Synthesis of Colloidal PbSe Nanoparticles Using a Microwave-Assisted Segmented Flow Reactor

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Abstract

Colloidal lead selenide nanoparticles (PbSe NPs) were synthesized using a microwave-assisted continuous flow reactor. Rapid heating of precursors was performed in the microwave reaction zone to initiate nucleation and was followed by an oil bath growth zone. In this study we have evaluated the effect of the nucleation temperature on the PbSe NP size distributions, crystallogeographic structure, particle shape, and particle composition. The PbSe NP size could be varied from 11.2 to 13.9 nm by adjusting the microwave nucleation temperature between 124 to 159 °C. It was found that nucleation of Pb rich species occurred in the microwave reaction zone, while PbSe NPs form in the growth zone.
Keywords: PbSe; Nanoparticles; Colloidal Processing; Microwave; Flow Synthesis
1. Introduction

Lead selenide nanoparticles (PbSe NPs) are of considerable interest due to their large Bohr exciton radius (46 nm) [1] and small direct bulk bandgap (0.28 eV) [2]. These properties make PbSe NPs useful for solar cells[3,4], photodetectors[5], and infrared emitters[6]. The large Bohr exciton radius allows the optical properties of PbSe NPs to be tuned by controlling their size. Solution-based approaches for the synthesis of colloidal PbSe NPs include solvothermal[7], sonochemical[8], photochemical[9], pH induced precipitation[10,11], microwave-assisted[12-14], continuous flow[15], and hot injection methods[16,17]. For these applications narrow PbSe NP size distributions are critical, and hot injection techniques are most commonly used for synthesis of PbSe NPs.

Hot injection techniques typically use small batch sizes to minimize NP size distributions by decreasing temperature and concentration gradients. Controlling these gradients becomes complicated with increasing batch size, which limits the potential for scale-up. Flow techniques offer a route toward large scale production by continuous synthesis[18]. The integration of continuous flow with microwave radiation allows rapid volumetric heating, which eliminates thermal gradients and wall effects present in conduction heating[12]. Continuous flow microwave methods have successfully synthesized a variety of NPs (e.g., Ag[19,20], Fe₃O₄[19], CuInSe₂[21], CuInS₂[21], Cu[22], and Ni[23]). Further improvements can also be obtained by segmented flow methods, which provide continued mixing, reduction in fouling, and reduced residence time distributions[18,24].

In this study, a microwave-assisted segmented flow reactor was used to synthesize colloidal PbSe NPs. We have found that chemistries developed for hot injection methods can be readily
adapted to the microwave-assisted segmented flow reactor and that the NP size could be controlled by varying the microwave nucleation temperature \( (T_{\mu W}) \).

2. Materials and Methods

2.1 Materials

Lead(II) oxide (PbO powder, >90 %), tri-n-octylphosphine (TOP, 90 %) and selenium powder (Se, 325 mesh, 99.5 %) were obtained from Alfa Aesar. Oleic Acid (OA, 90 %), toluene, and 1-octadecene (ODE, 90 %) were obtained from Aldrich. Acetone and methanol were obtained from Marcon, and acetonitrile was obtained from JT Baker. All chemicals were used with no further purification.

2.2 Methods

Two separate precursor solutions were formed in a nitrogen glovebox. The first contained 0.20 M PbO and 0.50 M OA in ODE. The second contained 0.40 M Se and 0.60 M TOP in ODE. The two solutions were stirred for 120 minutes at 150 °C. The precursors were transferred from the glovebox to the reactor in sealed sample containers. The precursors were held at 150 °C for 20 minutes under vacuum, then reduced to 90 °C while Ar gas was bubbled through the solution for an additional 20 minutes.

A peristaltic pump delivered the two precursors at a rate of 0.30 ml/minute into a polyether ether ketone (PEEK) micro T-mixer. A second PEEK micro T-mixer was connected downstream from the first to obtain segmented flow using Ar gas with a constant flow rate of 0.15 ml/minute. Initially the segmented solution flowed at a rate of 0.75 ml/minute, however the flow rate was not constant through the entire volume since the Ar gas expands with decreased pressure and
increased temperature. High temperature polytetrafluoroethylene (PTFE) tubing (1.6 mm inner diameter) was used for the nucleation, growth, and quench zones of the reactor.

