

Investigation on the large-scale synthesis of PbSe nanocrystals

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Abstract

Large-scale synthesis of high quality PbSe nanocrystals was conducted with the one-pot method. By this “greener” synthesis route, the use of traditional dangerous pyrophoric trioctylphosphine (TOP) and tributylphosphine (TBP) reagents was avoided. The crystal size and shape were controlled by the reaction time, reaction temperature, and the use of different combinations of surfactants. X-ray diffraction (XRD) and transition electron microscopy (TEM) were used to characterize as-synthesized nanocrystals and demonstrated the rock salt cubic structures and narrow size distributions. More than 3 g of high quality PbSe nanocrystals were synthesized in one reaction by this large-scale one-pot method. The uniform size of as-synthesized nanocrystals promoted the self-assembly of PbSe nanocrystals into large-area ordered superstructures.

Introduction

Since the introduction of size quantization effect by Brus in 1980s [1], semiconductor nanocrystals (NCs) attracted much attention from the researchers. Among various semiconductor nanocrystals, the small band gap and the large Bohr radius of the Pb-chalcogenides [2] make them interesting for fundamental researches and potential applications in many fields such as solar cells [3], thermoelectric devices [4], telecommunication [5], and field effect transistors [6]. Integrating Pb-chalcogenide nanocrystals in these devices requires the precise control of their properties by manipulating size and morphology of the nanocrystals.

The liquid-phase synthesis of PbSe colloidal nanocrystals was first reported by Murray et al. in 2001[7]. In the past several years, the synthesis of PbSe nanocrystals usually requires the use of toxic, dangerous, and expensive trioctylphosphine (TOP) and tributylphosphine (TBP) reagents. Moreover, most of the methods rely on a rapid precursor injection and this means only small quantities of nanocrystals could be synthesized in one reaction.

Herein we report the large-scale controlled synthesis of 3 g of high quality PbSe nanocrystals by the thermolysis of metal-acetylacetonates complexes with non-injection one-pot method. Se precursors were prepared by the protocols we had established before; the use of any pyrophoric reagents such as TBP and TOP was avoided [8-11]. Paraffin oil was chosen as the noncoordinating reaction solvent because the high boiling point and low cost. Because of the high chemical stability of paraffin oil and the avoidance of TOP/TBP, our new synthesis routes do not require the use of a glovebox. The size and shape were controlled by the reaction time, reaction temperature, and the combination of different surfactants. As-synthesized PbSe nanocrystals self-assembled into large-area ordered superstructures because of their monodispersities. The mechanism of this large-scale synthesis of PbSe nanocrystals was discussed in detail.

Experimental Section

Chemicals. Selenium (Se, 99.99%, powder), decanoic acid (DA, 99%), and oleylamine (OAM, 70%) were purchased from Aldrich. 2, 4-pentanedione (98%), triethylamine (99%), hexanes (analytical grade), methanol (analytical grade), acetone (analytical grade), ethanol (analytical grade), lead

chlorides (PbCl_2 , analytical grade), and paraffin oil (analytical grade) were obtained from Beijing Chemical Reagent Ltd., China. All reagents were used as received without further experimental purification.

Synthesis of Lead Acetylacetonates [$\text{Pb}(\text{acac})_2$] and Se precursor. 20 mmol PbCl_2 was dissolved in 10 mL of deionized water. Under magnetic stirring, 2, 4-pentanedione (5 mL, 50 mmol) was added into above solution and kept stirring for 15 minutes. $\text{Pb}(\text{acac})_2$ was precipitated after appropriate amount of triethylamine was added in the solution. Then, $\text{Pb}(\text{acac})_2$ precipitate was washed for several times by ethanol and water and finally was dried in vacuum at 50 °C for further use. Se powder (0.1578 g, 2 mmol) and 20 mL of ODE were mixed in a 50 mL three-neck flask, and then the mixture was heated to 220 °C and maintained for 180 min under nitrogen flow. During this time, the color of the mixture changed from transparent to orange, red, and finally turned into yellow.

