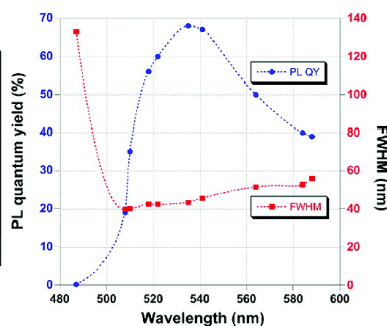


One-pot Synthesis of Highly Luminescent InP/ZnS Nanocrystals without Precursor Injection

Liang Li, and Peter Reiss

J. Am. Chem. Soc., **2008**, 130 (35), 11588-11589 • DOI: 10.1021/ja803687e • Publication Date (Web): 08 August 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

One-pot Synthesis of Highly Luminescent InP/ZnS Nanocrystals without Precursor Injection

Liang Li and Peter Reiss*

CEA Grenoble, INAC/SPRAM (UMR 5819 CEA-CNRS-UJF), 17 rue des Martyrs, 38054 Grenoble, France

Received May 25, 2008; E-mail: peter.reiss@cea.fr

The synthesis of colloidal semiconductor nanocrystals (NCs) has seen an impressive progress in the past two decades, fueled by the unique physical properties of these nano-objects arising from the quantum confinement effect. Precise control of size and shape is generally achieved by the temporal separation of NCs' nucleation and growth. The "hot-injection method", relying on the rapid injection of precursors into the hot reaction medium, fulfills this requirement and is extensively used.^{1,2} In the case of metal nanoparticles, the "heating-up method" constitutes an attractive alternative way to produce monodisperse samples.^{3,4} It consists of mixing all components at low/room temperature and subsequent heating to reflux. The absence of the pyrolytic event, which characterizes hot-injection approaches, strongly improves the reproducibility and possibility of large-scale nanoparticle production. Nevertheless similar synthetic procedures for semiconductor NCs are scarce and essentially restricted to cadmium chalcogenides.^{5,6} In view of the potential technological applications of NCs in biological labeling, lasers, LEDs, solar cells or sensors, alternative materials have to be developed. Indium phosphide is one of the most promising compounds in this context, combining size-tunable emission in the visible and near-infrared spectral range (bulk band gap: 1.35 eV) and low intrinsic toxicity.^{7–16} The aim of this Communication is to provide a heating-up pathway for the synthesis of high quality InP/ZnS core/shell NCs. The new synthetic approach, a *single-step procedure without precursor injection*, gives access to InP/ZnS NCs of unprecedented high fluorescence quantum yield (QY) (50–70%), comparably narrow emission line width (40–60 nm fwhm),¹⁷ and excellent photostability.

All precursors (indium myristate [In(MA)_x], zinc stearate, tris(trimethylsilyl)phosphine [P(TMS)₃], and dodecanethiol [DDT]) were mixed in 1-octadecene (ODE) under inert atmosphere at room temperature and subsequently heated to 300 °C within 3 min. Figure 1a presents the evolution of the UV–vis absorption and PL spectra with reaction time. The sample taken after 1 min exhibits a shoulder at 430 nm in its absorption spectrum and broad, weak emission. Within 3 min a sharp excitonic absorption peak becomes visible, accompanied by the narrowing of the fluorescence peak. These data indicate that the "size-focusing" growth regime is reached.^{6,18} The decomposition temperature of pure DDT is 350 °C. In the presence of the other compounds within the reaction mixture, we observed however that DDT already begins to react at around 230 °C, releasing sulfur for the formation of the ZnS shell. The emission efficiency increases significantly with reaction time, reaching a QY of up to 70% (Figure 1c). We attribute the in situ formation of the core/shell structure to the difference in reactivity of the applied InP and ZnS precursors.¹⁹ EDX analysis of samples taken at different reaction times (S1, Supporting Information) indicates that the reaction goes through several stages, starting with the decomposition of highly reactive P(TMS)₃ and formation of InP core NCs. The incorporation of P into the NCs stops with the starting reaction of the ZnS precursors, whereas the In content continues to increase,

