

Colloidal Synthesis of Octahedral Shaped PbSe Nanocrystals from Lead Oleate and Se : Temperature Effect

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Formation of octahedral shaped PbSe quantum dots at higher synthesis temperature is being reported in this paper. The synthesis includes the reaction between lead oleate and trioctylphosphine selenide under inert gas conditions to produce PbSe. TEM, SEM, XRD and EDS were used to characterize the samples. The SEM exhibited the formation of spherical shaped nanocrystals at temperature below 140 °C and octahedral shaped nanoparticles at higher temperatures. Moreover, the TEM also showed the well resolved (111) lattice fringes proving that the nanocrystals were crystalline in nature. Synthesis of highly pure PbSe nanocrystals was another interesting aspect of this research.

Key Words : Octahedral PbSe, Nanocrystals, Colloidal synthesis, Temperature effects, Lead oleate

Introduction

The past two decades have opened up new avenues in the field of optical and opto-electronic properties of semiconductor nanocrystals.¹⁻⁵ There has been a growing interest in the synthesis and characterization of colloidal semiconductor quantum dots (QDs) due to their wide applications in various fields such as sensors, light emitting diodes (LED), IR detectors, inorganic solar cells, tunnel diodes as well as photo-stable fluorescent tags in biological systems.⁶⁻¹¹ These nanocrystals will play a major role in future technologies such as nano-electronics, photonics, telecommunication and also in nano-biotechnology.

Recently, in the field of semiconductor nanomaterials, nanocrystals of lead chalcogenides such as PbS, PbSe and PbTe have gained a lot of importance as these exhibit extreme quantum confinement because the electron, hole and exciton, all have a large Bohr radii of the order of 23, 23 and 26 nm respectively.¹² These large radii bring about strong quantum confinement in PbSe QDs, which results in absorptive and dispersive nonlinearities which are 1000 times larger than those of CdSe nanocrystals of the same size.¹³ A bulk PbSe has a cubic (rock salt) crystal structure and a narrow direct band gap of 0.28 eV at the L point of Brillouin zone and nano crystals of PbSe exhibit the same cubic (rock salt) crystal structure.

The versatility of PbSe nanocrystals in opto-electronic devices in the IR spectral regime, in telecommunication applications and in thermoelectric devices is evident from the fact that PbSe QDs exhibit well defined band edge excitonic transitions in the range 0.5 eV-1.1 eV, sub-microsec. lifetime and increase in the Seebeck coefficient as compared to bulk PbSe.¹⁴ Despite, PbSe QDs exhibit strong

quantum confinement, synthesizing monodisperse dots with narrow size distribution and a well passivated surface is not an easy process. Although recently there have been a large number of reports on the synthesis of highly monodisperse PbSe QDs using various techniques,¹⁴⁻¹⁸ however, the effect of temperature on the shape of the nanocrystals has received much less attention, till date.

In this paper, we focus on the transformation in the morphology of the nanocrystals from spherical to octahedral shape by variation in the synthesis temperatures alone from 80 °C to 220 °C. There was no variation in the type of solvent used for bringing about this morphological change. The octahedral morphology is explained in terms of the rapid growth in the X-Ray peak intensity of the (111) plane which depends on the degree of adsorption of the stabilizing agents on the different crystallographic planes. The intensity ratio of the (111) plane to the (200) plane is seen to increase as the synthesis temperature increases. The main possible application of these kind of octahedral shaped quantum dots is for nanoantennas. Moreover, the synthesis of high purity PbSe quantum dots has been another highlighting factor of the present research. High purity QDs are necessary for device applications.

