A novel metalorganic route for the direct and rapid synthesis of monodispersed quantum dots of indium phosphide

Mark Green and Paul O'Brien*

Department of Chemistry, Imperial College of Science Technology and Medicine, South Kensington, London, UK SW7 2AY. E-mail: p.obrien@ic.ac.uk: Fax No., 0171-594-5825

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Nanometric particles of InP are readily prepared by the decomposition of the complex $In(PBu^t_2)_3$ at 167 °C in 4-ethylpyridine; the resulting materials show marked quantum confinement effects, and was investigated using optical absorption and photoluminescence spectroscopies, and transmission electron microscopy.

There is considerable current interest in the synthesis of compound semiconductors as isolated particles with dimensions of the order of nanometers.[1] Such materials are small enough to show quantum confinement effect and the electronic properties of the material depend on the size of the particles. The majority of work to date has concerned on II–VI materials[2] which are for many reasons easier to prepare than III–V or II–V semiconductors.[3] Initial attempts to prepare III–V materials focused on the reaction of separate sources in a high boiling point solvents[4] or an electrospray method.[5] However, the properties of the materials were somewhat disappointing. Recently better quality materials have been prepared by thermolysis reactions in TOPO (tri-*n*-octylphosphine oxide), an adaptation of the highly efficient route first described by Murray *et al.* for the preparation of CdSe from dimethylcadmium and tri-*n*-octylphosphine selenide.[2] These methods for III–V TOPO capped quantum dots were initially developed by Micic *et al.*[6,7] and have been further exploited by Alivisatos and co-workers[8,9] and materials with near band edge luminescence have been prepared. However, the methods used fairly ill-defined precursor systems such as an aged solution of $InCl_3$–TOPO in reaction with neat $E(SiMe_3)_3$ (E = As, P). Growth and annealing to form the final crystalline material can take up to a week (at 250 °C) and the resulting product is polydispersed and contaminated with In_2O_3 waste material

We have recently succeeded in using the phosphide compound $[MeCdPBu^t_2]_3$[10] for the preparation of high quality samples of nanocrystalline Cd_3P_2,[11] and have now developed the use of related compounds for the synthesis of III–V materials. We report here, the use of a single molecule precursor in the 'one pot' preparation of nanometric InP quantum dots.

The problems encountered in the synthesis of III–V dots can in part be attributed to covalent nature[3] of the semiconductor and the related effect of strong precursor–solvent interactions. In these systems, nucleation and growth tend to be high temperature processes and temporal separation of the two is difficult, the resulting products are hence often polydispersed and amorphous. The use of a reactive single-source precursor overcomes this problem.

The single source precursor $In(PBu^t_2)_3$ was prepared as described by Jones and coworkers, by reacting $InCl_3$ with 3 equiv. of $LiPBu^t_2$ in hexane.[12] Decomposition to InP was effected by reflux in 4-ethylpyridine (20 ml) for 0.5 h (167 °C, 0.4 g, 0.7 mmol).

$$In(PBu^t_2)_3 \xrightarrow{\text{heat}} \text{Q-InP}$$

Addition of a non-solvent (light petroleum) resulted in flocculation of the InP quantum dots. The powder was then re-dispersed in either pyridine or 4-ethylpyridine and centrifuged to remove waste material, an optically clear solution of nanoparticles resulted. At this point, addition of excess non-solvent produces a nanodispersed powder of the semiconductor. Electronic spectroscopy of this material showed a band edge of 1.92 eV, as determined by the direct band gap method[13] with an excitonic shoulder at *ca.* 2.72 eV (455 nm), a significant blue shift from the bulk band gap of 1.27 eV.[14] Luminescence spectroscopy shows strong broad near band edge luminescence with λ_{max}. at 2.32 eV (534 nm) (Fig. 1) slightly red shifted from the absorption. Size fractionation has little effect on band edge, indicating the system is highly monodispersed. The sample consists of a large number of relatively monodispersed dots, with an average diameter of 7.24 ± 1.24 nm which is easily observed in TEM experiments (Fig. 2).

