

One-pot synthesis and characterization of InP/ZnSe semiconductor nanocrystals

Paul Mushonga, Martin O. Onani, Abram M. Madiehe and Mervin Meyer

Abstract

We report on the one-pot synthesis of InP/ZnSe quantum dots (QDs) using a precursor-based colloidal synthesis in a noncoordinating solvent environment. The structural and optical studies were carried out on the as-prepared InPQDs. The quantum yield of the nanocrystals was recorded as 6% and a 1.4 times reduction in the ratio of trap-related emission to band edge emission was observed on ZnSe passivation of the InPQDs.

1. Introduction

The colloidal group III–V semiconductor nanocrystals (NCs) have attracted enormous interest in the past two decades [1]. The principal attraction to this class of nanocrystals lies in the robustness of their covalent bond compared to the ionic bond in group II–VI semiconductor systems [2,3]. This property carries along an enhanced optical stability and reduced toxicity as a result of non-erosion of constituent ions when they are used in biological milieu [4]. Within the group III–V semiconductor materials, the InP system appears popular due to its relatively narrow band gap (1.35 eV) and large excitonic Bohr radius (11.3 nm) [5]. These parameters allow for the tuning of the photoluminescence emission wavelengths from the blue to the near infrared regions [6]. Research in InP-based nanocrystals is also premised on the need to find less toxic non-cadmium based quantum dots for applications in biomedicine [7].

However, despite the fact that the covalent nature of the group III–V is acknowledged, it is unfavorable for their synthesis. The precursors of group III–V nanocrystals possess strong covalent bonding, and therefore demand high synthetic temperatures and long reaction times. In 2010, Kim et al. [8] reported the fabrication of trioctylphosphine oxide (TOPO)-capped InP/ZnSe using chloroindium oxalate as an indium precursor in a reaction carried out over several days with a quantum yield of 6.8. In this paper, we report a shorter route to the synthesis of palmitic acid-capped InP/ZnSe nanocrystals using a one-pot hot-injection [9] method. Further, weakly coordinating solvent, 1-octadecene (ODE), was used in our work because

strongly coordinating solvents lead to slow and continuous nucleation, thus making it difficult to attain discrete nucleation and growth steps which are essential in obtaining monodisperse quantum dots [5].

2. Experimental

The solvents used (acetone and *n*-hexane) were CHROMASOLV HPLC grade and were used as received from Sigma Aldrich. Indium acetate ($\text{In}(\text{OAc})_3$), palmitic acid, zinc undecylenate, selenium, trioctylphosphine (TOP), 1-octadecene (ODE) and tris-(trimethylsilyl)phosphine ($\text{P}(\text{TMS})_3$) were purchased from Sigma Aldrich.

Synthesis of InP/ZnSe NCs: The NCs were synthesized in a non-coordinating solvent, 1-octadecene according to the procedure by Ryuet al. with some modifications [10]. In a typical synthesis, indium acetate (0.15 mmol) was mixed with palmitic acid (0.45 mmol) and ODE (4 mL) in a three-necked flask in the glove box. The flask was sealed and transferred to a Schlenk line and heated to 120 °C and kept under vacuum for 1.5 h. The system was then purged with argon and then heated to 300 °C. On reaching 300 °C, a freshly prepared injection solution of $\text{P}(\text{TMS})_3$ in ODE (0.075 mmol in 1 mL ODE prepared in the glove box) was injected rapidly under argon flow. For the growth of the InP core, the reaction mixture was kept at 270 °C temperature was lowered to 150 °C. For the shelling process, the zinc injection solution (0.1 M) was prepared by dissolving zinc undecylenate in a mixture of ODE (9.5 mL) and TOP (0.5 mL) at 140 °C. Similarly the selenium injection solution (0.1 M) was prepared by dissolving selenium in a mixture of ODE (9.5 mL) and TOP (0.5 mL) at 140 °C. The zinc precursor solution (0.375 mmol, 0.375 mL) was added and the temperature was raised to 230 °C and maintained at that temperature for 4 h. A selenium precursor solution (0.15 mmol, 1.5 mL) was injected into the flask and kept at this temperature for 1 h. Aliquot portions were taken during core and shell growth for characterization. The InP/ZnSe nanocrystals were purified from the reaction mixture by precipitation with acetone and redissolving them in *n*-hexane.

