The Synthesis of a High Yield PbSe Quantum Dots by Hot Solution Method

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Colloidal solutions of crystalline PbSe nanoparticles have been synthesized by hot solution chemical process using PbO in oleic acid and tributylphosphine (TBP) bonded selenium. The use of TBP as a capping agent along with oleic acid gives a very good yield (around 10% at 180 ºC) with an average diameter of particle of about < 6.6 nm. The effects of temperature on size and production yield of PbSe quantum dots are studied. X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) and UV/VIS/NIR absorption spectroscopy were used to characterize the samples.

Key Words : PbSe, Quantum dots, Hot solution method

Introduction

Colloidal semiconductor metal chalcogenide quantum dots have attracted much attention on account of their quantum confinement effects and size-dependent photo-emission characteristics. These semiconductor quantum dots are used in different technological areas including biological labeling[1] and diagnostics,[2] light emitting diodes,[3] electro-luminescent devices,[4] photovoltaic devices,[5-8] lasers[9,10] and single-electron transistors. Quantum dots of IV-VI materials, particularly PbSe, offer a unique possibility of strong quantum confinement compared to II-VI semiconductor particles due to their large Bohr radii. The electron, hole and exciton Bohr radii of PbSe are 18, 23 and 46 nm respectively.[11] The Bohr a radius of PbSe is about eight times larger than the CdSe nanocrystal therefore the absorptive and dispersive non-linearities are theoretically predicted to be 1000 times larger than CdSe. Thus PbSe is a potential material for applications in opto-electronics devices such as solar cells, photocatalytic coatings, electrochromic windows and super-capacitors.[12-15]

Colvin and co-workers[16] synthesized monodisperse PbSe nanocrystals with diameters ranging from 3 to 13 nm using PbO and trioctylphosphine selenide (TOPSe) in 1-octadecene in the presence of oleic acid. Gokarna *et al.*[17] have synthesized octahedral shaped nanocrystals from lead acetate in the presence of oleic acid and TOPSe in phenyl ether. Murray *et al.*[18] also synthesized PbSe nanocrytals from lead oleate and TOPSe. It is observed that the diameter of PbSe nanocrystals can be controlled in the range 3.5-15 nm by varying the reaction temperature between 90 ºC and 220 ºC.[18] The initial size distribution of 10% was further narrowed down to 5% by size-selective precipitation. Houtepen *et al.*[19] have noticed that lead oleate, free from acetate, is essential for the synthesis of spherical PbSe nanocrystals. When acetate ions exist in the reaction mixture, star-shaped PbSe nanocrystals are formed by an oriented-attachment mechanism.

One step synthesis of TOP capped PbSe pyramidal nanocrystals are reported by Khanna *et al.*[20] Sashchiuk *et al.*[21] have reported the synthesis of PbSe from tributyl-phosphine-selenium (TBPSe) and lead 2-ethyl-hexanoate with average size of 1.2 and 5.0 nm. We have earlier reported the influence of acetic acid and hexanoic acids on the size and morphology of PbSe nanocrystals.[22] However, a high yield synthesis of PbSe quantum dots at low temperature, especially extremely small size below 7 nm, is not available. As a part of our comprehensive studies on quantum dot sensitized solar cells, we report a facile synthesis of size tunable and high yield colloidal PbSe quantum dots using PbO in oleic acid and TBPSe.

Experimental Procedure

Materials. Lead oxide (Kojundo Chemical Japan, 99.999%), selenium powder (Aldrich, 99.999%), phenyl ether (Aldrich, 99%), oleic acid (OA, Aldrich, 90%), tributylphosphine (TBP, Aldrich, 97%) and anhydrous chloroform (Aldrich, 99+%) were used as received without further purification. Hexane (HPLC grade) and methanol (HPLC grade) were purchased from Burdick & Jackson and were further purified prior to use. All manipulations were carried out under the atmosphere of argon using standard Schlenk type apparatus.

Preparation. The colloidal PbSe semiconductor quantum dots (QDs) were prepared according to our reported work, with slight modification, using diphenyl ether medium in the absences of water and oxygen.[22] OA and TBP were used as capping ligands. In a typical synthesis, lead oleate precursor was prepared in situ by heating lead oxide (4 mmol) and OA (18 mmol) in 25 mL of phenyl ether under Ar gas at 150 ºC for 30 min. One molar TBPSe stock solution was prepared by stirring elemental selenium in TBP. 12 mL of 1 M TBPSe was mixed with lead oleate precursor solution at room temperature with Pb/Se molar ratio of 1:3. The resulting solution containing lead and selenium was injected into the

vigorously stirring preheated phenyl ether solution (58 mL) at 110-180 °C (nucleation temperature) and aged at 84-147 °C (growth temperature) for 2 min to get PbSe QDs. Four samples with an average particle diameter from 3.5 nm to 6.6 nm have been synthesized by varying the nucleation and growth temperatures under the same experimental conditions and precursor ratio. A short chain alcohol, such as methanol, was used to precipitate the QDs out of the reaction mixture which were subsequently washed with methanol and redispersed in hexane. To insure adequate removal of the reaction solvents, precipitation and redispersion was repeated.