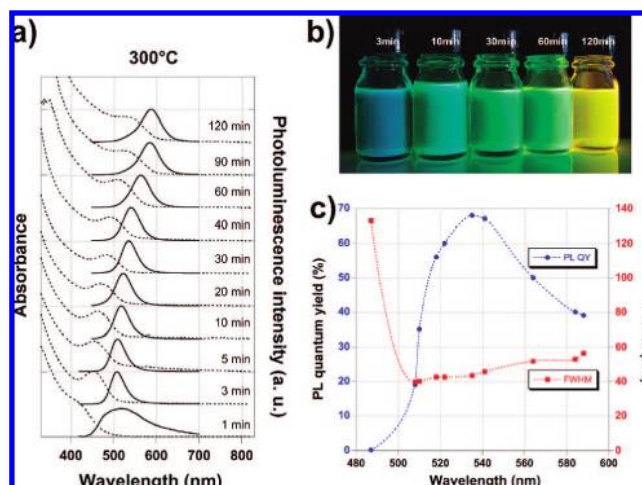


Figure 1. (a) Evolution of the PL ($\lambda_{\text{ex}} = 400$ nm) and absorption spectra with reaction time (vertically shifted for clarity). (b) Photograph of selected samples under UV light. (c) Evolution of the fluorescence QY and of the PL line width (increasing reaction time from left to right). Synthesis conditions: In:P:MA:Zn:S = 1:1:4.3:1:1, 300 °C.

leading to final In:P ratios of 1.5–1.9:1. The steady red-shift of the excitonic and PL peaks observed in this stage (cf. Figure 1a, 5–30 min) indicates that the resulting In-containing shell exhibits a lower conduction or valence band offset with InP as compared to pure ZnS. Remaining Zn and S precursors are deposited in the following, leading to a comparably small red-shift and high fluorescence QY (Figure 1a,c, 30–40 min). Finally, the reaction attains a "ripening stage", during which a further marked red-shift with concomitant peak broadening is observed (Figure 1 a,c, 60–120 min), attributed to the diffusion of In into the ZnS shell. The temporal evolution of the different stages strongly depends on the used precursor ratios (cf. Figure S2). In the case of intermediate In:MA ratios (1:2 or 1:3) leading to high monomer reactivity and fast depletion of the In precursor, the excitonic peak quickly reaches a stable position within the first 10 min. On the contrary, high stabilizer concentration (In:MA = 1:4.3, cf. Figure 1) leads to a continuous supply of In on a longer time scale. Regardless of the In:MA ratio, for extended reaction times and high temperature (300 °C) the ripening stage is reached. Concluding, the EDX data indicates that the obtained NCs possess a radial composition gradient. The latter efficiently relieves strain caused by the lattice mismatch between InP and ZnS. This "smooth" core/shell interface with few defect states likely is at the origin of the observed high fluorescence QY.

Figure S3 shows the TEM images of two typical InP/ZnS samples. Their PL (excitonic) peaks are located at 566 nm (527 nm) and at 537 nm (475 nm), and their average sizes determined from TEM are 3.5 and 4.1 nm, respectively. Literature data correlating the excitonic peak of pure InP NCs with their size results