Characterization Optical measurements: Photoluminescence (PL) spectra were recorded on a HORIBA Nanolog FL3-22-TRIAX. The photoluminescence quantum yield (QY) for the InP/ZnSe NCs was determined using Rhodamine 6G as a standard according to a published procedure [11]. The optical densities of all the solutions were adjusted to values below 0.05 at the excitation wavelength of 400 nm to avoid re-absorption effects. The absorbances for the standard in ethanol and the InP/ZnSe in hexane at this excitation wavelength and the photoluminescence spectra of the same solutions were measured respectively. The integrated fluorescence intensity from the corrected spectrum was calculated.

Transmission electron microscopy (TEM): TEM studies were performed on a TECNAI F30ST TEM. Samples for TEM studies were prepared by placing a hexane solution of the nanocrystals on ultrathin carbon-film-coated copper grids.

3. Results and discussion

Optical properties of the InP/ZnSe QDs: Highly fluorescent and monodisperse InP/ZnSe nanocrystals were synthesized by reacting indium acetate with tris(trimethylsilyl phosphine) (P(TMS)₃) using palmitic acid (PA) as the surfactant and 1-octadecene as the non-coordinating solvent. Palmitic acid, an intermediate chain length fatty acid, facilitates controlled nucleation and growth rates needed for the synthesis of monodisperse InP semiconductor nanocrystals in non-coordinating solvents [12]. We maintained the 1:3 ratio of indium precursor to surfactant as it yields high-quality nanocrystals [13]. Fig. 1 shows normalized photoluminescence (PL) spectra of three aliquots taken during the synthesis of the NCs. The spectra show that there is no significant change in the emission peak maximum for aliquots taken 30 min and 120 min into the core growth. Bawendi's group reported that in the synthesis of InP, molecular phosphorus precursors are completely used up at the InP nucleation step culminating in subsequent growth of nanocrystals exclusively being attributed to ripening from non-molecular InP species in the solution [14].

The as-prepared InP/ZnSe NCs showed a maximum emission wavelength at 574 nm. An aliquot taken 120 min into core growth gave an emission peak of 579 nm. The slight blue-shift observed for these type I core/shell systems is contrary to expectations and is attributed to the fact that photoluminescence in ZnSe shelled-InP is less contributed by defect emission in comparison to the bare InP NCs [7]. The photoluminescence quantum yield (QY) was measured as 6%.

Trap state-related emissions are also exhibited in the PL spectra. The surface states are a result of unsatisfied (dangling) bonds that are found at the reconstructed surface. In this work, we chose ZnSe with a lower lattice mismatch with InP as an inorganic shell instead of ZnS which has a relatively large lattice mismatch in the zinc blende phase of about 7.6% [15]. Fig. 2 shows each PL spectrum deconvoluted into two Gaussian peaks. The deep trap-related emissions for the InP/ZnSe and bare InP NCs are around 627 nm and 640 nm respectively. The blue-shift observed is an evidence of successful coating of the core and that the shell reduces the surface states. The ZnSe shell also greatly reduced the ratio of trap-related emission to band edge emission by a factor of 1.4 [16].

Structural properties of the InP/ZnSe QDs: Figs. 3 and 4 show the HRTEM micrographs and EDX results of the nanocrystals respectively. The InP/ZnSe nanocrystals had an average diameter of 1.95 nm and the lattice fringes in the HRTEM image confirm the good crystallinity of the nanocrystals with lattice-fringe distance of 0.29 nm (nanocrystals in white dotted circles) which is in good agreement with the plane spacing of 0.29343 nm for /200S planes of the zinc blende structure. These lattice fringes are continuous throughout the QD indicating the epitaxial nature of ZnSe shell growth [17]. The selected area electron diffraction (SAED) pattern (Inset, Fig. 3) confirmed the zinc blende structure

of the NCs with three rings indexed to $/111S$, $/220S$ and $/311S$ lattice planes with corresponding calculated d -spacing values of 0.3404, 0.2069 and 0.17716 nm in good agreement with the theoretical ones. The EDXS results for the InP/ZnSe NC sample showed an In:P:Zn:Se ratio of 1:0.96:1.47:0.17 showing an indium-rich core with a zinc-rich particle surface. Thus the InP core has an indium-terminated surface while the shell has zinc-terminated surface. The Zn/In ratio of 1.47 confirms that the InP cores are covered by a ZnSe shell. Even higher ratios (2.34) have been reported for ZnS-capped InP nanocrystals [18].