Characterization. X-ray diffraction (XRD) patterns were recorded using x-ray diffractometer (Rigaku D/Max-2200V) employing Cu$K\alpha$ (1.5418 Å) radiation. Samples for XRD measurement are prepared by evaporating several drops of reaction mixture onto a sample holder plates. A Varian Cary 5000 UV/VIS/NIR spectrometer was used to monitor the reaction. The morphology of the PbSe QDs was analyzed by transmission electron spectroscopy (TEM, Tecnai GII, FEI) operating at 200 kV. The samples for TEM were prepared by depositing one drop of solution in hexane on a carbon coated copper grid (300-mesh). The particle yield of PbSe QDs dispersed in hexane was evaporated in oven and measured.

Results and Discussion

In the present modified method, TBP is used as co-capping agent instead of tri-n-octyl phosphine (TOP).[22] It is noticed that a high yield PbSe QDs can be prepared under optimized reaction conditions using this method. The production yield obtained in this method of preparation is about 4 times higher than those reported earlier.[22] Two sets of experiments were carried out: (i) varying growth temperature for a given nucleation temperature and (ii) repeating step (iii) with varying nucleation temperature.

Table 1 gives a comparison of yield of PbSe QDs obtained under different experimental conditions. It is observed that an increase in the nucleation temperature increases the particle yield. The highest yield of 9.5% is obtained at 180 °C (nucleation temperature) and 147 °C (growth temperature) which is about 5 times compared to the reaction carried out at 110 °C (nucleation temperature) and 84 °C (growth temperature). Similarly the yield of 9.5% using OA + TBP is about 5-6 times compared to our earlier result using OA + TOP with same nucleation temperature. The increased yield in OA + TBP system might be attributed by the faster rate of the forward reaction, when R = ^{t}Bu, of the following equilibrium due to a sterically less hindrance of TBP than TOP; $Pb(OA)_2 + R_3P = Se \rightarrow PbSe + R_3P = O + (OA)_2O$ [23] (Where R = ^{t}Bu or *n*-octyl).

Table 1. The yield of PbSe QDs obtained with different nucleation temperature, growth temperature and capping agent

Nucleation Temperature (°C)	Growth Temperature (°C)	Reaction Time (min)	Collected yield (%)	Co-capping Agent
180	130	2	1.4	OA+TOP[22)]
180	136	2	1.4	OA+TOP[22)]
110	84	2	2.0	OA+TBP
110	91	2	4.0	OA+TBP
150	113	2	4.2	OA+TBP
150	126	2	7.8	OA+TBP
180	136	2	5.0	OA+TBP
180	147	2	9.5	OA+TBP

Figure 1 shows the powder XRDs of PbSe QDs prepared under different conditions. The typical line broadening of peaks suggests the nano size nature of particles. The observed XRD peaks are exactly similar to those reported PbSe rock salt structure (JCPDF #00-006-0354). We could not measure the particle size using Schrrer's formula due to difficulty in obtaining the full width at half maximum (FWHM) of (200) peak. The NIR absorption spectra of PbSe QDs are shown in Figure 2. It is observed that the λ_{max} of

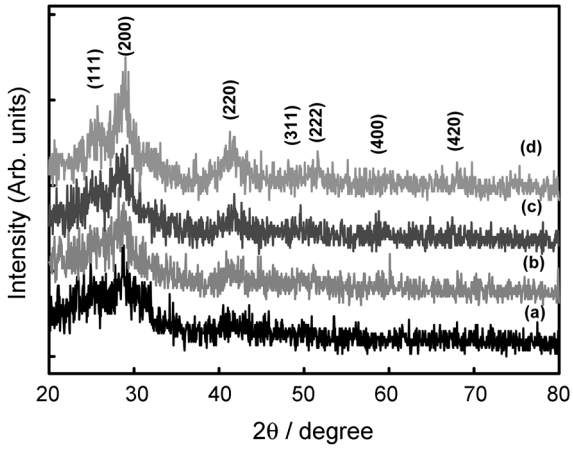

Figure 1. X-ray diffraction patterns of the PbSe QDs prepared with different nucleation and growing temperature [Nucleation temperature - Growing temperature - Reaction time; (a) 110 °C - 84 °C - 2 min., (b) (a) 150 °C - 113 °C - 2 min., (c) 180 °C - 136 °C - 2 min. and (d) 180 °C - 147 °C - 2 min., respectively].