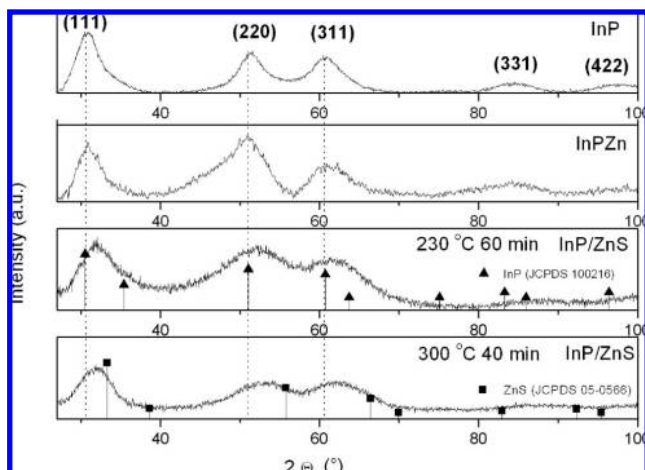


Figure 2. Powder X-ray diffractograms (Co K α) of InP NCs, of InP NCs synthesized in the presence of zinc stearate (InPZn), and of InP/ZnS core/shell NCs prepared at different temperatures (In:P:MA:Zn:S = 1:1:3:1:1). For comparison the diffraction patterns of bulk cubic InP (triangles) and ZnS (squares) are displayed.

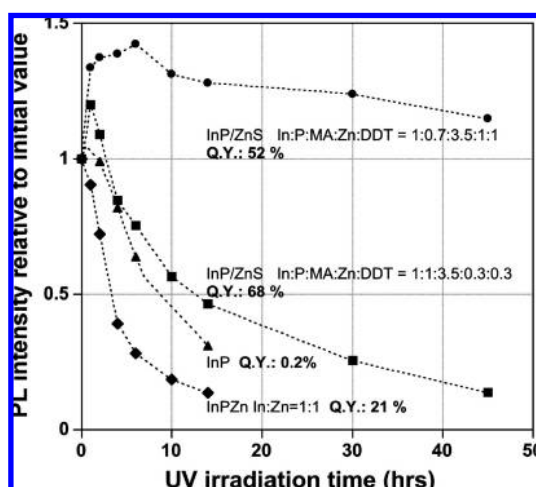


Figure 3. PL intensity of core and core/shell samples as a function of irradiation time with UV light (365 nm, 3 mW).

in 2.35 and 2.1 nm.^{8,20} These values are slightly overestimated in the case of the present core/shell samples, as the red-shift of the excitonic peak due to the penetration of the wave function into the shell is not taken into account. Therefore it can be concluded that the shell thicknesses are at least 0.6 and 1.0 nm, respectively.

In Figure 2, the X-ray diffractograms of InP NCs emitting at 640 nm and of two InP/ZnS samples prepared with different experimental conditions are compared to a sample synthesized using the standard procedure without DDT (InPZn). In all cases, the three predominant peaks can be attributed to the cubic zinc blende structure of InP. However, a significant shift of these peaks toward the characteristic positions of cubic ZnS is observed for the two core/shell samples, whereas no shift occurs in the case of the sample without DDT.

A crucial point for the application of fluorescent NCs is their photostability, which can be assessed by continuous irradiation with UV light in the presence of oxygen. Using this method, the photostability of purified InP/ZnS NCs prepared with varying amounts of ZnS precursors and thus presumably different shell thicknesses has been evaluated. Figure S4 shows the UV–vis

absorption and PL spectra of these samples and exhibits that zinc stearate and DDT not only act as the zinc and sulfur sources, respectively, but also influence the NCs' growth rate. Using a low concentration of ZnS precursors (In:Zn:S = 1:0.3:0.3) yields bigger NCs than the standard protocol (1:1:1), while the size dispersion remains narrow and an excellent QY is obtained (68%). However, lowering the ZnS precursor concentration also dramatically affects the photostability, which decreases to 50% of its initial value after 15 h of UV irradiation (Figure 3). In the case of the InP/ZnS NCs prepared with a In:Zn:S ratio of 1:1:1, even after 45 h of continuous irradiation no signs of photodegradation are visible. Samples prepared without DDT (InPZn) present a rather high initial QY (21%). However, similar as standard core InP NCs, they show a rapid decrease of their fluorescence intensity within 5–10 h of irradiation.

In conclusion, a convenient single-step method without precursor injection for the synthesis of highly luminescent InP/ZnS core/shell NCs has been introduced. Their optical properties make them promising candidates for use in displays and light-emitting devices or as fluorescent biological labels.

