

Nanoparticles from the decomposition of the complex [InN₃(CH₂CH₂CH₂NMe₂)₂]^{†‡}

Paul S. Schofield,^a Wuzong Zhou,^a Phillip Wood,^b Ifor D. W. Samuel^b and David J. Cole-Hamilton^{*a}

^aSchool of Chemistry, University of St. Andrews, St. Andrews, Fife, UK KY16 9ST.

E-mail: djc@st-and.ac.uk; Fax: 44-1334-463808; Tel: 44-1334-463805

^bOrganic Semiconductor Centre, School of Physics and Astronomy, University of St. Andrews, St. Andrews, Fife, UK KY16 9SS

Received 31st March 2004, Accepted 25th June 2004

First published as an Advance Article on the web 20th September 2004

Particles with diameters in the 2–10 nm range have been synthesised from the decomposition of InN₃(CH₂CH₂CH₂NMe₂)₂ in trioctylphosphine oxide; XPS, EDX and HRTEM studies are consistent with particles of cubic indium nitride. Size fractionated particles with average diameters of 4.5 nm show luminescence at 690 nm (1.82 eV), consistent with the band-gap of the bulk material being near 0.7 eV.

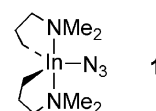
Particles with dimensions between 1 and 10 nm occupy a state of matter somewhere between molecular compounds and bulk solid state materials. In the particular case of semiconductors, the band structure is altered relative to that of the bulk by quantum confinement effects, which are manifested by an increase in the band gap and a move towards discrete energy levels rather than continuous bands. The band gap can hence be tuned by varying the particle size, with small particles having larger band gaps than bulk material.

Group 13 nitrides are of particular interest because of their importance in blue emitter technologies. InN¹ is especially interesting because its bandgap has recently been remeasured as 0.7 eV rather than the previously accepted value of 1.9 eV.^{2,3} Theoretical support for the new value has been provided.⁴ Thus, nanoparticles of InN would be expected to have band-gaps varying from the near infra-red region of the electromagnetic spectrum, close to wavelengths of especial interest in telecommunications, through much of the visible region.

There have been only three reports of nanoparticles of InN and none of these reports luminescence or band-gap measurements. In one, Pr₂InN₃ was decomposed at 203 °C in diisopropylbenzene to give an “amorphous black powder”.⁵ This material was not further characterised as the authors were more concerned with the InN nanotubes that grew on In metal seeds when 1,1-dimethylhydrazine was added to the reaction mixture. InN particles of ca. 100 nm were prepared from the reaction of nanoparticles of In₂O₃ with ammonia at 580–620 °C, close to the temperature at which nitrogen is lost from the lattice.⁶ The third report is of the reaction between InCl₃ and Li₃N in xylene at 250 °C which led to mixed cubic and hexagonal InN with diameters of ca. 30 nm.⁷ Very recently, nanowires of InN (25 nm in diameter) surrounded by InP have been prepared from In₂O₃, In and InP under ammonia.⁸

We focussed on the precursor, **1**, which, unlike many azides, is not explosive and has been used by Fischer and co-workers

for the epitaxial growth of InN thin films.⁹ A related gallium diazide has been used for the synthesis of GaN nanoparticles.¹⁰ Bawendi and coworkers pioneered the use of trioctylphosphine oxide (TOPO) as a medium for the high temperature preparation of nanoparticles such as CdSe. TOPO not only acts as the solvent, but also controls particle growth and aggregation by binding to the surface of the growing particles.¹¹ We now report that a similar procedure using **1** leads to the production of nanoparticles of InN.



A toluene solution of **1** was injected into TOPO at 250 °C and the resulting solution held at 230 °C for 3.5 h. The resulting brown solution was treated with methanol to precipitate a solid, **A**, which was washed with butanol. This yielded a solid **B** and a butanol solution, **C**. These three samples were evaporated onto carbon supports and examined by high resolution transmission electron microscopy (HRTEM). They were also analysed by X-ray diffraction, whilst sample **B** was analysed by X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDX). The XPS studies showed the characteristic peaks for In and N with a separation of 46.3 eV, close to the value obtained for bulk material grown by low pressure chemical vapour deposition (46.4 eV),¹²

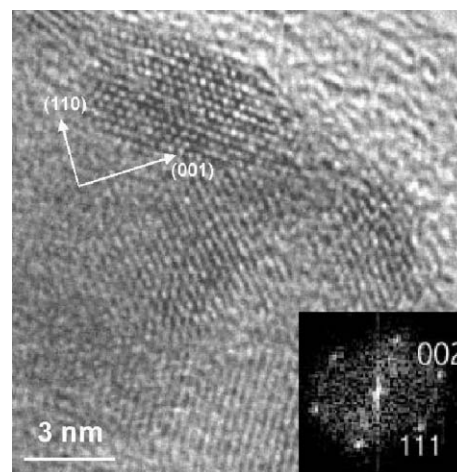


Fig. 1 HRTEM image of nanoparticles in sample **B**. The principal zone axes of the cubic unit cell are indicated for the top particle. Inset is the Fourier transform electron diffraction pattern of the particle in the top of the image.