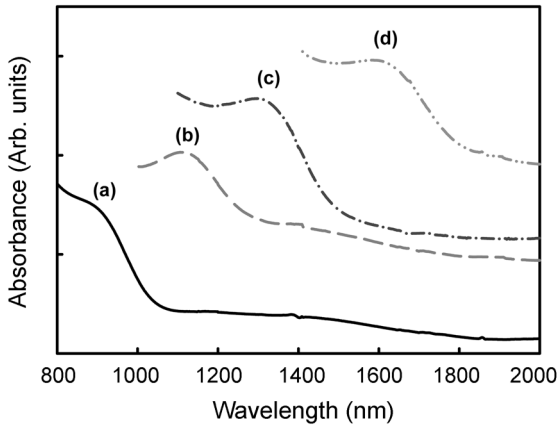

Figure 2. Near-infrared absorption spectra of PbSe QDs prepared with different nucleation and growing temperature. [Nucleation temperature - Growing temperature - Reaction time; (a) 110 °C - 84 °C - 2 min., (b) (a) 150 °C - 113 °C - 2 min., (c) 180 °C - 136 °C - 2 min. and (d) 180 °C - 147 °C - 2 min., respectively].

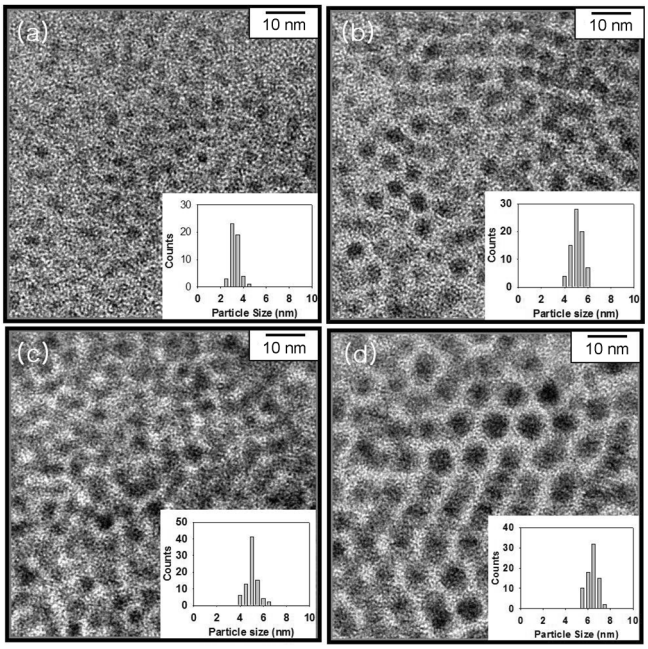

Figure 3. TEM micrographs of PbSe QDs prepared with different nucleation and growing temperature [Nucleation temperature - Growing temperature - Reaction time; (a) 110 ^{o}C - 84 ^{o}C - 2 min., (b) (a) 150 ^{o}C - 113 ^{o}C - 2 min., (c) 180 ^{o}C - 136 ^{o}C - 2 min. and (d) 180 ^{o}C - 147 ^{o}C - 2 min., respectively].

samples shifts to lower wavelength with decrease in the particle size in agreement with quantum confinement effect. These spectra are similar to those reported earlier.[22]

Figure 3 shows TEM micrographs of PbSe QDs synthesized with different nucleation and growth temperatures. It shows that the nanocrystals of PbSe develop as highly mono-dispersed QDs without the size selection. The dispersibility of the PbSe QDs increases with nucleation and growth temperature. The particle size from TEM micrographs were measured (± 10% uncertainty) by image analyzer. The histograms (inset in Fig. 3) of the PbSe QDs give average diameters of 3.51, 5.3, 5.31 and 6.61 nm with narrow size distributions. It is observed that as size increases the particles tend to arrange as ordered array as shown in Figure 3d.

Conclusion

Highly dispersed size-tunable PbSe QDs were synthesized using TBPSe as selenium source. A high production yield of 9.5%, about 5-6 times compared to the result using TOPSe, was achieved in this process. The good dispersibility and high yield of colloidal QDs are cost-effective for the industrial scale production of various optoelectronics materials like solar cells etc.

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