This work clearly shows that the use of defined precursors has potential in the preparation of high quality quantum dots. Indeed, the presently reported procedure is both simpler and

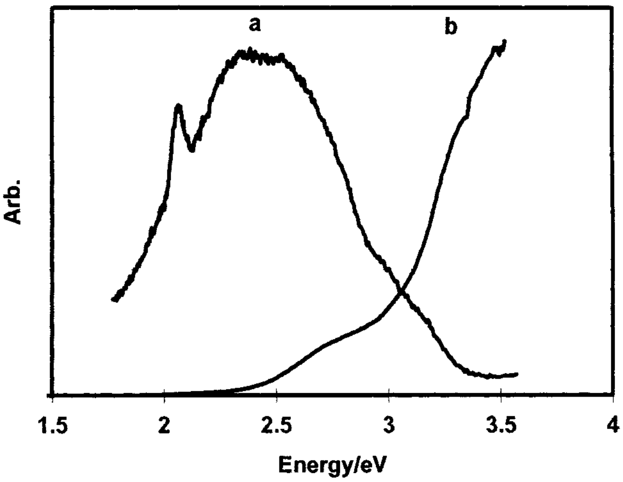

Fig. 1 Luminescence (a) and UV (b) spectra of Q-InP synthesised at 167 °C. Feature at *ca.* 2 eV is a second order excitation (λ_{exc} = 300 nm).

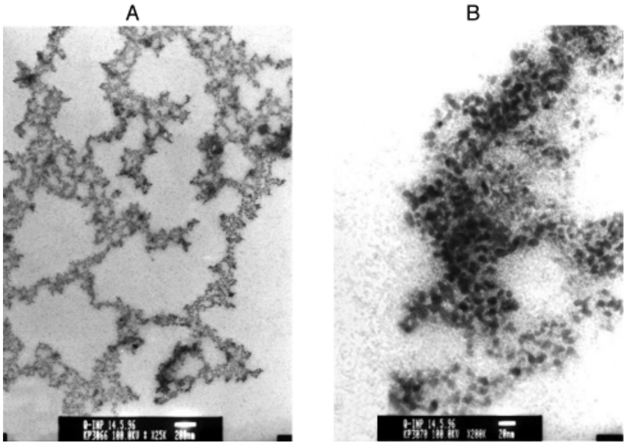

Fig. 2 TEM of Q-InP dispersed on a copper grid: (A) bar = 200 nm, (B) bar = 20 nm.

more rapid than those known to date. Work on other III–V materials is continuing in our laboratory and preliminary results have been obtained which show that organically passivated GaP and InAs can be prepared by related methods.

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Notes and references

1 M. L. Steigerwald and L. E. Brus, *Acc. Chem. Res.*, 1990, **23**, 183.
2 C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am.Chem. Soc*., 1993, **115**, 8706
3 J. R. Heathand and J. J. Shiang, *Chem. Soc. Rev*., 1998, **27**, 65.
4 M. A. Olshavsky, A. N. Goldstein and A. P. Alivisatos, *J. Am. Chem. Soc*., 1990, **112**, 9438.
5 O. V. Salata, P. J. Dobson, P. J. Hull and J. L. Hutchinson, *Appl. Phys. Lett*., 1994, **65**,189.
6 O. I. Micic and Nozik, *J. Lumin*., 1996, **70**, 95.
7 O. I. Micic, C. J. Curtis, K. M. Jones, J. R. Sprague and A. J. Nozik, *J. Phys. Chem*., 1994, *98*, 4966.
8 A. A. Guzelian, U. Banin, A. V. Kadavanich, X. Peng and A. P. Alivisatos, *Appl. Phys. Lett*., 1996, **69,** 1432
9 A. A. Guzelian, J. E. B. Katari, U. Banin, A. V. Kadavanich, X. Peng, A. P. Alivisatos, K. Hamed, E. Juban, R. H. Wolters, C. C. Arnold and J. R. Heath, *J. Phys.Chem*., 1996, **100**, 7212.
10 B. L. Benac, A. H. Cowley, R. A. Jones, C. M. Nunn and T. C. Wright, *J. Am. Chem. Soc.*, 1989, **111**, 4986.
11 M. Green and P. O'Brien, *Adv. Mater*., 1998, **10**, 527.
12 A. M. Arif, B. L. Benac, A. H. Cowley, R. A. Jones, K. B. Kidd and C. M. Nunn, *New. J. Chem*., 1988, 12, 553.
13 J. I. Pankove, *Optical Processes In Semiconductors*, Dover Publication Inc, New York, **1970.**
14 D. R. Lide, *Handbook of Chemistry and Physics*, CRC press, 1997.

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