Journal of Nano Research
ISSN: 1661-9897, Vol. 34, pp 79-89
doi:10.4028/www.scientific.net/JNanoR.34.79

Submitted: 2015-04-07
Accepted: 2015-05-26
Online: 2015-07-15

Effects of reaction parameters on the growth and optical properties of PbSe nanocrystals

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Keywords PbSe, Nanocrystals (NCs), nucleation, non-coordinating, photoluminescence (PL)

Abstract
Colloidal syntheses of PbSe nanocrystals (NCs) have been widely investigated and the properties of nanocrystals have been shown to vary with reaction conditions, time, concentration and chemistry of reagents as well as the surfactants used. In this work the effects of reaction temperature, solvents, ligand purity, lead and selenium sources on the optical and structural properties of PbSe nanocrystals were investigated. PbSe NCs synthesized at 90 °C were observed to be spherical and had a narrower size distribution as compared to those synthesized at higher temperatures. 1-octadecene, trioctylphosphine and oleylamine were investigated as solvents for NC synthesis with the non-coordinating solvent octadecene showing the fastest growth rate with medium sized NCs. The coordinating solvents trioctylphosphine and oleylamine produced larger and smaller NCs respectively; this could be attributed to solvent interference during NC nucleation and growth phases. Oleate ligands were used during these syntheses and the ligand purity was not observed to have a significant effect on the NC optical and structural properties. The selenium precursor used affected the NC size and their optical properties while the lead source influenced both the NC shape and size. Lead acetate produced cubic NCs which were larger than the spherical NCs obtained when lead oxide was used.

1 Introduction

Colloidal NCs of group IV-VI compounds have received widespread attention due to their unique electronic structures and superior optical properties [1]. They provide size-tuneable interband absorption and luminescence emission at technologically important infrared wavelengths including the best spectral region for biological tissue imaging [2,3]. Specifically, lead salt NCs have provided the platform to allow for the investigation of strong quantum confinement regimes which were previously impossible using NCs of groups II-VI or III-V compounds [4,5,6]. The lead salt NCs have large exciton Bohr radii with small electron and hole masses which imply large confinement energies. In these NCs the electron and hole contribute equally to the exciton Bohr radii [2,4]. The semiconductor NCs which are synthesized using colloidal methods have been reported to possess unique properties dictated by reaction conditions, time, concentration and chemistry of reagents and surfactants [7]. These factors control the size and size distribution of NCs by either controlling their nucleation or growth. The parameters growth temperature, choice of capping agent and ligand ratios have been reported to majorly determine the size and shape of NCs while other factors such as type of noncoordinating solvent and monomer concentration are lesser factors in the NC size and shape evolution [8]. In this work the effects of reaction temperature, growth time and type of solvent on the optical properties of PbSe nanocrystals were investigated.

2 Experimental

2.1 Materials

Lead (II) oxide (PbO, 99.99%), Lead acetate trihydrate ($Pb(OAc)_2.3H_2O$), selenium powder (100 mesh, 99.99%), trioctylphosphine (TOP, 90%), tributylphosphine (TBP, 97%), oleic acid (OA, 90%), (OA, 99%), 1-octadecene (ODE, 90%), oleylamine, hexane and acetone were all purchased from Sigma Aldrich. The chemicals were used as received without further purification.

2.2 Synthesis of PbSe NCs

PbSe NCs were prepared according to a reported procedure with some modifications [9]. The reaction was carried out using standard air free procedures using a glove box and Schlenk line. Lead oleate was prepared by drying 223mg (1 mmol) of PbO or $Pb(OAc)_2 \cdot 3H_2O$ under vacuum at 130 °C for 15 min, followed by the addition of 20 mL of octadecene (ODE) and 0.6 mL (2 mmol) of oleic acid (OA). This mixture was heated under vacuum for 15 min at 130 °C to form Pb-$(oleate)_2$ and remove excess H_2O and acetic acid followed by bubbling argon gas through the solution for 1 hr. In a 2-neck flask, 158 mg (2 mmol) of elemental selenium was dissolved in 5 mL of TOP or TBP inside the glove box. The mixture was stirred at room temperature till all the selenium was dissolved. The reaction flask was brought to the injection temperature of 90 °C and TOPSe rapidly injected into the flask. The NCs were allowed to grow for a maximum of 30 min with samples being taken at various intervals for optical characterization. The reaction was repeated at different injection temperatures, solvents and oleic acid purity.