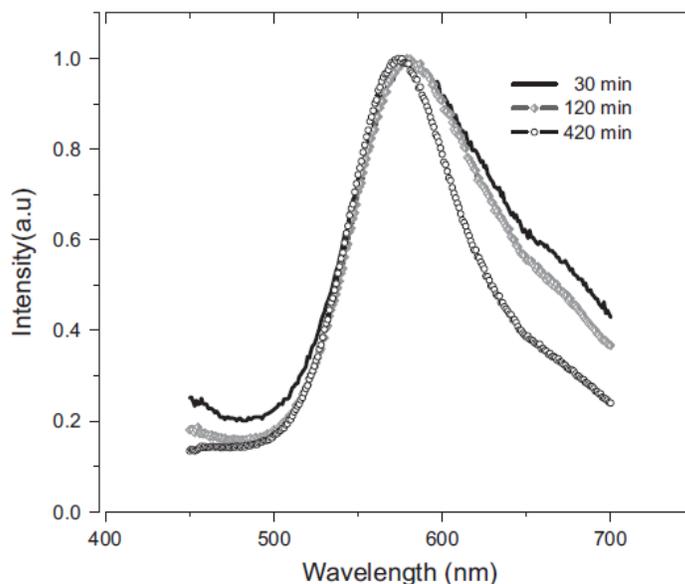


Fig. 1. Normalized photoluminescence spectra of three aliquots taken during the synthesis of the NCs.

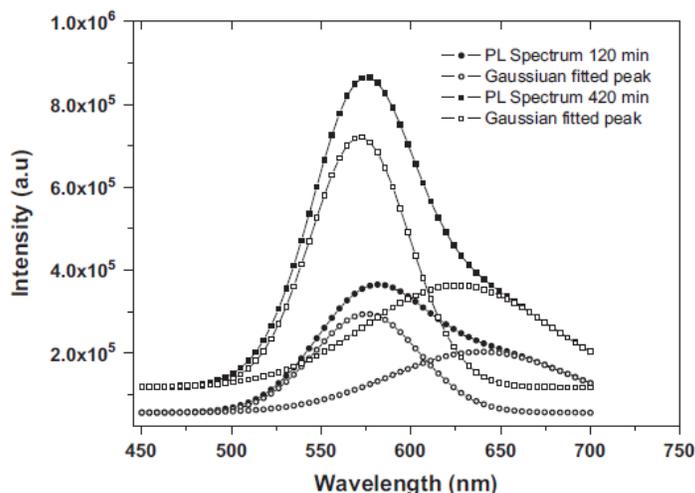


Fig. 2. Photoluminescence spectra deconvoluted into Gaussian peaks.

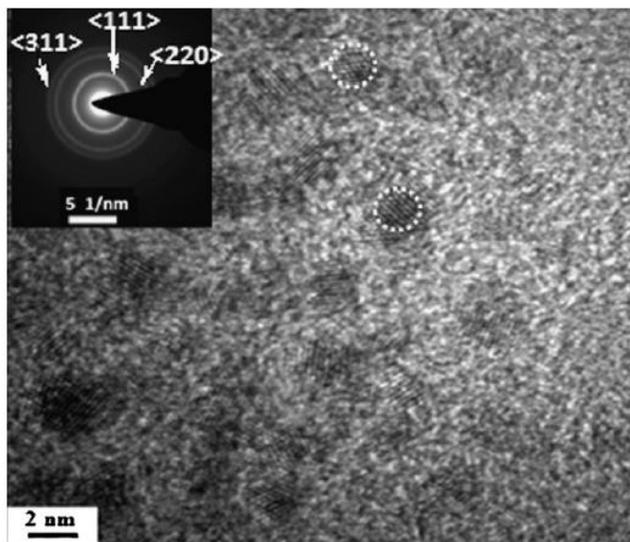


Fig. 3. HRTEM micrograph of the InP/ZnSe NCs (Insert is an SAED pattern).