The segmented solution entered the nucleation zone through an aluminum chimney and was irradiated over a 4 cm length using a microwave reactor (Sairem model PCCMWR340PVMR1PE GMP 30K; 3kW; 2.45 GHz) with a residence time of ~6 seconds. A Pyrex tube was used to center the top and bottom of the PTFE tube in the microwave reactor. A fiber optic probe (Neoptix) was attached to the outside of the PTFE tube using PTFE tape and was positioned in the center of the microwave region. The $T_{\mu W}$ was controlled by setting the microwave power between 270 to 360 W and then adjusting the reflector to achieve a maximum temperature. After exiting the microwave the segmented solution entered the growth zone which consisted of 350 cm of coiled tubing submerged in a 140 °C oil bath, resulting in a growth zone residence time of ~9 minutes. Upon exiting the oil bath the solution entered the quench zone where the tubing was cooled by ambient air over the last 10 cm prior to collection in a glass vial. During the PbSe NP synthesis the reactor was run continuously for 3.5-6 hours. For each sample the $T_{\mu W}$ was adjusted and allowed to stabilize prior to collecting the product for 10 minute. Addition of methanol followed by centrifugation was used to precipitate the PbSe NPs, which were resuspended in toluene. This process was repeated a minimum of three times prior to analysis, and NPs remained stable in solution for several weeks.

Compositions were determined using energy dispersive X-ray spectroscopy (EDS) with a FEI Quanta 3D (30 kV beam energy). Crystal structures were determined using X-ray diffraction (XRD) with a Bruker D8 Discover diffractometer (Cu Kα radiation). Size and crystal structures were determined using a FEI Titan FEG transmission electron microscope (TEM) (200 kV beam energy), where the TEM images were analyzed with ImageJ software. A minimum of 500 NPs
were counted and sized for each condition to find an average diameter ($\bar{x}$) and standard deviation ($\sigma$). To determine if the mean nanoparticle size obtained for different experimental conditions were statistically significant we performed an analysis of variance (ANOVA).

3. Results and Discussion

A series of reactions were performed with $T_{\mu W}$ varied between 124, 142, and 159 °C followed by a constant growth zone temperature (140 °C). Dropcast films of PbSe NPs were characterized using XRD and a typical diffraction pattern is shown in Figure 1 (upper). The XRD patterns have eight main diffraction peaks at $2\theta = 25.2^\circ$, $29.1^\circ$, $41.7^\circ$, $49.3^\circ$, $51.7^\circ$, $60.4^\circ$, $68.5^\circ$, and $76.1^\circ$, which correspond to the (111), (200), (220), (311), (222), (400), (420), and (422) planes of PbSe clausthalite (JCPDS 00-006-0354) and are indicated in the bottom of the figure. No impurity peaks were observed in the XRD patterns, suggesting phase pure PbSe NPs. An XRD pattern from a sample that had a $T_{\mu W}$ of 159 °C but no growth zone is shown in Figure 1 (lower). In this case only a broad diffraction feature is observed suggesting very small particle sizes and/or amorphous materials.

EDS was performed on dropcast films to determine the Pb:Se stoichiometry for different growth conditions. Table 1 indicates that $T_{\mu W}$, with a 140 °C growth zone, influenced the stoichiometry of the PbSe NPs, where lower $T_{\mu W}$ resulted in a slight excess of Se. However it should be noted that the PbSe NP stoichiometries for these three conditions were within the standard deviation of the desired 1:1 atomic composition. EDS obtained from a sample synthesized using a $T_{\mu W}$ of 159 °C, but without the growth zone, indicated formation of Pb rich material. We were unable to obtain HR-TEM images from these samples despite thorough cleaning procedures due to
significant carbon contamination during imaging, and possibly due to the amorphous nature of
the particles as suggested by the XRD.