2.3 Characterization of NCs

Optical properties were determined using photoluminescence (PL) spectroscopy carried out on a Horiba Nanolog FL3-22-TRIAX. Samples for PL analyses were dispersed in hexane. The structural and morphological properties were determined using high-resolution transmission electron microscopy (HR-TEM). The HR-TEM characterization was carried out on a TECNAI F30ST TEM. Samples for TEM analysis were dispersed in hexane and dropped on carbon film-coated copper grids forming ultrathin layers.

3 Results and discussion

The formation of NCs in colloidal solutions occurs majorly in two distinct stages i.e. nucleation and growth stages. The two stages are extensively discussed by Murray *et al.* [7] and Viswanatha and Sarma [10]. Conclusively, the nucleation stage occurs when there is a sudden supersaturation of monomers in solution resulting in the formation of nuclei in a short period of time. This results in the lowering of monomer concentration in solution till they are insufficient to form new nuclei. The remaining monomers can only add to the existing pre-formed nuclei which occurs during the growth stage. With increased growth time, smaller NC clusters aggregate to form larger NCs. This occurs through Ostwald ripening where smaller particles dissolve in solution and the NCs material gets deposited on larger NCs [7]. Murray *et al.* [7] attribute Ostwald ripening to high surface energies on the smaller NCs, a process which is enhanced by high solution temperatures.

3.1 Temperature effects

The effect of temperature on the optical properties of PbSe NCs was investigated by carrying out similar reactions at different temperatures i.e. 90 °C, 120 °C and 150 °C. These reactions were carried out in 1-octadecene. At higher temperatures the growth of NCs occurred rapidly as shown by the red shift in emission maxima over time (Figure 1). Higher reaction temperatures have been reported to accelerate the chemical reaction producing a burst of nucleation [11]. With an increase in growth time at high reaction temperatures, Lu *et al*. observed that the formed nuclei agglomerate into octahedrons which with the addition of monomers grow into nanocubes [11]. Dai *et al.* [12] observed a similar growth trend at 140 °C while observing the shift in emission spectra. At higher reaction temperatures, ligands are likely to desorb from the surface of NCs allowing monomers to add to NC surface forming larger sized NCs [7]. With decrease in temperature, a narrowing of

emission spectra was observed corresponding to a narrower size distribution. The narrower size distribution was further confirmed from the reduction of full width at half maximum (FWHM) with decreasing temperatures (Figure 2). FWHM was observed to be 76 nm, 86 nm and 110 nm at 90 °C, 120 °C and 150 °C respectively. The control of size and size distribution of NCs can be attributed to crystal focussing which is hampered by fast growth of NCs [12]. The emission is however observed to stagnate at approximately 1600 nm at all the temperatures. The stagnation occurred faster at higher temperatures occurring after 30 min, 10 min and 8 min at 90 °C, 120 °C and 150 °C respectively (Figure 1). This could be attributed to depletion of starting materials or the reaction equilibrium having been reached and the NCs having reached their critical size [12]. Murray *et al.* reported that PbSe QDs are able to grow at relatively low temperatures with solution temperatures being used to tune the QD size from 3.5 nm at 90 °C to 15 nm at 220 °C [7]. Smaller sized NCs were obtained at lower temperatures with an increase in NC size with growth temperature with spherical NCs being obtained at 90 °C, 120 °C and cubic NCs at 150 °C (Figure 3).

