$ , QD-2 of 8.3 nm with  $\sigma = 1.9\%$ , QD-3 of 9.5 nm with  $\sigma = 5.7\%$ , QD-4 of 12.1 nm with  $\sigma = 6.9\%$ , QD-5 of 15.0 nm with  $\sigma = 6.1\%$ , and QD-6 of 15.5 nm with  $\sigma = 5.9\%$ .

The selected stability test results of 2 PbSe QDs synthesized in Fig. 4 demonstrated that the as-synthesized PbSe QDs were not air-sensitive, but

with a long-term air-stability when stored as thin film because TEM measurement results show no size, size distribution, and shape variations of PbSe QDs for at least 22 months. Both QD-3 of size 9.5 nm (Fig. 4a and Fig. 4b) and QD-6 (Fig. 4c and Fig. 4d) of size 15.5 nm were air-stable for 22 months. The protection shields formed by chloride anions (exclude oxygen),  $PbCl_2$ -OLA complex (the amine group of OLA can form hydrogen bond with water, while it can also neutralize the acid), OLA (the amine group of OLA can form hydrogen bond with water, the double bond of OLA can eliminate oxygen), and probably the organic and inorganic hybrid formed with the presence of moisture and weak acid in air during storage, made the PbSe QDs air-stable for at least 22 months. We propose that excess  $PbCl_2$ , OLA, and trace water may generate organic and inorganic hybrid  $CH_3(CH_2)_7CH=CH(CH_2)_8(NH_3^+)2Pb(OH)_2Cl_2$  on the surface of PbSe QDs and maintain the basicity condition of the surface to protect the PbSe core from oxidation as Fig. 5 indicated, similar to the Koutselas<sup>18</sup> et al reported recently that  $PbCl_2$  and OLA can form organic cation  $(CH_3(CH_2)_7CH=CH(CH_2)_8(NH_3^+))$ . The enhanced surface stability of PbSe QDs is the direct result of using the simple  $PbCl_2$ -OLA system in QD synthesis. The PbSe QDs synthesized were not air-sensitive because they were protected from the oxygen, the water (moisture), and trace acid attacks during storage in air. Fig. 5 illustrates the interactions of species adsorbed (including excess amount of  $Pb^{2+}$  cations and  $Cl^-$  anions) on the surface of PbSe QDs and how the combined attacks from oxygen, water, and trace acid failed to oxidize the PbSe QD core.



**Fig.2.** FT-IR spectra of QD-3.

**Table 3: EDS Results of PbSe Sample QD-3**

Element	Weight (%)	Atomic (%)
PbL	74.9	53.2
SeK	25.1	46.8
Total	100.0	100.0

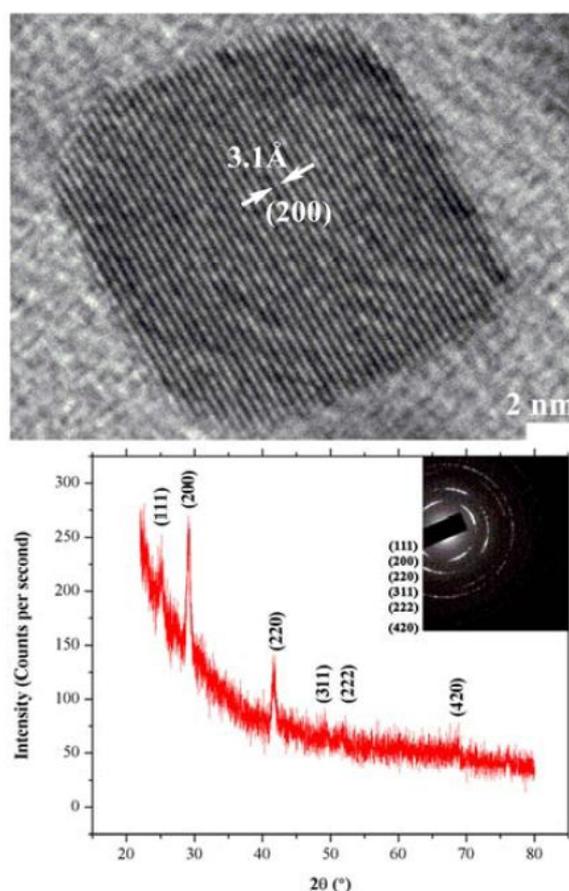


Fig.3. HRTEM image, XRD curve, and SAED patterns of PbSe sample QD-3. The size of QD-3 calculated from the full-width-half-maximum (FWHM) of the (200) peak of XRD using the Scherrer equation was 9.7 nm. The plot is the actual XRD curve. It matches the ICDD, PDF card file no. 01-071-4753 cubic phase PbSe. Inset in the top right of the bottom of Fig. 3 shows electron diffractogram linked with the main diffraction rings of sample QD-3.