Our results provide insights into PbSe NP growth mechanisms. Two possible routes for PbSe
synthesis are shown in Equation 1 and 2[25,26] where \( R_a = (CH_2)_7CH=CH(CH_2)_7CH_3 \), \( R_b = 
Phenyl \), and \( (R_aCO)O(OCR_a) \) is oleic anhydride. The large excess of Pb in the microwave only
sample suggests that nucleation of PbSe NPs occurs via equation 2 where reduction of lead
oleate \((\text{Pb}(\text{OA})_2)\) to \( \text{Pb}^0 \) by diphenyl phosphine (a contaminant in 90% TOP) precedes the
formation of PbSe and may be accelerated by microwave radiation.

\[
\text{Equation 1} \\
(R_a\text{COO})_2\text{Pb} + \text{Se} = \text{P}(\text{C}_8\text{H}_{17})_3 \rightarrow [\text{PbSe}] + O \\
= \text{P}(\text{C}_8\text{H}_{17})_3 + (R_a\text{CO})\text{O}(\text{OCR}_a)
\]

\[
\text{Equation 2} \\
(R_a\text{COO})_2\text{Pb} + \text{PH}(R_b)_2 \rightarrow [\text{Pb}^0] + O = \text{PH}(R_b)_2 + (R_a\text{CO})\text{O}(\text{OCR}_a) \\
[\text{Pb}^0] + \text{Se} = \text{P}(\text{C}_8\text{H}_{17})_3 \rightarrow [\text{PbSe}] + \text{P}(\text{C}_8\text{H}_{17})_3
\]

Excess Pb may indicate either the presence of Pb nanoparticles[27] or PbSe nuclei with a Pb
shell. Previous reports of Pb rich PbSe NPs have shown increasing Pb content with decreasing
particle size[28,29]. We found that samples synthesized using a \( T_{\text{µW}} \) of 159 °C, but without the
growth zone, resulted in Pb:Se ratios \( \sim 9 \times \) larger than previously reported for 3.3 nm in diameter
PbSe NPs having a Pb shell. This suggests that our nuclei have a Pb shell and are much smaller than 3nm in diameter, or they are inherently Pb rich.

Typical TEM images and size histograms for each $T_{\mu W}$ followed by a 140 °C growth zone are shown in Figure 2. Average PbSe NP diameters are found to decrease with increasing $T_{\mu W}$ (Table 1). Average PbSe NP diameters were found to be 13.9, 12.5, and 11.2 nm for $T_{\mu W}$ of 124, 142, and 159 °C, respectively. A coefficient of variation (100% × $\sigma$/$\bar{x}$) of ~15-16% was obtained without further size selection. Further analysis was performed to confirm that $\bar{x}$ and $\sigma$ are statistically distinct using the ANOVA method for the three sets of data [30]. The analysis indicated that the three distributions are significantly different where the calculated F value of 272 is significantly higher than the critical F value of 3.0. The smaller PbSe NP size for higher $T_{\mu W}$ is likely due to an increase in the number of nuclei generated in the microwave nucleation zone, with a corresponding decrease in dissolved precursor available during the growth stage. Additionally, increased heating ramp rates are expected to cause a more rapid and uniform nucleation event. With further optimization of nucleation and growth stages, the microwave-assisted segmented flow synthesis may approach the state of the art coefficient of variation (~5%) for hot injection [16,17].

High-resolution TEM (HR-TEM) images of individual NPs were used to determine crystal structure by indexing fast Fourier transforms (FFT) of the images shown in Figure 3. Only select planes in the FFT were labeled for clarity. The analyzed particles are shown along the [101] zone axis for $T_{\mu W}$ of 159 and 142 °C, and the [112] zone axis for a $T_{\mu W}$ of 124 °C. In all cases the atomic spacings matched that expected for cubic PbSe and are in agreement with XRD results. TEM images (Figure 2) of PbSe NPs synthesized using a $T_{\mu W}$ of 159 and 124 °C shows particles with semispherical to rounded square shapes and more rectangular shapes, respectively. Closer
examination of HR-TEM images for PbSe NPs from these reactions is shown in Figure 4. For \( T_{\mu W} \) of 159 °C the dominant sides of the square shaped PbSe NPs correspond primarily to the \{111\} surface planes and minority \{100\} surface planes that result in an octahedral or truncated octahedral morphology. For \( T_{\mu W} \) of 124 °C the dominant sides of the particles correspond primarily to the \{111\} surface planes, however facets in these surface planes are readily observed and we find these facets correspond to \{100\} surface planes. A statistical analysis was performed on over 500 PbSe NPs for each growth condition, and we found that 52, 25, and 10% had \{100\} surface plane facets for \( T_{\mu W} \) of 124, 142, and 159 °C. The (100) PbSe surface is significantly lower in energy than the (111) surface, which would suggest that the lowest energy state for PbSe NPs is cubic structures with exposed \{100\} surfaces [31,32]. However, these studies also show the modification of relative surface energies due to adsorbed surface ligands.