Experimental Section

Lead acetate (99.8%), selenium metal powder and anhydrous TOP were purchased from Aldrich Chemical Co. All experiments were carried out under an inert argon atmosphere using standard Schlenk type apparatus. PbSe nanocrystals were synthesized in the following manner, a stock solution of 1 M trioctylphosphine selenide (TOPSe) was prepared by completely dissolving selenium in TOP at

100-150 °C. Lead oleate was prepared by heating a mixture of 3 g lead acetate, 10 mL oleic acid and 50 mL phenyl ether at a temperature of 100-150 °C for 2-3 hours. It was cooled down to about 70 °C and 24 mL of TOPSe was injected into this flask. This formed the precursor solution, which was then rapidly injected into another flask containing 80 mL of vigorously stirred phenyl ether pre-heated to 80 °C. The reaction mixture was further stirred at the desired temperature for one hour. Different experiments were carried out by varying the temperature from 80-220 °C. The colloidal solution was then cooled to room temperature and stored in hexane. The residue after centrifugation was washed several times with methanol to remove impurities. The black powders were then vacuum dried. The NIR absorption spectra were measured on Bruker Vector/22 Near-IR spectrometer. X-ray diffraction (XRD) measurements were done on Rigaku D/MAX IIIB X-ray diffractometer at room temperature using $\text{CuK}\alpha$ with a wavelength of 1.542 Å. Transmission electron microscopic (TEM) experiments were carried out on Philips CM 20T/SREM electron microscope. Scanning electron microscopic (SEM) and energy dispersive X-ray spectroscopic (EDS) analyses were performed on Philips XL30S FEG microscope/EDAX Phoenix spectrometer.

Results and Discussion

The synthesis of nanocrystals of PbSe were carried out by direct reaction between TOPSe and lead oleate precursors in phenyl ether at a temperature varying between 80 °C to 220 °C. The overall growth time was maintained constant at 60 minutes. The use of tributylphosphine (TBP) and TOP has been documented in literature,^{14,15,19} with or without the presence of trioctylphosphine oxide (TOPO) for more effective capping thus avoiding agglomeration when re-dispersed in desired solvents. During the formation of the product in the present study, the lead ions from lead oleate directly react with Se^{2-} (from trioctylphosphine selenide) to form PbSe. The complete intake of selenium ions by lead ions is confirmed from EDS and XRD analysis.

Figure 1 represents the EDS result of PbSe quantum dots. The ratio of Pb : Se was estimated to be 1 : 0.75. EDS also

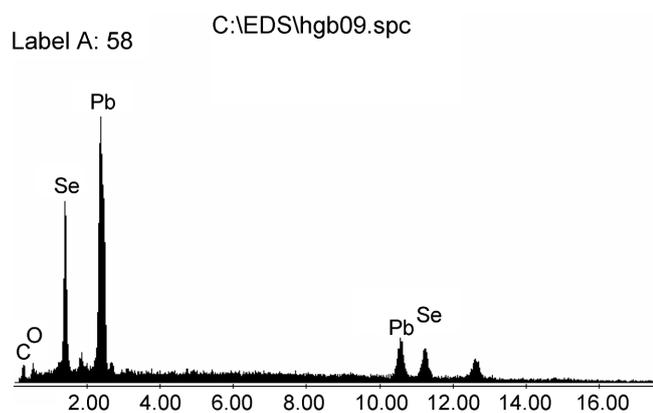


Figure 1. EDS spectra of PbSe Quantum dots synthesized at 150 °C.

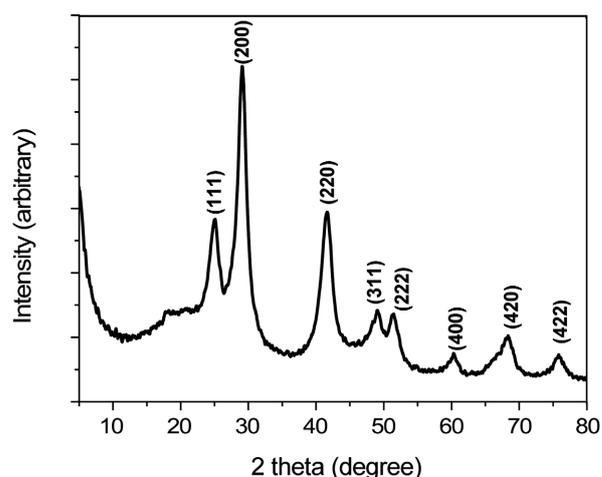


Figure 2. XRD pattern of PbSe quantum dots synthesized at 80 °C.

showed the presence of carbon (C) arising from TOP, thus confirming the presence of organics around the particles.