[†] Basis of a presentation given at Materials Discussion No. 7, 13–15th September 2004, London, UK.

[‡] Electronic supplementary information (ESI) available: HRTEM images of several particles from samples **A**, **B**, **C** and In₂O₃, together with EDX data. See <http://www.rsc.org/suppdata/jm/b4/b404767b/>

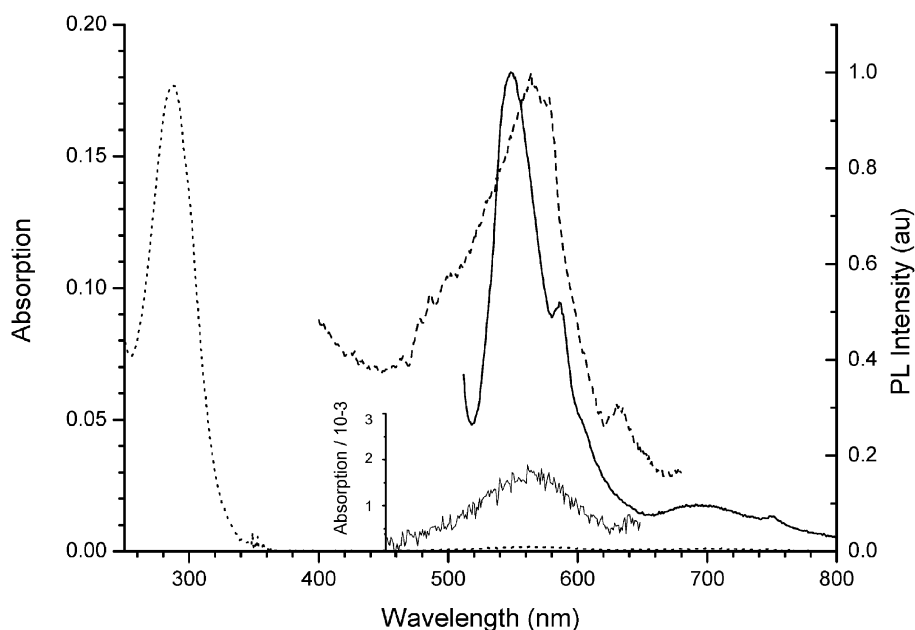


Fig. 2 Absorption (dotted), emission with excitation at 500 nm (solid) and PLE with detection at 700 nm (dashed) spectra of sample **B**. Inset is the weak absorbance at 550 nm. The emission at 550 nm is from TOPO.¹⁷

perhaps suggesting a similar environment; X-ray diffraction revealed only features too broad for indexing. EDX showed strong absorptions for In and a feature due to nitrogen, a weak shoulder on the dominant peak from carbon, when an accelerating voltage of 20 kV was used. The N feature became more prominent when the energy of the electron beam was reduced to 5 kV. EDX mapping (see ESI† Fig. 8) showed that In, N, C, O and P map together.

The most compelling evidence for the formation of InN comes from HRTEM studies (Fig. 1 and ESI†). Samples **A** (wide size distribution), **B** (diameters 2–10 nm, av. 4.5 nm) and **C** (diameters ca. 2 nm) show lattice fringes from well formed nanoparticles embedded in an organic matrix. An examination of the particle at the top right hand side of Fig. 1 suggests that cubic InN has been formed. The angles of the hexagons in the two dimensional pattern of the particle at the top of Fig. 1 and in the electron diffraction pattern are 70°, 55° and 55° and the lattice spacings parallel to the edges of the hexagons are not all the same (2.93, 2.93 and 2.56 Å). The spacings correspond to the [111] planes (2.93 Å) and the [002] planes (2.56 Å) of an fcc unit cell. These measurements give an average cell parameter, a , of 5.09 Å, consistent with literature values. Lattice parameters for cubic InN of 5.09,¹³ 4.98,¹⁴ 4.932¹⁴ and 4.532 Å¹⁵ have all been reported. The one other possibility is that the nanoparticles might be of In₂O₃. These have been reported by Chaudret and co-workers,¹⁶ who have also carried out HRTEM studies. In₂O₃ has a lattice parameter of 10.17 Å, almost exactly double that of the nanoparticles we observe, but is bcc rather than fcc. This manifests itself by an electron diffraction pattern which contains extra spots compared with those which we observe and a clear superlattice structure in the HRTEM image corresponding to four [440] planes in each repeat unit (see ESI† Fig. 7). Again, this superlattice structure is not observed in any of our particles. The d -spacings of all the observed nanoparticles from sample **B** with 1D and 2D fringes were also measured and all of them matched an fcc unit cell. A few other particles are present in Sample **A** (for HRTEM image see ESI† Fig. 3), with a lattice spacing of (2.7 Å). These particles are clearly of indium metal.