We have found that varying microwave intensity in the microwave zone, and the resulting nucleation temperature, affected both size and shape of particles. Increasing the microwave intensity in the nucleation zone increases the heating rate of the solution and maximum temperature obtained. The increased microwave intensity causes an increase in the nucleation rate, resulting in a lower monomer concentration in the growth bath. With an increased number of nuclei and a lower concentration of monomers during the growth phase, the resulting PbSe NPs have a smaller average diameter and a spherical shape. The variation in morphology for different microwave intensities is more difficult to explain. It is possible that the different nucleation temperatures cause a relative change in surface ligand coverages, which can then modify the relative surface energies of the nuclei. Further studies that compare the different retention times for the various \( T_{\mu W} \) may provide insights into the shape evolution during PbSe NP growth but is beyond the scope of this study.
4. Conclusion

In summary, a microwave-assisted segmented flow reactor was used to synthesize high quality PbSe NPs with low coefficients of variation (~15%). No additional crystalline impurities were observed in XRD. PbSe NP diameters were found to increase from 11.2 to 13.9 nm with decreasing $T_{\mu W}$. As the PbSe NP size increased the shapes of the particles were observed to evolve from semi-spherical and octahedral to multi-faceted structures. Observation of crystalline planes indicates that particles have a $\{111\}$ truncated octahedral morphology for a $T_{\mu W}$ of 159 °C, but have both $\{111\}$ and $\{100\}$ facets for a $T_{\mu W}$ of 124 °C. Pb rich nucleates were observed directly after the microwave indicating that reduction of Pb occurs during the nucleation zone, and that PbSe NPs form in the growth zone. These results demonstrate the use of a microwave-assisted segmented flow reactor as an effective method for the synthesis of high quality colloidal NPs.

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References


Table 1: Summary of PbSe NP composition and size after synthesis with different reaction conditions

<table>
<thead>
<tr>
<th>$T_{\mu W}$ (°C)</th>
<th>EDS (Pb At%)</th>
<th>EDS (Se At%)</th>
<th>Average Diameter (nm)</th>
<th>Diameter Standard Deviation (nm)</th>
<th>Coefficient of Variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>159</td>
<td>47</td>
<td>53</td>
<td>11.2</td>
<td>1.7</td>
<td>15</td>
</tr>
<tr>
<td>142</td>
<td>46</td>
<td>54</td>
<td>12.5</td>
<td>2.0</td>
<td>16</td>
</tr>
<tr>
<td>124</td>
<td>44</td>
<td>56</td>
<td>13.9</td>
<td>2.1</td>
<td>15</td>
</tr>
<tr>
<td>159 without growth zone</td>
<td>93</td>
<td>7</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Figure 1: XRD patterns for material synthesized with a $T_{\mu W}$ of 159 °C with (upper) and without (lower) a growth temperature of 140 °C.
Figure 2: TEM images and particle size histograms for PbSe NPs synthesized with a $T_{pw}$ of 124, 142, and 159 °C and a growth temperature of 140 °C.
Figure 3: HR-TEM and FFT images for PbSe NPs synthesized with a $T_{\mu W}$ of 124, 142, and 159 °C and a growth temperature of 140 °C.
Figure 4: HR-TEM images showing the shape of PbSe NPs synthesized with a $T_{\text{w}}$ of 159 and 124 °C followed by a growth temperature of 140 °C.