It was noticed that the previous preparations of PbSe quantum dots have highlighted the presence of impurities of the starting materials in their final product. In the present case, however emphasis was laid down to synthesize the nanocrystals without impurity. Thorough washing of the centrifuged product with methanol leads to highly pure and re-dispersible PbSe nanocrystals as is clearly evident from the XRD spectra in Figure 2 and Figure 3. Figure 2 represents the XRD spectra for PbSe QDs synthesized at 80 °C. The peaks at 2θ values of 22° and 32° are due to the impurities arising from lead oleate¹⁵ but in the present case these were not observed thus indicating that the product is free from unreacted lead oleate. Figure 3 represents the XRD pattern of the PbSe nanocrystals synthesized at different temperatures.

All peaks could be indexed as cubic phase PbSe having a lattice constant of bulk PbSe. The diffraction peaks at 2θ

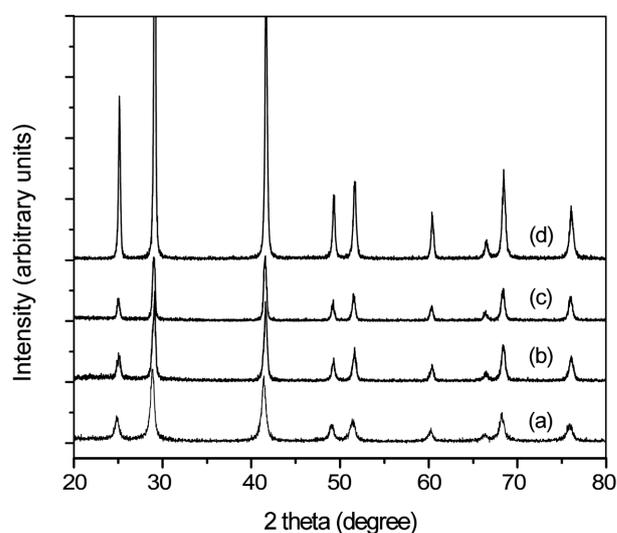


Figure 3. XRD of PbSe quantum dots synthesized at (a) 120 °C, (b) 150 °C, (c) 200 °C, and (d) 220 °C.

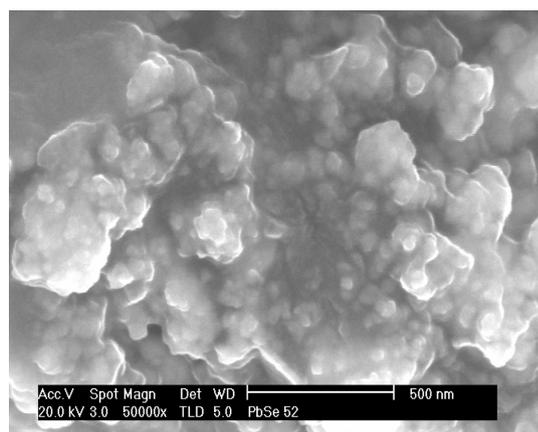


Figure 4. SEM image of PbSe quantum dots synthesized at 120 °C.

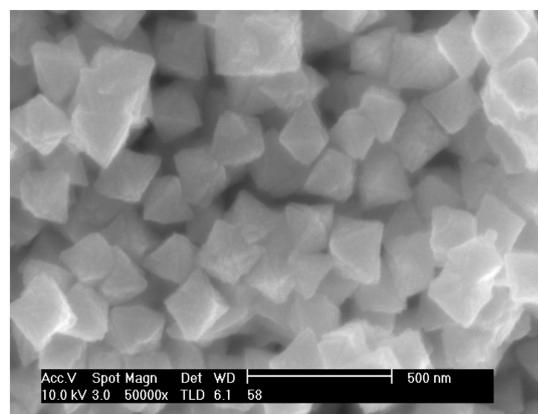


Figure 5. SEM image of PbSe quantum dots synthesized at 150 °C.

values of 24° , 29° and 42° correspond to (111), (200) and (220) planes of the PbSe structure. Moreover, in the case of the peaks at 2θ values of 24° , (111) plane and 29° (200) plane, the ratio of intensity of (111) to the (200) plane is seen to increase as the synthesis temperature increases. This proves that the (111) peak becomes more dominant with increasing temperature.

