

# One-pot Synthesis of Monodisperse PbSe Quantum Dots and Graphene Oxide Nanocomposites

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## ABSTRACT

A new, one-pot method to synthesize monodisperse PbSe quantum dots (QDs) and graphene oxide (GO) nanocomposites (GO-PbSeQDs) is reported here. PbCl<sub>2</sub> complexed with oleylamine was used as the Pb precursor. Se powder dissolved in 1-tetradecene (TDE) was used as the Se precursor (SeTDE). The Pb precursor, the Se precursor, and GO were mixed together and heated to elevated temperatures; monodisperse GO-PbSeQDs nanocomposites were obtained by controlling the heating rate for the nucleation and growth of the nanocomposites. GO-PbSeQDs nanocomposites with PbSe QDs of 6.4 nm and a size distribution of 7.3% and with PbSe QDs of 7.2 nm and a size distribution of 5.3% were synthesized.

The as-synthesized GO-PbSeQDs nanocomposites were characterized by transmission electron microscopy, high resolution transmission electron microscopy, selected area X-ray diffraction, and energy-dispersive X-ray spectroscopy.

**Keywords:** PbSe semiconductor quantum dots, PbCl<sub>2</sub>, one-pot monodisperse colloidal synthesis, oleylamine, graphene oxide, 1-tetradecene, nanocomposites

## 1 INTRODUCTION

The semiconductor PbSe QDs and GO nanocomposites are 2D (dimension) confined nanomaterials, which incorporate 0D QDs into a 2D graphene oxide sheets. These kinds of nanocomposites are hot-spots for material scientists [1], [2], [3]. They are energy-efficient materials that may have potential for fabricating solar cells.

However, the methods to produce the nanocomposites lag behind their applications. A typical example to synthesize the QD and GO nanocomposites involves two steps: to obtain the individual components QD and GO first, and then combine them together [4], [5]. QD synthesis is a complicated process. Two synthetic methods are widely used for the colloidal synthesis of QD: hot-injection (two-steps) and non-injection (one-step) approaches [6], [7]. Hot-injection method was first reported by Bawendi's group [8] in 1993 for the synthesis of monodisperse cadmium chalcogenide QDs. The non-injection method was revealed by Cao's group [9], [10] in 2005 for the synthesis of CdSe and CdTe QDs. Although most of the QDs are synthesized using the hot-injection

method [11], the non-injection method is preferred for the synthesis of QD and GO nanocomposites because of its simplicity. It is also convenient, and efficient for large scale monodisperse QD synthesis or industrial tailored QD synthesis due to the less experimental requirements. Therefore, more reports of this method have been published within the last several years [12], [13]. However, the current non-injection method still requires high reaction temperature and long reaction time due to the fact that non-metal precursors used are solids and need to be dissolved at elevated temperature to achieve the burst nucleation for nanocrystal formation.

We have discovered a new Se precursor solution—SeTDE to solve the non-metal precursor problem. We also developed a non-injection method to synthesize Se-containing QDs with the SeTDE precursor [14]. Among them, the successful synthesis of monodisperse PbSe QDs made it possible to develop a new, one-pot method to obtain PbSe QDs and GO nanocomposites.

In this paper, we report a new, one-pot, single step synthesis of GO-PbSeQDs nanocomposites using SeTDE as Se precursor. The paper also reveals the following discoveries: (1) A new, selenide-containing Se stock solution—SeTDE, Se powders dissolved in TDE at elevated temperatures, as Se precursor. (2) Design and develop a PbCl<sub>2</sub> model system to demonstrate size controlled monodisperse GO-PbSeQDs nanocomposites can be obtained in a dramatically reduced reaction time by our one-pot synthetic method. To the best of our knowledge, there are no reports of these kinds of synthesis until now. The reaction scheme of the synthetic method was shown in Figure 1.