The presented synthetic approach opens the way for the large-scale production of high quality InP/ZnS NCs and it can be assumed that by proper choice of the reaction conditions, core/shell structures of other materials can be synthesized in a similar manner.

Acknowledgment. Financial support from CEA (program “Technologies pour la Santé”, project TIMOMA2) and from the ANR (project SYNERGIE) are acknowledged. Maxime Guinel is thanked for assistance with transmission electron microscopy.

Supporting Information Available: Synthesis details, EDX data, UV–vis spectra, and TEM images of the prepared NCs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706–8715.
- (2) Donega, C. D.; Liljeroth, P.; Vanmaekelbergh, D. *Small* **2005**, *1*, 1152–1162.
- (3) Kwon, S. G.; Piao, Y.; Park, J.; Angappane, S.; Jo, Y.; Hwang, N. M.; Park, J. G.; Hyeon, T. *J. Am. Chem. Soc.* **2007**, *129*, 12571–12584.
- (4) Park, J.; Joo, J.; Kwon, S. G.; Jang, Y.; Hyeon, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 4630–4660.
- (5) Cao, Y. C.; Wang, J. H. *J. Am. Chem. Soc.* **2004**, *126*, 14336–14337.
- (6) Yang, Y. A.; Wu, H. M.; Williams, K. R.; Cao, Y. C. *Angew. Chem., Int. Ed.* **2005**, *44*, 6712–6715.
- (7) Micic, O. I.; Sprague, J. R.; Curtis, C. J.; Jones, K. M.; Machol, J. L.; Nozik, A. J.; Giessen, H.; Fluegel, B.; Mohs, G.; Peyghambarian, N. *J. Phys. Chem.* **1995**, *99*, 7754–7759.
- (8) Guzelian, A. A.; Katari, J. E. B.; Kadavanich, A. V.; Banin, U.; Hamad, K.; Juban, E.; Alivisatos, A. P.; Wolters, R. H.; Arnold, C. C.; Heath, J. R. *J. Phys. Chem.* **1996**, *100*, 7212–7219.
- (9) Haubold, S.; Haase, M.; Kornowski, A.; Weller, H. *Chemphyschem* **2001**, *2*, 331–334.
- (10) Battaglia, D.; Peng, X. G. *Nano Lett.* **2002**, *2*, 1027–1030.
- (11) Talapin, D. V.; Gaponik, N.; Borchert, H.; Rogach, A. L.; Haase, M.; Weller, H. *J. Phys. Chem. B* **2002**, *106*, 12659–12663.
- (12) Lucey, D. W.; MacRae, D. J.; Furis, M.; Sahoo, Y.; Cartwright, A. N.; Prasad, P. N. *Chem. Mater.* **2005**, *17*, 3754–3762.
- (13) Xu, S.; Kumar, S.; Nann, T. *J. Am. Chem. Soc.* **2006**, *128*, 1054–1055.
- (14) Xie, R.; Battaglia, D.; Peng, X. J. *Am. Chem. Soc.* **2007**, *129*, 15432–15433.
- (15) Li, L.; Protière, M.; Reiss, P. *Chem. Mater.* **2008**, *20*, 2621–2623.
- (16) Liu, Z. P.; Kumbhar, A.; Xu, D.; Zhang, J.; Sun, Z. Y.; Fang, J. Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 3540–3542.
- (17) Narayanaswamy, A.; Feiner, L. F.; van der Zaag, P. J. *J. Phys. Chem. C* **2008**, *112*, 6775–6780.
- (18) Peng, X. G.; Wickham, J.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1998**, *120*, 5343–5344.
- (19) Bae, W. K.; Char, K.; Hur, H.; Lee, S. *Chem. Mater.* **2008**, *20*, 531–539.
- (20) Baskoutas, S.; Terzis, A. F. *J. Appl. Phys.* **2006**, *99*, n/a.

JA803687E