Synthesis of PbSe Nanocrystals. In a typical synthesis of spherical PbSe nanocrystals, 0.2 mmol $\text{Pb}(\text{acac})_2$, 0.8 mmol DA, 0.2 mmol OAM, 2 mL Se precursor solution, and 5 mL of paraffin oil were added into a three-neck flask at room temperature, and the resultant reaction mixture was heated to 120 °C under nitrogen flow. The solution color gradually changed from yellow to deep-brown and finally to dark. Different sized PbSe nanocrystals were prepared at different reaction time. The solution was then cooled down to room temperature and excess ethanol was added in to yield a dark precipitate, which was then separated by centrifuging. The synthesis of cube-shaped PbSe nanocrystals is similar to the synthesis of sphere-shaped PbSe nanocrystals except that 0.2 mmol OAM was replaced by 2.4 mmol OAM and the reaction temperature was elevated to 180 °C.

Large-scale Synthesis of PbSe Nanocrystals. The large-scale synthesis of PbSe nanocrystals was carried out in a 1000 mL three-neck flask. In a typical large-scale synthesis of PbSe nanocrystals, 20 mmol $\text{Pb}(\text{acac})_2$, 80 mmol DA, 20 mmol OAM, 200 mL Se precursor solution, and 200 mL of paraffin oil were added into a three-neck flask at room temperature, and the resultant reaction mixture was degassed and then heated to 150 °C or 200 °C for the synthesis of sphere- or cube- shaped PbSe nanocrystals under nitrogen flow. After the synthesis, the reaction solution was cooled down to room temperature and acetone was added to precipitate as-synthesized PbSe nanocrystals.

Characterization. X-ray diffraction (XRD) studies of nanocrystals were carried out with a Philips X' Pert Pro X-ray diffractometer using Cu $K\alpha$ radiation (wavelength = 0.154 nm). The specimens were prepared as follows: about 20 mg of the purified nanocrystals were dissolved in 0.5 mL toluene and then dropped on a low-scattering quartz sample-holder, then it was dried in air and kept overnight in a vacuum dessicator. Transmission electron microscopy (TEM) studies were performed using a JEOL-100 CX II microscope operating at 100 kV and JEOL JEM-2010 electron microscope operating at 200 kV.

Results and Discussion

Shown in Figure 1 are the TEM images of as-synthesized sphere- and cube-shaped PbSe nanocrystals. Different shaped nanocrystals were obtained by changing the reaction temperatures and the molar ratios between DA and OAM. When the molar ratio of DA/OAM was 4:1 and the reaction temperature was set of 120 °C, spherical PbSe nanocrystals were prepared as shown in Fig. 1A. When the reaction temperature was elevated to 180 °C and the molar ratio of DA/OAM was changed to 1:3,

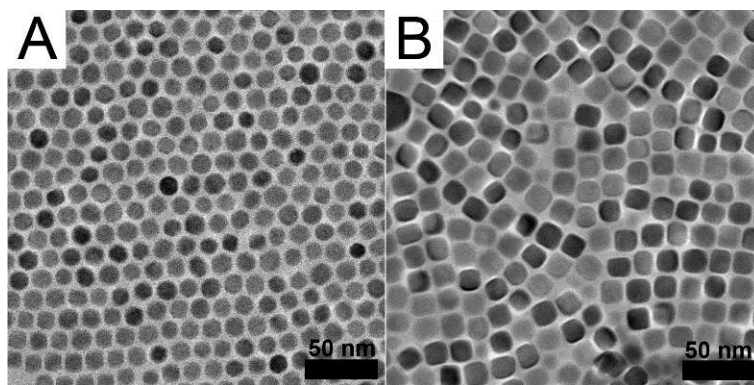


Figure 1. TEM images of as-synthesized sphere (A) and cube (B) shaped PbSe nanocrystals.

cube-shaped PbSe nanocrystals were obtained as shown in Fig. 1B. As-synthesized sphere- and cube-shaped PbSe nanocrystals had narrow size distributions, in fact, the nanocrystals self-assembled into ordered structures because of their monodispersity.

The phase identification of as-synthesized PbSe nanocrystals was performed using XRD and selected-area electron diffraction (SAED) measurements (Fig. 2). For both the sphere- and cube-shaped PbSe nanocrystals, the XRD patterns are almost the same and the diffraction peaks are well corresponded to the reflections of rock salt cubic structured PbSe (JCPDS, 78-1903). The peak broadening of the XRD patterns of both specimens was due to the finite particle size. And the peaks of cubic PbSe nanocrystals are a little narrower because of their larger size. The SAED patterns of sphere- and cube-shaped PbSe nanocrystals were totally the same, and the SAED pattern is shown in Fig. 2B, which can be indexed to a single rock salt phase.