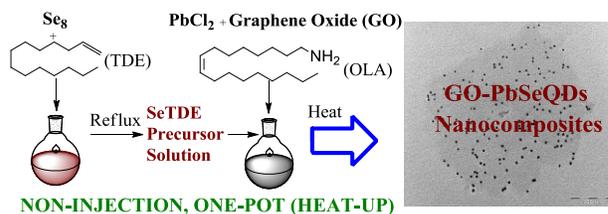


Figure 1. GO-PbSeQDs Nanocomposite Synthesis

The synthetic 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. This synthetic method can also be extended to

obtain reduced GO (RGO) and QDs nanocomposites (RGO-QDs).

## 2 EXPERIMENTAL SECTION

### 2.1 Chemicals

PbCl<sub>2</sub> (99-100%) was from J.T. Baker Chemical Company. Graphene oxide was from SinoCarbon (>95%). Methanol (absolute reagent, 99.8%, A.C.S.) was purchased from Spectrum Chemical. Tetrachloroethylene (TCE, 99%, extra pure), selenium (Se, 99.5%, powder, 200 mesh), oleylamine (OLA, 80-90%), 1-tetradecene (TDE, 94%), acetone (99.5+%), and n-hexane (99+%) were purchased from ACROS Organic. All chemicals were used as received without further purification.

### 2.2 SeTDE Precursor Preparation

0.6 M SeTDE precursor stock solution was prepared by dissolving 0.917 g (11.61 mmol) of Se powder in 15.000 g TDE and heated with vigorous stirring at 260-270°C for 2-3 hr. Then it was cooled to room temperature for storage.

### 2.3 Non-injection Synthesis of PbSe QDs

In a typical temperature-based controlled non-injection synthesis of the 5.5 nm PbSe QDs sample QD-1, 0.094 g (0.34 mmol) PbCl<sub>2</sub>, 3.39 g (10.14 mmol, 4.19 mL) OLA, and 1.1 mL 0.6 M SeTDE solution were introduced into a three-neck round-bottom flask at room temperature. The mixture was magnetically stirred and heated to 30°C under vacuum for 15 min. Then, the vacuum was removed and the temperature of the mixture was further raised to 160°C with a heating rate at about 20.1°C/min. The temperature of the mixture was maintained at that level for 5 min. Then, the crude solution was cooled immediately in a water bath. The crude was centrifuged and washed with methanol. Next, 5 mL of TCE or n-hexane was added into the crude to extract the PbSe QDs. After centrifuging, the as-synthesized PbSe QDs were stored in TCE.

The temperature-based controlled non-injection synthesis was used to obtain various sizes of PbSe QDs by running various batches of the synthesis under the same conditions: the same amounts of chemical reagents were used, Pb to OLA feed mole ratio of 1:30, Pb to Se feed mole ratio of 1:2, the growth time of 5 min., but at a variety of reaction temperatures. The synthetic conditions and results are listed in Table 1.

### 2.4 Non-injection Synthesis of GO and PbSe QDs Nanocomposites

In a typical synthesis of the 6.4 nm GO-PbSeQD nanocomposites sample GO-QD-1, 0.094 g (0.34 mmol) PbCl<sub>2</sub>, 3.39 g (10.14 mmol, 4.19 mL) OLA, 1.1 mL 0.6 M SeTDE solution, and 25 mg GO were introduced into a

three-neck round-bottom flask at room temperature. The mixture was magnetically stirred and heated to 30°C under vacuum for 30 min. Then, the vacuum was removed and the temperature of the mixture was further raised to 160°C with a heating rate at about 20.1°C/min. The temperature of the mixture was maintained at that level for 5 min. Then, the crude solution was cooled immediately in a water bath. The crude was centrifuged and washed with acetone. Next, 5 mL of TCE was added into the crude to extract the nanocomposites. After centrifuging, the as-synthesized GO-PbSeQD nanocomposites were stored in TCE.

The temperature-based controlled non-injection synthesis was used to obtain various sizes of GO-PbSeQDs by running various batches of the synthesis under the same conditions, but at a variety of reaction temperatures. The synthetic conditions and results are listed in Table 1.

