

How to make decent quantum dots on the southern hemisphere

Geoffry Laufersky, Thomas Nann

The MacDiarmid Institute & School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, New Zealand

Colloidal indium phosphide (InP) quantum dots are an attractive alternative to the frequently studied and used cadmium selenide (CdSe) ones. They luminesce in a similar range of the visible spectrum while being much less toxic. However, synthesis methods that result in high-quality InP quantum dots require tris-trimethylsilylphosphine ((TMS)₃P) as a reagent.¹⁻³ Unfortunately, (TMS)₃P is not commercially available in some countries including Australia and New Zealand. This makes the synthesis of high-quality InP quantum dots extremely difficult for researchers in these countries. Recently, Song *et al.* and Tessier *et al.* described a new synthesis method that does not require (TMS)₃P, thus allowing Aussis and Kiwis to fabricate InP quantum dots.^{4,5} Compared with the more hazardous methods mentioned above, the new synthesis results in particles of moderate optical quality and the synthesis mechanism is poorly understood.^{6,7} We present a study that aims at elucidating the synthesis mechanism of InP quantum dots using the non-(TMS)₃P route.

While implementing tris-dialkylaminophosphines has allowed us to fabricate our favourite QDs again, it has also presented us with a number of new problems to which previous literature has limited utility. For example, despite Song *et al.* having published the ground-breaking work on this phosphine several years ago, only recently has a viable scheme been presented to describe why this reaction must be undertaken in a primary amine as solvent,⁶ contrasting the bulk of (TMS)₃P-based research.⁸⁻¹⁰ Similarly, the choice in indium and zinc halide starting materials seems to have an unprecedented effect on the final nanoparticle size: moving down the halogen group results in smaller nanoparticle radii. While this trend could be rationalised for the indium salts as increased sterics and therefore reduced reaction rates, the same effect can be seen with changing zinc halides. Historically, despite being necessary for most high-quality InP syntheses, zinc salts have been generally regarded as uninvolved in precursor conversion, presenting as surface passivants¹¹ or alloyed gradient-shell materials.¹² This striking effect of ZnX₂ choice yields a potential insight into previously-ignored components of the reaction mixture, perhaps explaining how a P(III) species can come to produce P(-III) materials.

Using the hot-injection, one-pot core/shell growth scheme outlined by Tessier *et al.*, various indium and zinc precursors were used to synthesise InP/ZnS nanoparticles. Final samples were characterised by a gambit of spectroscopic data to determine the effect of precursor conversion on particle size, quality, quantum yield, and fluorescence lifetimes. Reaction solutions were also examined with MALDI-MS, ³¹P- and ¹H-NMR throughout and compared to careful reaction-in-a-tube studies to determine intermediates.

While the above experimental techniques have been useful in designing hypotheses for the conversion mechanism, density functional theory (DFT) calculations were performed in concert to identify a more fully-realised reaction scheme. Identifying minima and transition states along the reaction pathway allowed for the calculation of kinetic rates to rationalise the shifting size dependence with zinc salt composition. Similarly, the identified geometries allowed for the calculation of NMR spectra to provide firmer identification of peaks in the otherwise confusing reaction mixtures.

With the information gathered from this in-depth study, new prospects for faster, cheaper, and higher quality indium phosphide quantum dots emerge. Improvements of rational design and control could allow for the realisation of a full-spectrum synthetic route, opening opportunities for a number of industrial and biological applications.

- (1) Li, L.; Reiss, P. *J. Am. Chem. Soc.* **2008**, *130* (35), 11588.
- (2) Lucey, D. W.; MacRae, D. J.; Furis, M.; Sahoo, Y.; Cartwright, A. N.; Prasad, P. N. *Chem. Mater.* **2005**, *17* (14), 3754.
- (3) Xu, S.; Kumar, S.; Nann, T. *J. Am. Chem. Soc.* **2006**, *128* (4), 1054.
- (4) Song, W.-S.; Lee, H.-S.; Lee, J. C.; Jang, D. S.; Choi, Y.; Choi, M.; Yang, H. *J. Nanoparticle Res.* **2013**, *15* (6), 1.
- (5) Tessier, M. D.; Dupont, D.; De Nolf, K.; De Roo, J.; Hens, Z. *Chem. Mater.* **2015**, *27* (13), 4893.
- (6) Tessier, M. D.; De Nolf, K.; Dupont, D.; Sinnaeve, D.; De Roo, J.; Hens, Z. *J. Am. Chem. Soc.* **2016**, *138* (18), 5923.
- (7) Buffard, A.; Dreyfuss, S.; Nadal, B.; Heuclin, H.; Xu, X.; Patriarche, G.; Mézailles, N.; Dubertret, B. *Chem. Mater.* **2016**, *28* (16), 5925.
- (8) Lim, J.; Bae, W. K.; Lee, D.; Nam, M. K.; Jung, J.; Lee, C.; Char, K.; Lee, S. *Chem. Mater.* **2011**, *23* (20), 4459.
- (9) Kim, S.; Kim, T.; Kang, M.; Kwak, S. K.; Yoo, T. W.; Park, L. S.; Yang, I.; Hwang, S.; Lee, J. E.; Kim, S. K.; Kim, S.-W. *J. Am. Chem. Soc.* **2012**, *134* (8), 3804.
- (10) Xie, L.; Harris, D. K.; Bawendi, M. G.; Jensen, K. F. *Chem. Mater.* **2015**, *27* (14), 5058.
- (11) Mordvinova, N.; Vinokurov, A.; Kuznetsova, T.; Lebedev, O. I.; Dorofeev, S. *Dalton Trans.* **2017**.
- (12) Pietra, F.; De Trizio, L.; Hoekstra, A. W.; Renaud, N.; Prato, M.; Grozema, F. C.; Baesjou, P. J.; Koole, R.; Manna, L.; Houtepen, A. J. *ACS Nano* **2016**, *10* (4), 4754.