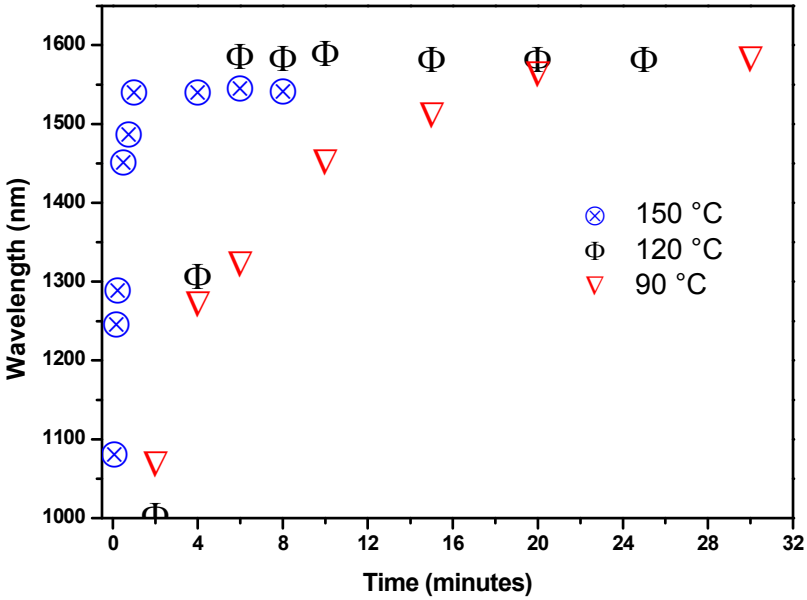

Figure 1 Variation of emission maxima with time at different reaction temperatures