All other conditions for the synthesis of PbSe QDs and GO-PbSeQDs nanocomposites were same. Except that there was no GO added in the non-injection synthesis of PbSe QDs.

Sample #	QD-1	QD-2	GO-QD-1	GO-QD-2
<b>Pb to Se Feed Ratio</b>	1:2	1:2	1:2	1:2
<b>Pb to OLA Mole Ratio</b>	1:30	1:30	1:30	1:30
<b>GO (mg)</b>	-	-	25	25
<b>Heating Rate (°C/min.)</b>	20.1	20.1	20.1	20.1
<b>Growth Temp (°C)</b>	<b>160</b>	<b>180</b>	<b>160</b>	<b>180</b>
<b>TEM Size (nm)</b>	<b>5.5</b>	<b>8.4</b>	<b>6.4</b>	<b>7.2</b>
<b>σ</b>	5.6%	5%	7.3%	5.3%

**Table 1.** Reaction Conditions and Results

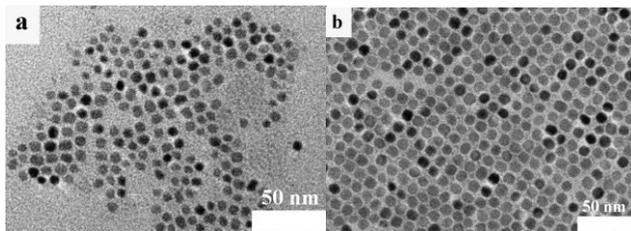
### 2.5 Sample Characterization

Transmission electron microscope (TEM), high resolution transmission electron microscope (HRTEM), selected area x-ray diffraction (SAED), and energy-dispersive x-ray spectroscopy (EDS) were used to characterize the size, shape, crystal structure, and composition of PbSe QDs and GO-PbSeQD nanocomposites. TEM images of PbSe QDs and GO-PbSeQD were taken by a Zeiss EM 920 instrument operated at 80 kV. High resolution TEM images of PbSe QDs were taken using a JEOL, JEM-2100F instrument operated at 200 kV. The TEM samples were prepared by

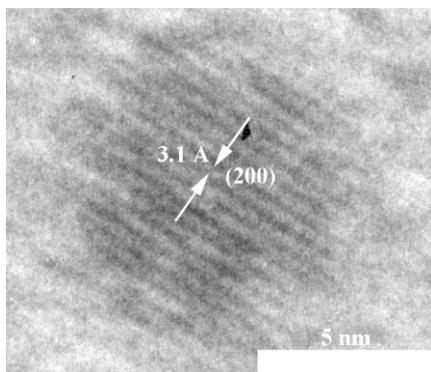
drop casting one drop of a dilute solution of PbSe QDs or GO-PbSeQD in TCE or n-hexane on a 300 mesh carbon-coated, copper grid from Electron Microscope Sciences. The grid was dried by evaporating the solvent in air. The sizes and size distributions (relative standard deviation) of the PbSe QDs or GO-PbSeQD were measured from TEM images using iTEM 5.1 of Olympus Soft Imaging Solutions GmbH. A minimum of 120 particles were counted on each image to obtain the average diameter of the nanoparticles. SAED patterns were obtained using JEM-2100F. The EDS spectra were recorded using EDS attached to JEM-2100F.

### 3 RESULTS AND DISCUSSIONS

TEM images of the non-injection controlled synthesis of PbSe QDs were shown in Figure 2. QD-1 has a size of 5.5 nm with size distribution  $\sigma = 5.6\%$ . QD-2 has a size of 8.4 nm with size distribution  $\sigma = 5.0\%$ . The results are in accordance of the synthetic condition: the higher the growth temperature, the larger the size.