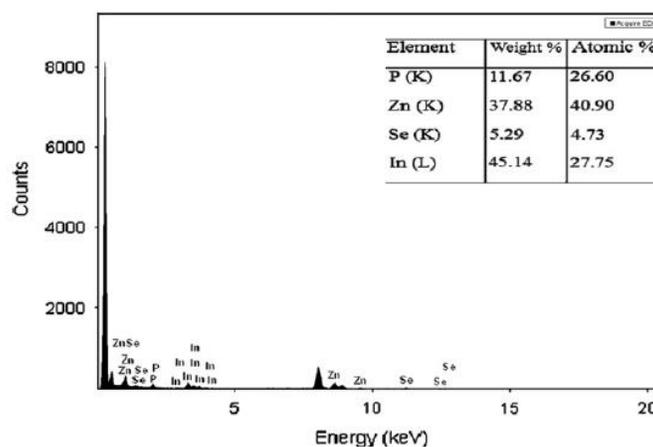


Fig. 4. EDX results of the InP/ZnSe NCs.

4. Conclusion

In conclusion, we have successfully synthesized InP/ZnSe QDs emitting at 574 nm with a QY of 6%. We have also demonstrated that indeed ZnSe shell passivates the InP core QDs with a blue-shift in the emission profiles and a 1.4 times reduction in the ratio of trap-related emission to band edge emission. The nanocrystals will undergo ligand exchange reactions as a functionalization step before they are applied in biological imaging studies.

Acknowledgments

The authors acknowledge the NIC/DST and UWC Senate Research for financial support.

References

- [1] Pham TT, Tran TKC, Nguyen QL. *Adv Nat Sci Nanosci Nanotechnol* 2011;2(025001):1-4.
- [2] Narayanaswamy A, Feiner LF, Van der Zaag PJ. *J Phys Chem* 2008;C 112(17):6775-80.
- [3] Bharali DJ, Lucey DW, Jayakumar H, Pudavar HE, Prasad PN. *J Am Chem Soc* 2005;127(32):11364-71.
- [4] Yong K-T, Ding H, Roy I, Law W-C, Bergey EJ, Maitra A, et al. *ACS Nano* 2009;3:502-10.
- [5] Langof L, Fradkin L, Ehrenfreund E, Lifshitz E, Micic OI, Nozik AJ. *Chem Phys* 2004;297(1-3):93-8.
- [6] Xu S, Ziegler J, Nann T. *J Mater Chem* 2008;18:2653-6.
- [7] Paul Mushonga P, Onani MO, Madiehe AM, Meyer M. *J Nanomater* 2012;2012(869284):1-11.
- [8] Kim MR, Chung JH, Lee M, Lee S, Du-Jang D-J. *J Colloid Interface Sci* 2010;350(1):5-9.
- [9] Murray CB, Norris DJ, Bawendi MG. *J Am Chem Soc* 1993;115(19):8706-15. [10] Ryu E, Kim S, Jang E, Jun S, Jang H, Kim B, et al. *Chem Mater* 2009;21(4):573-5.
- [11] Byun H-J, Song W-S, Yang H. *Nanotechnology* 2011;23(235605):1-622 2011;23(235605):1-6.
- [12] Battaglia D, Peng X. *Nano Lett* 2002;2(9):1027-30.
- [13] Xu S, Kumar S, Nann T. *J Am Chem Soc* 2006;128(4):1054-5.
- [14] Allen PM, Walker BJ, Bawendi MG. *Angew Chem Int Ed* 2010;49(4):760-2. [15] Huang K, Demadrille R, Silly MG, Sirotti F, Reiss P, Renault O. *ACS Nano* 2010;4(8):4799-805.
- [16] Protiere M, Reiss P. *Chem Commun* 2007:2417-9.
- [17] Gao S, Zhang C, Liu Y, Su H, Huang T, Dellas N, et al. *Opt Exp* 2011;19(6):5528-35.
- [18] Byun H-J, Lee JC, Yang H. *J Colloid Interface Sci* 2011;355(1):35-41.