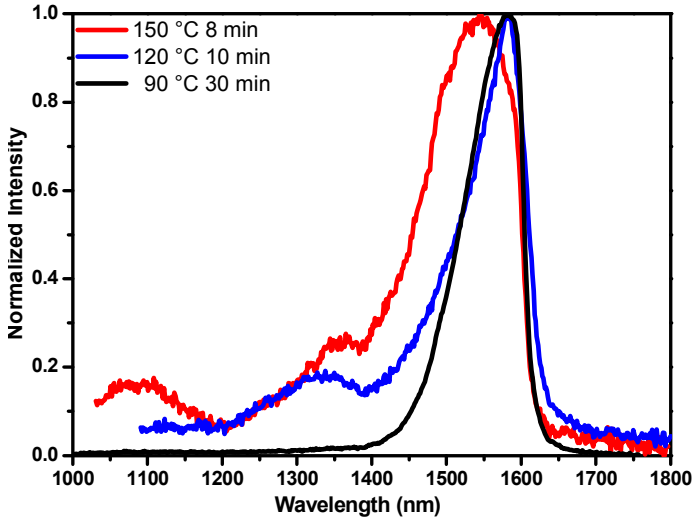

Figure 2 Emission spectra of NCs synthesized at different reaction temperatures

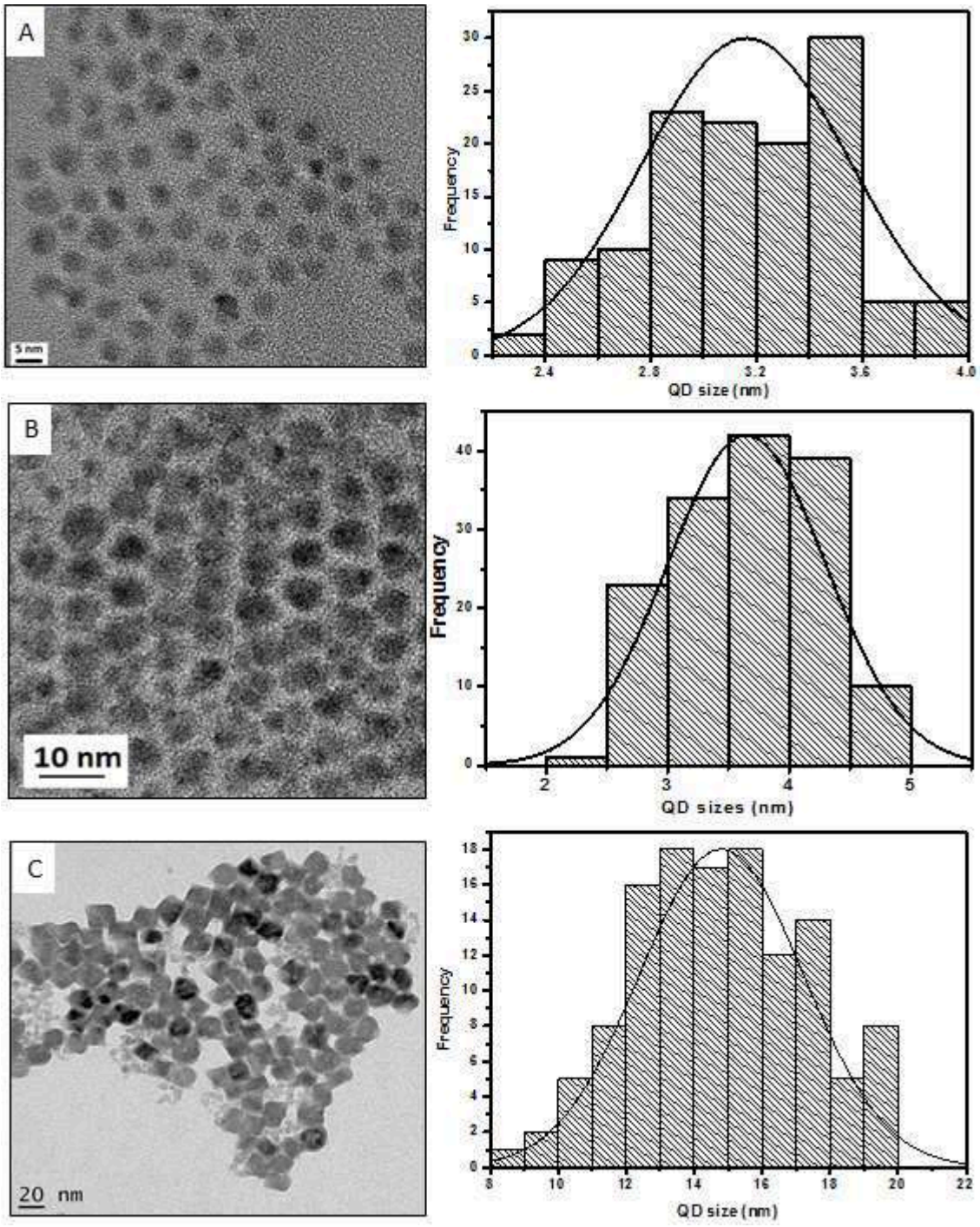

Figure 3 TEM micrographs and size distribution of PbSe NCs synthesized at A: 90 °C, B: 120 °C and C: 150 °C

3.2 Solvent effects

Colloidal synthesis of PbSe NCs has widely been studied following the pioneering work by Murray *et al.* [7]. Most of the reported syntheses make use either of the noncoordinating solvent 1-octadecene (ODE) or diphenylether. These solvents are preferred because of their high boiling points and non-coordinating nature, which allows the tunable reactivity of monomers which in turn leads to a better control of NC sizes [7,13]. However, the coordinating solvents particularly trioctylphosphine oxide (TOPO), have been used in the synthesis of group II-VI NCs [14]. In this work 1-octadecece (ODE), trioctylphosphine (TOP) and oleylamine (OLA) were used in the synthesis of PbSe NCs to provide a better insight into the effects of solvent on NC growth. The

effects of the different solvents was determined at 90 °C for all solvents and a reaction time of 30 min. ODE was observed to exhibit the fastest growth rate as observed from the emission profiles (Figure 4) and produced NCs with an average size of 3.2 ± 0.4 nm (Figure 5A). This can be attributed to its non-coordinating nature which implies that it does not take part in the reaction. Trioctylphosphine (TOP), a coordinating solvent, produced larger NCs with an average size of 4.58 ± 0.50 nm (Figure 5B) though with an average growth rate as observed from the progression in NC emission profiles (Figure 4). The TOP being a coordinating solvent may inhibit nucleation of NCs by slowing down the selenium exchange between trioctylphosphine selenide and lead oleate to form PbSe nuclei allowing more monomers in solution for NC growth [15]. The coordinating solvent oleylamine [16] gave the growth rate which rated lowest among the investigated solvents (Figure 4). The relatively slow growth and smaller NCs produced in oleylamine (Figure 5C), can be attributed to the activation of metal species which promotes nucleation leading to a higher number of NCs in solution [16], while at the same time the desorption of oleic acid from the NC surface and the bonded Pb surface atoms leads to NC shrinkage [12].