In order to correlate the effect of the growth kinetics of the (111) plane and the morphology of the nanocrystals, SEM studies were conducted. Figure 4, Figure 5 and Figure 6 represents the SEM micrographs of the nanocrystal synthesized at 120 °C, 150 °C and 200 °C temperatures respectively. Temperature, type of surfactants and the concentration of the surfactants as well as the chemical nature of the stabilizing agents can significantly affect the surface energy of the different crystallographic planes of quantum dots. At low synthesis temperature (temperature varying from 80 °C to about 120 °C) spherical nanocrystals are observed which later on evolve into octahedral shaped nanocrystals at higher temperatures. This change in morphology from the spherical shape to the octahedral shape can be correlated to various factors namely 1) surface energy of the particle, 2) surface energy of various planes of crystals and 3) the growth kinetics of crystal planes. The chemical bonding of the elements forming nanocrystal with capping agents or the

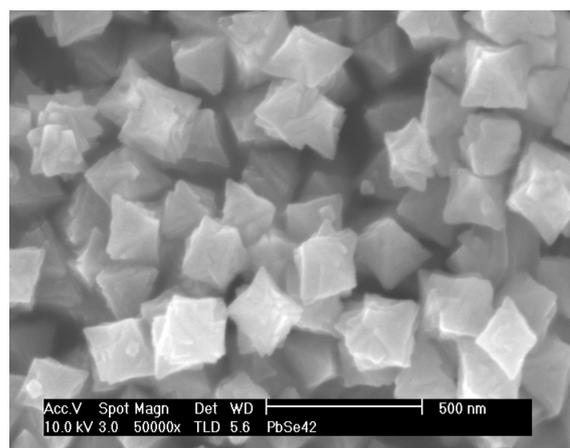


Figure 6. SEM image of PbSe quantum dots synthesized at 200 °C.

adsorption of the chemical species formed during processing are known to affect the kinetics of growth of crystal planes. In CdSe, TOPO interacts strongly with Cd and therefore planes involving Se are prone to higher reactions when compared to capped Cd containing planes.²⁰ The interaction of TOP with Pb and Se atoms is also likely to affect the growth of planes dominated by these atoms.

At low temperatures of PbSe formation, the particle size is small as revealed by SEM studies. The surface energy would be dominating the shape of the crystal and therefore the spherical crystallites are observed; in spite of clear evidence of presence of (111) plane. As the size of the crystallite increases, the surface energy decreases and other factors become more important in deciding the shape of the crystals. It is known that the {111} facets of cubic metals have lowest energy as compared to the other facets. PbSe structure is also made up of two interpenetrating elemental lattices. Therefore, it is not surprising to observe this plane at all temperatures of formation. The lowest energy plane growth is a consequence of thermodynamic origin. At still higher temperatures, however, the kinetics of the growth of various faces decide the shape of the crystallites. Every alternate plane will be made up of same atoms. Because of the chemical similarity of PbSe and CdSe, we propose that TOP would be strongly interacting with Pb. The alternating planes made up of Se atoms, on the other hand are not capped and therefore the growth of (220) and (200) planes is more. In fact, the planes with even number of (hkl) are dominating, supporting the proposed effect of preferential capping in PbSe. The formation of square pyramids of PbS confined by (220) and (400) planes has been reported²¹ as due to experimental constraints. PbSe is very similar to PbS structurally, physically and chemically. Therefore, formation of octahedral prisms confined by (220) and (200) planes is supported.