Fig. 3 shows the HRTEM images of spherical and cubic PbSe nanocrystals. Both the PbSe nanocrystals in HRTEM images have well-resolved lattice fringes, which imply good crystallinities. The most obvious lattice fringes observed from the nanocrystals in Fig. 3A, 3B were measured with the same d-spacing of 3.06 Å, which is in accordance with the (200) planes of the rock salt cubic structured PbSe.

Considering the surface ligands molar ratio dependence of nanocrystal shapes, we attribute the shape control of PbSe nanocrystals to the increasing and/or decreasing of the growth rate in different directions because the rock salt structured PbSe possesses different surface energies in different facets [12].

Because of the narrow size distributions of as-synthesized PbSe nanocrystals, they self-assembled into large-area ordered superlattices as shown in Fig. 4. We examined the self-assembly process and found that OAM molecules played an important role to promote the self-assembly behavior of as-synthesized NCs [13]. With the evaporation of solvent, the unafaced sphere-shaped PbSe nanocrystals self-assembled into superlattices with compact hexagonal packing because this structure could most reduce the total surface energy (Fig. 4A). The van der Waals interactions between the surfactants of NCs determined this assembly process. For the cube-shaped PbSe nanocrystals, the (100) planes approached to each other and simple square assemblies were formed (Fig. 4B).

The most important success in these series of experiments was the large-scale synthesis of PbSe nanocrystals with more than 3g by one reaction. We attributed this large-scale synthesis to the introduction of Pb(acac)₂ as the precursor and the one-pot method. Pb(acac)₂ was chosen as the cationic precursor because metal acetylacetonates are very suitable to synthesize nanocrystals by the one-pot method. Metal acetylacetonates will fast decomposed in a very short time if the certain temperatures are reached [14]. This fast decomposition is propitious to the “burst nucleation” mechanism proposed by LaMer [15] and favors the synthesis of uniform NCs. So the particle size and

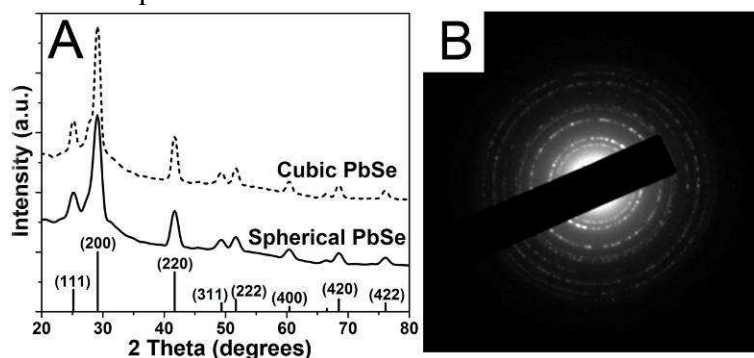


Figure 2. XRD patterns and SAED pattern of sphere and cube shaped PbSe nanocrystals. The diffraction lines of rock-salt structured PbSe are indicated.

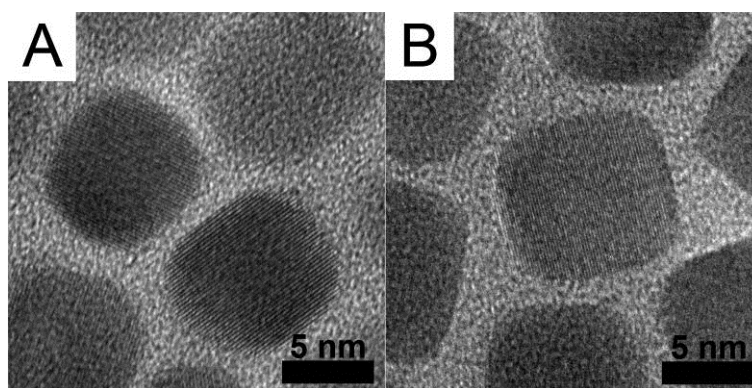


Figure 3. HRTEM images of sphere- (A) and cube- (B) shaped PbSe nanocrystals.

shape are still uniform even the synthesis was largely scaled up. Paraffin oil was chosen as the noncoordinating reaction solvent because the high boiling point and low cost. And selenium powder was directly dissolved in ODE at elevated temperature as the Se precursor so the use of traditional pyrophoric TBP/TOP was avoided. Because of the high chemical stability of paraffin oil and the avoidance of TBP/TOP, this new synthesis route does not require the use of a glovebox. By the use of Se-ODE precursor, paraffin oil, and the large-scale synthesis, the total cost could be saved as much as 60% compared with traditional TOP/TBP based methods.