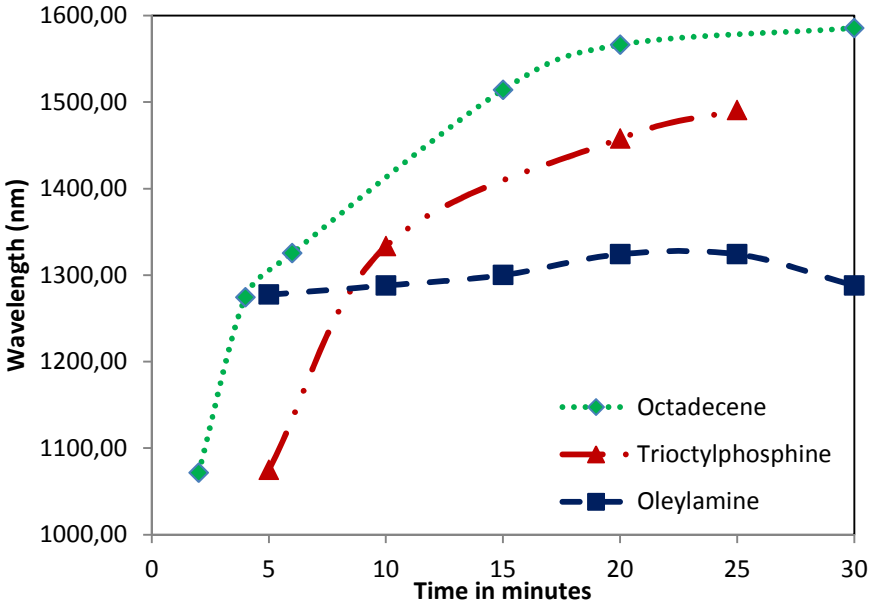

Figure 4 Summary of emission maxima with time in different solvents

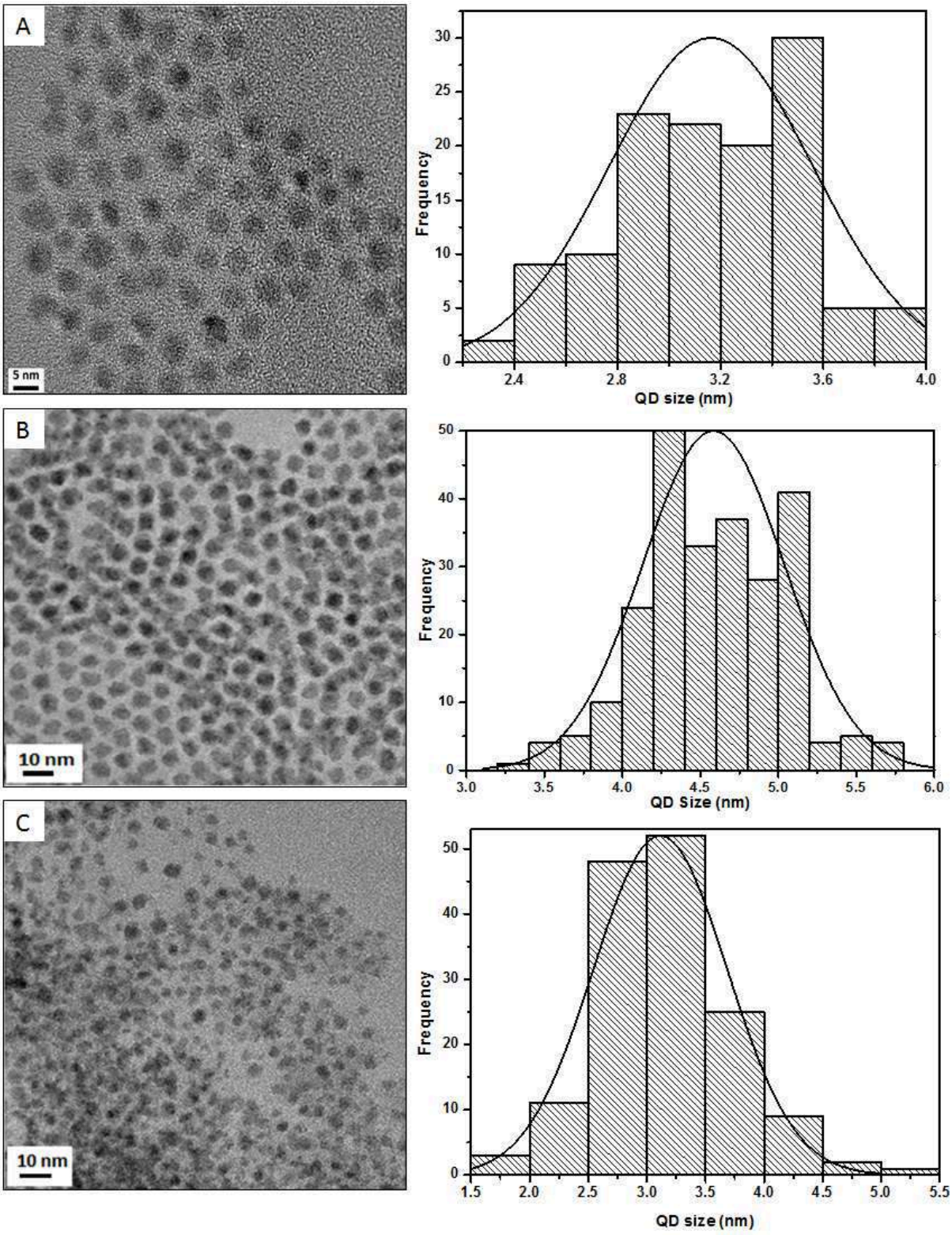

Figure 5 TEM micrographs and size distribution of PbSe NCs synthesized in A: 1-Octadecene (ODE), B: Trioctylphosphine (TOP) and C: Oleylamine (OLA)

3.3 Effect of Lead and Selenium sources on the optical and structural properties of PbSe NCs

In this study, lead oxide (PbO) and lead acetate ($Pb(Ac)_2$) were used as the sources lead ions while Trioctylphosphine-selenium (TOP-Se) and tributylphosphine-selenium (TBP-Se) were used as selenium precursors. The PbSe NCs synthesized from lead oxide (Figures 6A and 6B) were spherically shaped and monodispersed and were generally smaller than those synthesized from lead acetate (Figure 6C) which were cubic and agglomerated. The cubic shape can be attributed to the

effects of free acetic acid which may result during the formation of lead oleate in case of the presence of residual water from the hydrated lead acetate [17]. Houtepen *et al.* provided great insight into the growth of PbSe NCs when they investigated the effects of acetic acid on the growth of these nanocrystals [17]. They observed that using lead acetate which is not completely dried before the injection of the chalcogen precursors, allows the free acetate groups to combine with water molecules (from the hydrated lead acetate) to form acetic acid. They investigated the effects of acetic acid on the growth of PbSe QDs following the addition of free acetic acid into the reaction mixture. They concluded that the addition of acetic acid influenced the size and shape evolution of NCs producing starlike nanoparticles. Acetic acid being smaller than oleic acid partially replaces oleic acid on NC surfaces and due to the lower steric hindrance allows monomers to add to existing nuclei promoting growth in different directions.

TOPSe produced generally larger NCs as compared to TBPSe with longer emission wavelengths (Table 1). This could be attributed to better size control by tributylphosphine. Both tributylphosphine (TBP) and trioctylphosphine (TOP) form a P=Se double bond with selenium which is cleaved during nucleation when Se^{2-} ions react with Pb^{2+} ions to form QDs. The length of the alkyl chain indirectly affects the nucleation of the QDs but has not been shown to directly affect QD growth [12]. The longer TOP chain offers steric hindrance during the P=Se bond cleavage leading to the formation of fewer nuclei. TBP on the other hand favours the formation of nuclei leaving fewer monomers in solution for NC growth. This in turn leads to the formation of smaller QDs with a narrower size distribution [12].