A rough estimate of the particle size was obtained by using the Debye Scherrer formula. With the increase in temperature, the particle size is seen to increase and the broad peaks at 80 °C become narrower as the temperature increases. The approximate particle sizes of the samples at

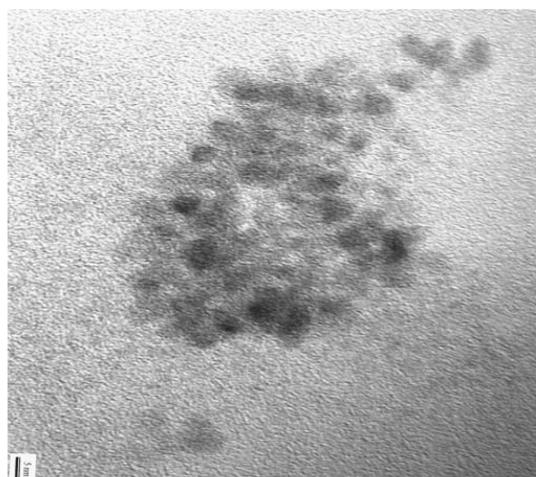


Figure 7. TEM image of PbSe quantum dots synthesized at 80 °C.

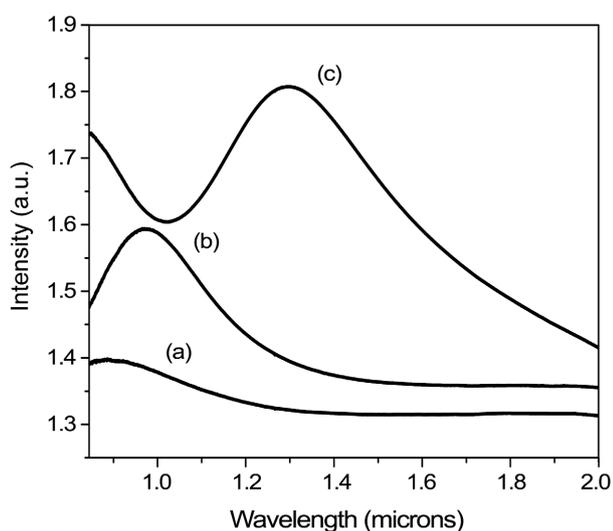


Figure 8. NIR spectra of PbSe nanocrystals synthesized at (a) 80 °C, (b) 150 °C, and (c) 220 °C.

80 °C, 120 °C, 150 °C, 200 °C and 220 °C are estimated to be 6, 14, 19, 20 and 32 nm, respectively.

The particle size for PbSe nanocrystals synthesized at 80 °C was also examined using TEM. A typical TEM image is shown in Figure 7. Some of the unagglomerated particles exhibit sizes *ca.* 5 nm. However, at some spots agglomeration is also observed. The TEM also shows well resolved (111) cubic lattice fringes. This implies that the nanocrystals are highly crystalline in nature.

The increase in the particle size with temperature was further confirmed by using room temperature NIR spectral analysis of PbSe synthesized at 80 °C, 150 °C and 220 °C, respectively, as shown in Figure 8. It is seen that increase in the synthesis temperature leads to a red shift in the peak wavelength, λ_{\max} . When the temperature is increased from 80 °C to 150 °C a shift of 0.1 μm is observed in λ_{\max} value but when the synthesis temperature is further increased to 220 °C, λ_{\max} shifts by about 0.4 μm . The band gap energy of the samples prepared at 80 °C, 150 °C and 220 °C are

estimated to be 1.39, 1.27 and 0.95 eV, respectively. These values are blue shifted as compared to the bandgap of bulk PbSe (0.28 eV), indicating the quantum confinement effect.

Conclusion

Highly pure PbSe nanocrystals were synthesized from lead oleate and Se(TOP). The main highlight of this study was the change in morphology from spherical to octahedral shaped nanocrystals with increase in synthesis temperature only. This change in the morphology was correlated to the growth kinetics. These kind of octahedral shaped quantum dots can have large scale applications in the fabrication of nanoantennas.

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