All of the samples show bright blue luminescence when irradiated with a UV lamp. However, this emission arises from the TOPO¹⁷ and is obtained if TOPO is treated under the same conditions in the absence of **1**. If the band-gap of cubic InN is close to 0.7 eV, as seems likely since, for example, the band gaps

of cubic and hexagonal GaN differ by only 0.192 eV,¹⁸ emission from cubic InN nanoparticles would be expected in the near IR or red region of the spectrum. We have therefore carried out photoluminescence studies with an excitation wavelength of 500 nm (see Fig. 2). Two emission bands are observed. One centred at 550 nm is the excitation frequency dependent emission expected from TOPO after heating,¹⁷ whilst the other is a broad emission centred at 690 nm. PLE measurements indicate that this arises from an absorption centred at 570 nm, which is also weakly observed in the absorption spectrum (see inset in Fig. 2). The absorption at 570 nm and emission at 690 nm are absent when the indium precursor is omitted from the preparation, so we assume that they arise from the nanoparticles. Calculations suggest that nanoparticles of diameters around 4.5 nm will have a band-gap of the observed 1.8 eV (emission at 690 nm) if the bandgap of bulk InN is much closer to 0.7 eV, the value recently reported for epitaxially grown hexagonal InN,^{2,3} than to 1.7 eV, the value previously accepted for cubic InN.¹⁹

In conclusion we have discovered a simple method for the synthesis of nanoparticles from a stabilised indium azide. XPS, EDX and electron microscopy are consistent with nanoparticles of InN capped with TOPO. These are hence the first InN nanoparticles for which near band edge emission has been observed. Calculations based on the size of the particles and the wavelength of this emission suggest that the band-gap of cubic InN is much less than the 1.7 eV.

We thank the Dr. B. N. Chaudret for the image of In₂O₃ and Professor P. O'Brien for helpful comments on the manuscript. We also thank the EPSRC and Epichem Ltd. for a studentship (P. S. S.) and the Scottish Higher Education Funding Council for funding of the Organic Semiconductor Centre and the Electron Microscope Laboratory

Notes and references

- 1 A. G. Bhuiyan, A. Hashimoto and A. Yamamoto, *J. Appl. Phys.*, 2003, **94**, 2779.
- 2 J. Wu, W. Walukiewicz, K. M. Yu, J. W. Ager, E. E. Haller, H. Lu, W. J. Schaff, Y. Saito and Y. Nanishi, *Appl. Phys. Lett.*, 2002, **80**, 3967.
- 3 T. Matsuoka, H. Okamoto, M. Nakao, H. Harima and E. Kurimoto, *Appl. Phys. Lett.*, 2002, **81**, 1246.
- 4 S. H. Wei, X. L. Nie, I. G. Batyrev and S. B. Zhang, *Phys. Rev. B*, 2003, **67**, 165209.

-
- 5 S. D. Dingman, N. P. Rath, P. D. Markowitz, P. C. Gibbons and W. E. Buhro, *Angew. Chem., Int. Ed.*, 2000, **39**, 1470.
 - 6 L. Gao, Q. H. Zhang and J. G. Li, *J. Mater. Chem.*, 2003, **13**, 154.
 - 7 Y. J. Bai, Z. G. Liu, X. G. Xu, D. L. Cui, X. P. Hao, X. Feng and Q. L. Wang, *J. Crystal Growth*, 2002, **241**, 189.
 - 8 L. W. Yin, Y. Bando, Y. C. Zhu, D. Golberg and M. S. Li, *Appl. Phys. Lett.*, 2004, **84**, 1546.
 - 9 R. A. Fischer, H. Sussek, A. Miehr, H. Pritzkow and E. Herdtweck, *J. Organomet. Chem.*, 1997, **548**, 73.
 - 10 A. Manz, A. Birkner, M. Kolbe and R. A. Fischer, *Adv. Mater.*, 2000, **12**, 569.
 - 11 C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706.
 - 12 B. J. Bae, J. E. Park, B. Kim and J. T. Park, *J. Organomet. Chem.*, 2000, **616**, 128.
 - 13 P. Bhattacharya, T. K. Sharma, S. Singh, A. Ingale and L. M. Kukreja, *J. Crystal Growth*, 2002, **236**, 5.
 - 14 A. F. Wright and J. S. Nelson, *Phys. Rev. B*, 1995, **51**, 7866.
 - 15 C. Falter, M. Klenner and Q. Chen, *Phys. Rev. B*, 1993, **48**, 16690.
 - 16 K. Soulantica, L. Erades, M. Sauvan, F. Senocq, A. Maisonnat and B. Chaudret, *Adv. Funct. Mater.*, 2003, **13**, 553.
 - 17 O. I. Micic, J. R. Sprague, C. J. Curtis, K. M. Jones, J. L. Machol, A. J. Nozik, H. Giessen, B. Fluegel, G. Mohs and N. Peyghambarian, *J. Phys. Chem.*, 1995, **99**, 7754.
 - 18 H. Okumura, S. Yoshida and T. Okahisa, *Appl. Phys. Lett.*, 1994, **64**, 2997.
 - 19 O. Ambacher, *J. Phys. D: Appl. Phys.*, 1998, **31**, 2653.