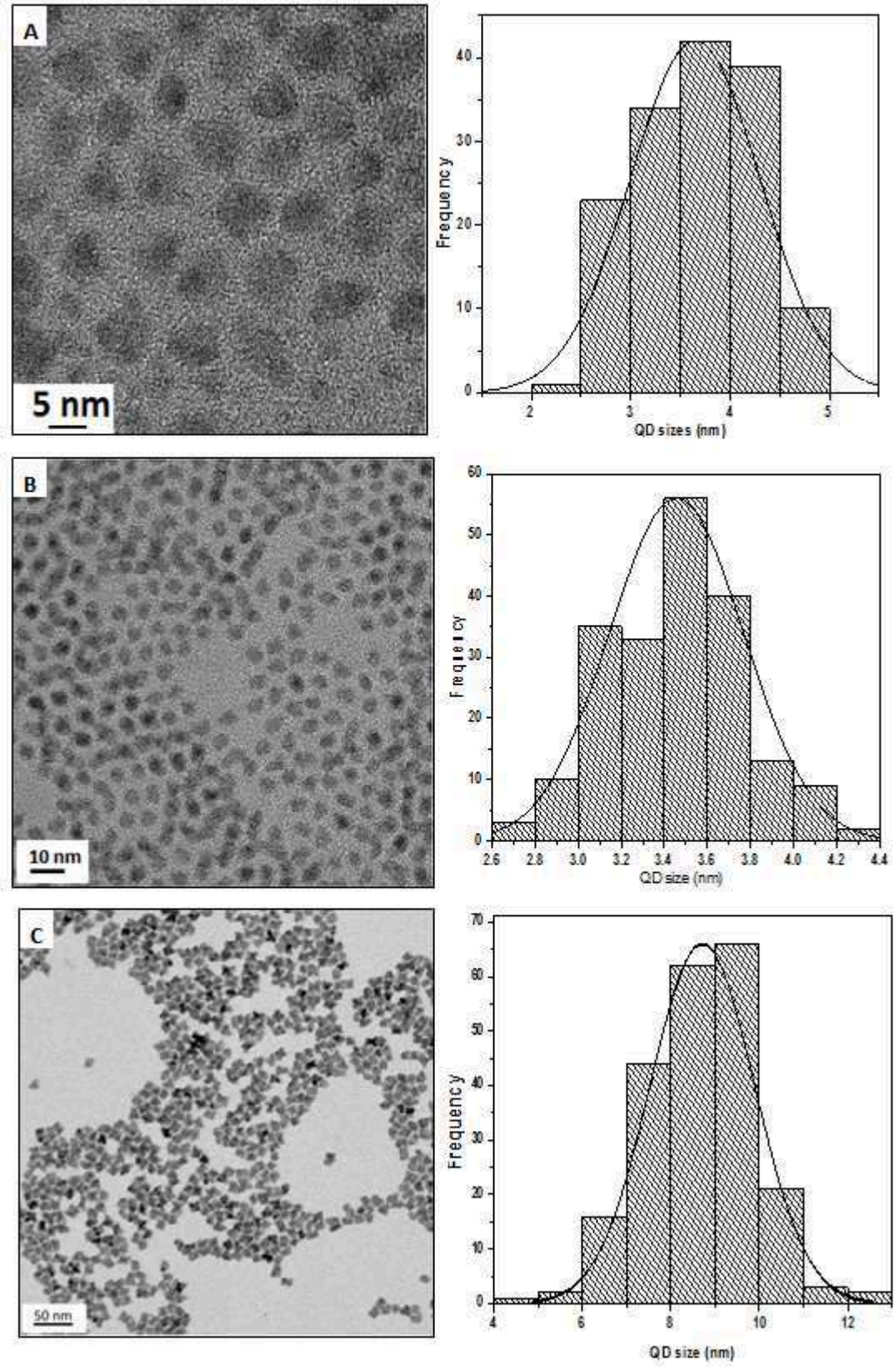

Figure 6 TEM micrographs and size distribution of PbSe NCs synthesized from A: PbO/TOP-Se, B: PbO/TBP-Se and C: $Pb(Ac)_2$/TOP-Se

Table 1 Effect of lead and selenium sources on the optical and structural properties of PbSe NCs.

Ligand	Pb source	Se source	Max. Emission	NC size
OA	PbO	TOPSe	1320 nm	3.7 ± 0.6 nm
OA	PbO	TBPSe	1034 nm	3.5 ± 0.3 nm
OA	$Pb(Ac)_2$	TOPSe	1590 nm	8.7 ± 1.2 nm

Figure 7 shows an EDS spectrum of some of the synthesized NCs, from the spectrum it can be confirmed that the synthesized PbSe NCs were indeed non-stoichiometric consisting of more lead atoms than selenium atoms as shown by the atomic percentages. This is consistent with reports that PbSe NCs are off-stoichiometric consisting of a stoichiometric PbSe core wrapped with a single layer of Pb atoms [18,19,20].