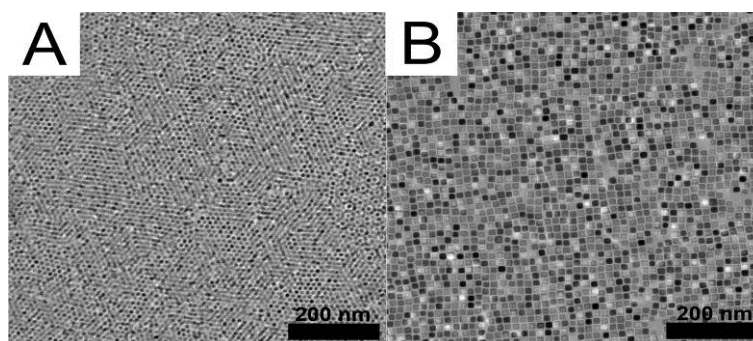


Figure 4. Large-area assemblies of spherical (A) and cubic (B) PbSe nanocrystals.

Conclusions

In summary, large-scale synthesis of more than 3 g of high quality PbSe nanocrystals was successfully conducted by a low-cost, green, environmentally friendlier one-pot synthesis route. Paraffin oil was chosen as the noncoordinating reaction solvent because the high boiling point and low cost. Selenium powder was directly dissolved in ODE at elevated temperature as the Se precursor and the use of traditional pyrophoric TBP/TOP was avoided. The total cost could be saved as much as 60% compared with traditional TBP/TOP based synthesis routes. The crystal shape was controlled by the use of different combinations of surface ligands. As-synthesized PbSe nanocrystals self-assembled into ordered superstructures because of their monodispersities with the assistance of surface ligands.

Acknowledgements

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References

- [1] L.E. Brus: *Journal of Chemical Physics*, Vol. 80 (1984), p. 7
- [2] F.W. Wise: *Accounts Chem Res* Vol. 33 (2000), p. 773
- [3] R.J. Ellingson, M.C. Beard, J.C. Johnson, P. Yu, O.I. Micic, A.J. Nozik, A. Shabaev and A.L. Efros: *Nano Letters* Vol. 5 (2005), p. 865
- [4] M. Fardy, A.I. Hochbaum, J. Goldberger, M.M. Zhang and P. Yang: *Adv. Mater* Vol. 19 (2007), p. 3047
- [5] M. Harrison, S. Kershaw, M. Burt, A. Rogach, A. Kornowski, A. Eychmuller and H. Weller: *Pure Appl Chem* Vol. 72 (2000), p. 295
- [6] D.V. Talapin and C.B. Murray: *Science* Vol. 310 (2005), p. 86
- [7] C. Murray, S. Sun, W. Gaschler, H. Doyle, T. Betley and C. Kagan: *Ibm J Res Dev* Vol. 45 (2001), p. 47
- [8] H. Shen, H. Wang, Z. Tang, J.Z. Niu, S. Lou, Z. Du and L.S. Li: *Crystengcomm* Vol. 11 (2009), p. 1733
- [9] J.Z. Niu, H. Shen, H. Wang, W. Xu, S. Lou, Z. Du and L.S. Li: *New J. Chem.* Vol. 33 (2009), p. 2114
- [10] H. Shen, H. Wang, X. Li, J.Z. Niu, X. Chen and L.S. Li: *Dalton Trans.* (2009), p. 10534
- [11] J.Z. Niu, H. Shen, C. Zhou, W. Xu, X. Li, H. Wang, S. Lou, Z. Du and L.S. Li: *Dalton Trans.* Vol. 39 (2010), p. 3308
- [12] T. Mokari, M. Zhang and P. Yang: *Journal of the American Chemical Society* Vol. 129 (2007), p. 9864
- [13] H. Shen, H. Wang, H. Yuan, L. Ma and L.S. Li: *Crystengcomm* (2011).
- [14] X. Li, J.Z. Niu, H. Shen, W. Xu, H. Wang, L.S. Li: *Crystengcomm* Vol. 12 (2010), p. 4410
- [15] V.K. LaMer and R.H. Dinegar: *Journal of the American Chemical Society* Vol. 72 (1950), p. 4847