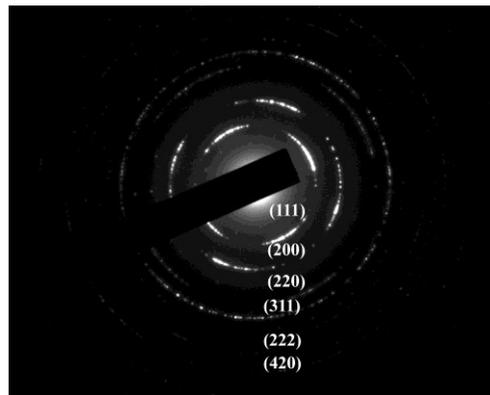
**Figure 2.** TEM images of size and size distribution of PbSe QDs. (a) PbSe QD-1 of 5.5 nm with size distribution  $\sigma = 5.6\%$ . (b) PbSe QD-2 of 8.4 nm with size distribution  $\sigma = 5.0\%$ .



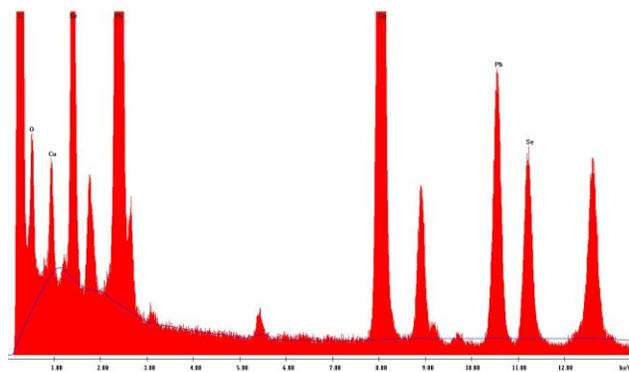
**Figure 3.** PbSe QD sample QD-1 HRTEM image.

Figure 3 lists sample QD-1's HRTEM image. The HRTEM measurement of the lattice fringe is 3.1 Å, which matches the standard card data [15] of 3.07 Å. Both HRTEM result and SAED diffraction pattern (Figure 4) confirm that the nanoparticles are single crystals. The EDS results (Figure 5) reveal that the PbSe QDs consist of Pb and Se elements. The TEM, HRTEM, SAED, and EDS

data prove that sample QD-1 of 5.5 nm with a size distribution of 5.6% are PbSe QDs.

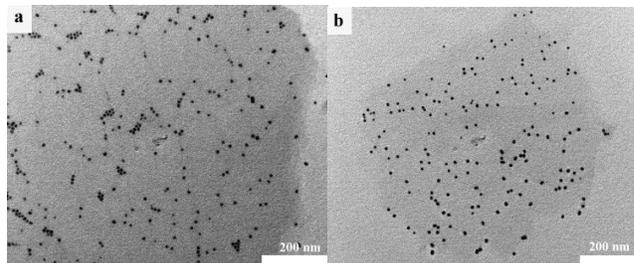


**Figure 4.** PbSe QD sample QD-1 SAED data.



**Figure 5.** PbSe QD sample QD-1 EDS result.

The TEM images of GO-PbSeQDs nanocomposites sample GO-QD-1 and GO-QD-2 were shown in Figure 6. Sample GO-QD-1 has PbSe QDs of 6.4 nm with size distribution  $\sigma = 7.3\%$  attached to the GO layer. Sample GO-QD-2 has PbSe QDs of 7.2 nm with size distribution  $\sigma = 5.3\%$  attached to the GO layer.



**Figure 6.** TEM images of size and size distribution of PbSe QDs of GO-PbSeQDs nanocomposites sample GO-QD-1 and GO-QD-2. (a) GO-QD-1 with PbSe of 6.4 nm with size distribution  $\sigma = 7.3\%$ . (b) GO-QD-2 of 7.2 nm with size distribution  $\sigma = 5.3\%$ .