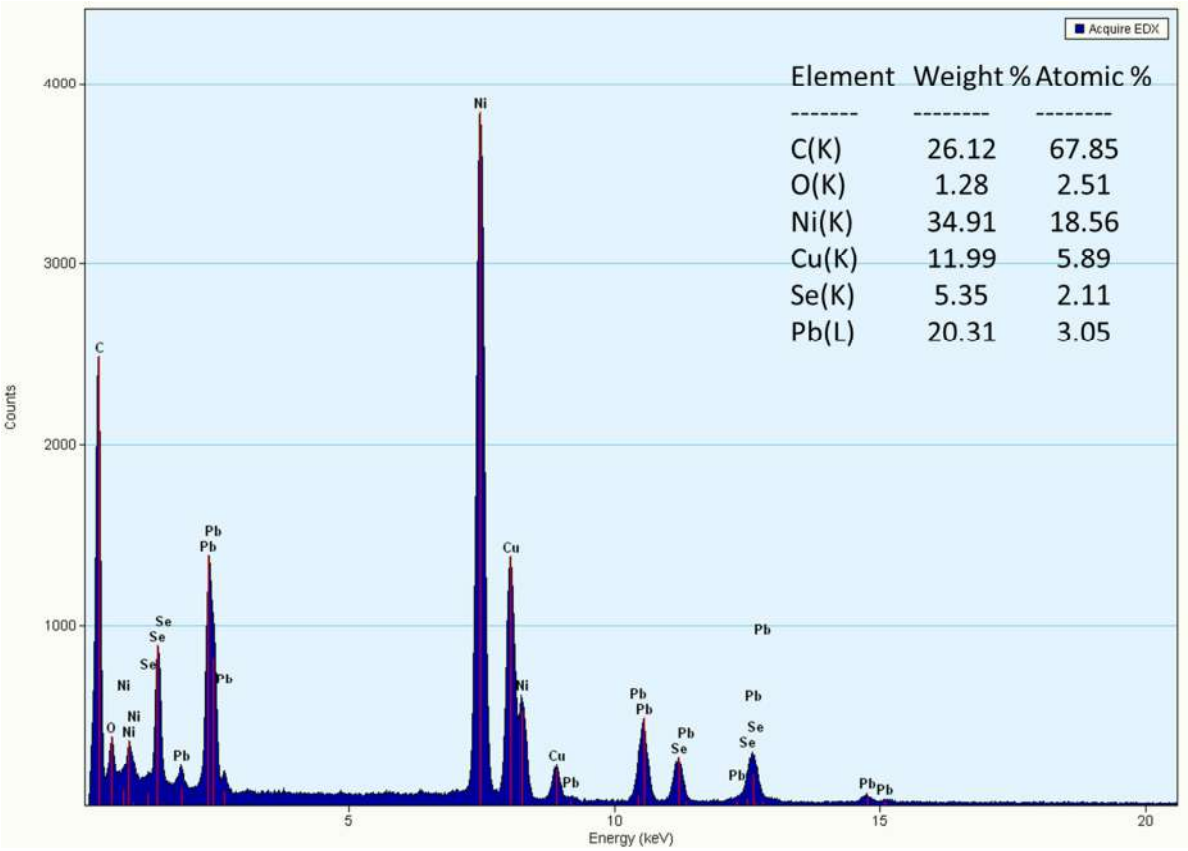

Figure 7 EDS spectrum of PbSe quantum dots

4 Conclusion

The effects of temperature, ligand purity, lead and selenium sources on the optical and structural properties of PbSe NCs were investigated. With increase in temperature, the NC sizes and size distribution increased as observed from the TEM micrographs and PL spectra. The NC growth was also shown to be influenced by the choice of solvent with 1-octadecene showing the fastest growth rate with medium sized NCs and oleylamine recording the slowest growth rate and smallest NCs. Trioctylphosphine recorded a moderate growth rate but with the largest NCs. The ligand purity however did not have a significant effect on the NC sizes as observed from the TEM micrographs of NCs synthesised using oleic acid of 90 % and 99 % purity. TEM micrographs of NCs synthesized from lead acetate and lead oxide showed that lead acetate produced cubic shaped NCs which were large compared to the spherical NCs produced from lead oxide. The selenium source was observed to affect the NC size with trioctylphosphine producing larger NCs than

tributylphosphine. The EDS spectrum of the synthesized PbSe NCs revealed that they were non-stoichiometric consisting of more lead atoms than selenium atoms.

5 Acknowledgements

The authors acknowledge DST/Mintek Nanotechnology Innovation Centre for funding this research and University of the Western Cape where the work was carried out.

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10.4028/www.scientific.net/JNanoR.34

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