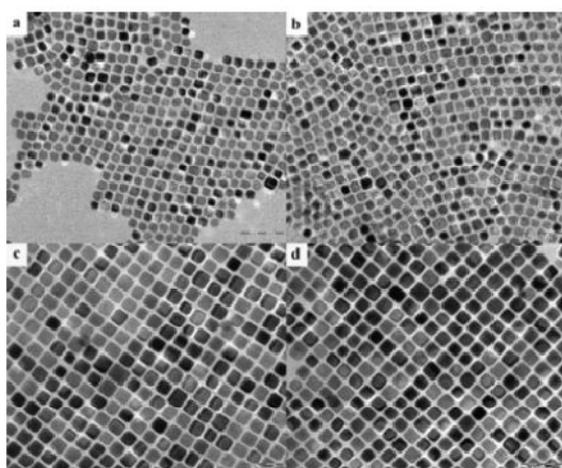


Fig.4. TEM images of the PbSe QDs stability test of QD-3 and QD-6. The scale bar from a to d is 50 nm. a and b corresponding to the TEM measurement results of the size, the size distribution, and the shape changes of QD-3:  $9.5 \pm 0.5$  nm ( $\sigma = 5.7\%$ ) on TEM grid right after the synthesis (a) and  $9.7 \pm 0.5$  nm ( $\sigma = 4.7\%$ ) on TEM grid for 22 months (b). c to d corresponding to measurement results of the size, the size distribution, and the shape changes of QD-6:  $15.5 \pm 0.9$  nm ( $\sigma = 5.9\%$ ) on TEM grid right after the synthesis (c) and  $15.0 \pm 0.8$  nm ( $\sigma = 5.2\%$ ) on TEM grid for 22 months (d).

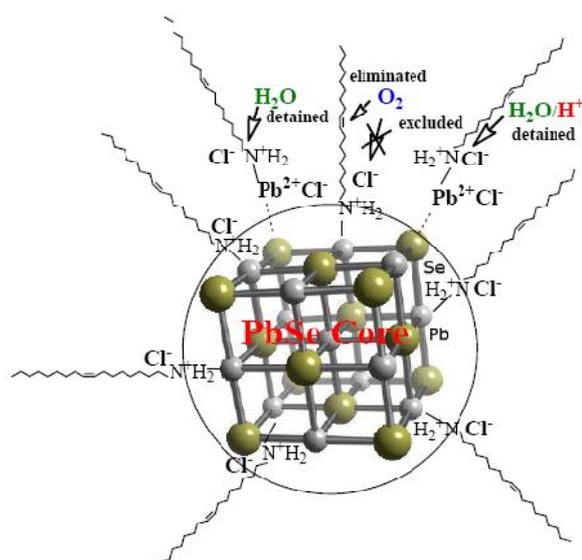


Fig.5. Enhanced surface stability of PbSe QDs (the PbSe crystal structure used is from WebElements).<sup>19</sup> The combined attacks from oxygen, water, and water plus acid in air failed to oxidize the PbSe core protected by the shields consisting of chloride anions (exclude oxygen), PbCl<sub>2</sub>-OLA complex (detain water and trace acid), OLA (detain water and eliminate oxygen), and probably the organic and inorganic hybrid formed (detain water and trace acid).

Sample QD-7 was synthesized using the same condition as QD-5, except under nitrogen protection. Fig. 6 demonstrated that there are no size, size distribution, and shape variations between QD-5 and QD-7. It clearly demonstrated that the open air method should be the choice due to the simplified process and the reduced cost. The detailed analysis of the actual synthetic conditions also supports the open air approach: first, the reaction is carried on at high temperature to reduce the amount of oxygen in the reaction mixture (low solubility of oxygen at high temperature); second, the reaction mixture consists of excess amount of reducing reagents: both ODE and OLA, which can eliminate the small amount of oxygen in the mixture; and last, the surface of the PbSe QDs are well protected from oxygen attack. The stability results proved that even when oxygen was on the surface of PbSe QDs, the PbSe QD core were still air-stable for 22 months. Therefore, air-stable PbSe QD synthesis does not require any routine inert environment, but needs a correct synthetic system: PbCl<sub>2</sub>-OLA.

Although near-IR spectra can also measure the optical properties of QDs to determine the air-stability of PbSe QDs, we selected TEM as a tool to assess the air-stability of QDs because the stability can be visualized in terms of sizes, size distributions, and shapes. The upper limit of the size of the PbSe QDs synthesized is extended from 13.9 nm to 15.5 nm probably due to the solvent effect and the reduced Pb to Se ratio of 1:1.5 instead of 1:3. There are relatively less OLA available to cap the PbSe cores when SeODE is used as the Se precursor. Fig.6. TEM images of the PbSe QDs synthesized. a is QD-5 size

of 15.0 nm with  $\sigma = 6.1\%$  (synthesized in open air). b is QD-7 size of 15.0 nm with  $\sigma = 4.9\%$  (synthesized under nitrogen protection).

## CONCLUSIONS

Air-stable lead selenide quantum dots were synthesized with a simple PbCl<sub>2</sub>-oleylamine system in open air, using ODE as the Se Precursor. The as-synthesized PbSe QDs were long term air-stable. This project and our previous studies demonstrate that the PbCl<sub>2</sub>-oleylamine system has the advantages to generate air-stable lead chalcogenide quantum dots. Further, metal chlorides and OLA system may be used in the synthesis of other air-stable binary chalcogen-containing quantum dots.

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