Comparing the sizes of PbSe QDs synthesized with PbSe QDs attached to the GO-PbSeQDs nanocomposites under the same conditions, we found that the sizes of the PbSe QDs are almost the same within the experimental errors. PbSe QDs QD-1 has a size of 5.5 nm, while PbSe QDs in GO-QD-1 has a size of 6.4 nm. PbSe QDs QD-2 has a size of 8.4 nm, while PbSe QDs in GO-QD-2 has a size of 7.2 nm. The experimental results indicate: (1) Different sizes of PbSe QDs attached to GO-PbSeQDs nanocomposites can be synthesized using the temperature-based non-injection method. (2) Other Se-containing binary QDs and GO nanocomposites can also be synthesized if these QDs can be obtained independently using the one-pot synthetic method. (3) GO may be used as a template for the synthesis of QD and GO nanocomposite materials because it has functional groups containing oxygen attached to the graphene.

#### 4 CONCLUSIONS

We have developed a new, simple non-injection, one-pot method to synthesize monodisperse GO-PbSeQDs nanocomposites. We selected SeTDE as Se precursor, PbCl<sub>2</sub> as Pb metal source, OLA as the only capping ligand, and GO as the complex materials. GO-PbSeQDs nanocomposites of PbSe QDs of 6.4 nm with a size distribution of 7.3% and PbSe QDs of 7.2 nm with a size distribution of 5.3% were synthesized simply by changing the growth temperature.

This non-injection synthetic method can be extended to obtain reduced GO (RGO) and QDs nanocomposites (RGO-QDs). It can also be used to synthesize nanocomposites of GO and other Se-containing QDs. The large two-dimension flexible layer of GO provides easy control of the distribution of QDs on the GO sheet. The new nanocomposite materials may have great potential for fabricating optoelectronic devices.

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#### REFERENCES

- [1] X. Huang, Z. Yin, S. Wu, X. Qi, Q. He, Q. Zhang, Q. Yan, F. Boey, and H. Zhang, *Small* **2011**, *7*, 1876.
- [2] S. Stankovich, D. A. Dikin, G.H.B. Dommett, K. M. Kohlhaas, E. J. Zimney, E.A. Stach, R. D. Piner, S. T. Nguyen, and R. S. Ruoff, *Nature* **2006**, *442*, 282.
- [3] O. V. Prezhdo, P. V. Kamat, G. C. Schatz, *The Journal of Physical Chemistry C* **2011**, *115*, 3195.
- [4] R. Narayanan, M. Deepa, and A. K. Srivastava, *Phys. Chem. Chem. Phys.* **2012**, *14*, 767–778.
- [5] H. Hu, W. Chen, T. Hung, W. Chen, and Y. Chen *Adv. Mater.* **2012**, *24*, 1748–1754.
- [6] S. G. Kwon and T. Hyeon *Small* **2011**, *7*, 2685.
- [7] C. de Mello Donegá, P. Liljeroth, and D. Vanmaekelbergh *Small* **2005**, *1*, 1152.
- [8] C. B. Murray, D. J. Norris, and M. G. Bawendi *J. Am. Chem. Soc.* **1993**, *115*, 8706.
- [9] Y. A. Yang, H. Wu, K. R. Williams, and Y. C. Cao, *Angewandte Chemie International Edition* **2005**, *44*, 6712.
- [10] Y. C. Cao, and J. Wang *J. Am. Chem. Soc.* **2004**, *126*, 14336.
- [11] Y. Pan and J. R. Lombardi In Nanotech 2011-- NanoTech Conference & Expo 2011; NSTI: Boston, USA, **2011**; Vol. 1, p 303.
- [12] N. Li, X. Zhang, S. Chen, X. Hou, Y. Liu, and X. Zhai *Materials Science and Engineering: B* **2011**, *176*, 688.
- [13] Z. Li, Y. Ji, R. Xie, S. Y. Grisham, and X. Peng *J. Am. Chem. Soc.* **2011**, *133*, 17248.
- [14] Y. Pan (2012) Synthesis, Characterization, Raman, and Surface Enhanced Raman Studies of Semiconductor quantum dots. (Doctoral Dissertation). Retrieved from ProQuest/UMI.
- [15] ICDD PDF Card 01-071-4753.