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The synthesis of cadmium phosphide nanoparticles using cadmium diorganophosphide precursors†

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An investigation into the thermolysis of diorganophoshides in co-ordinating Lewis base solvents has revealed the importance of not only reaction conditions such as time and temperature, but also the importance of organic groups on the precursor. Nanoparticles of Cd_3P_2 have been synthesised using compounds such as $[MeCd(PBu^t_2)]_3$ in tri-*n*-octylphosphine oxide (TOPO) and 4-ethylpyridine at elevated temperatures. Distinct optical characteristics of quantum confinement effects are observed as the particle's dimensions decrease below the excitonic radius of 180 Å.

Quantum dots are a novel form of semiconductor of theoretical interest but also with the potential to develop as an important class of materials for the electronics industry of the 21st century.[1–3] The properties of semiconductors are usually best described by a model which describes the properties of the material as a continuous solid. The resulting electronic properties of a bulk semiconductor are described in terms of a band gap and its type. Typically bulk samples of CdS, irrespective of their size once greater than around 20 nm, will absorb all electromagnetic radiation with an energy greater than the band gap ($h\nu > 2.42$ eV, 512 nm).[4] The band gap is classified as direct. However, as particles become smaller their electronic structure changes, eventually the description of the material as containing continuous bands breaks down and there are discrete bonding and anti-bonding levels in the material. The electronic structure resembles that of a molecule rather than that of the bulk material. The electronic, and other, properties of the particle will then depend on both its size and the material of which it is composed.

An alternative view of such structures, which has some conceptual appeal, is that they may be viewed as 'super atoms'.[5] Electrons within the solids are confined within an approximately spherical particle with the radius of the quantum dot. The solutions of the Schrödinger equation for this 3-dimensional confinement can be viewed for a single electron as resembling a super atom with electronic states which resemble the orbitals of atoms (s,p,d...). The transitions observed are analogous to those observed in atomic spectroscopy. Consequently one way to view the current excitement, and interest, in this area of science is that we are put into a position in which we can produce a material which has the electronic properties of a 'tailor-made atom'. In the case of the semiconductor CdS these effects were predicted, some years ago, to become important in the size range from around 2–10 nm and Brus and co-workers published a number of keynote papers.[6]

The preparation of stable particles in this size range has presented a considerable challenge to the chemist and such materials have been synthesised from aqueous solutions, adapting the approaches of colloid chemistry,[7] or from organometallic or metal organic compounds.[8] Such small particles have relatively large surface areas and control of their surface chemistry has been important in developing stable forms of these materials and in controlling their properties. The approach can be traced to work by colloid chemists in the 1950s and is used in this work to produce small particles which in size are at the limits of those considered in classical colloid chemistry. Matijevic demonstrated[9] that in a system in which nucleation is rapid and extensive, the set of nuclei initially formed will grow in concert to produce a final product with a narrow particle size distribution.

Not only do these materials represent an interesting challenge as a new class of materials, they may also have practical applications. Quantum dots have been used to make very simple blue light emitting diodes.[10–12] Other potential uses include: amplifying electromagnetic radiation in fibre optic communication systems, and in the use of non-linear optical effects in the region of absorption edges.[13]

From a chemist's point of view, one interest in these materials is that they can be prepared by methods which resemble traditional wet chemical methods.[14] Using this fundamental approach, three distinct schools in the synthetic chemistry of nanocrystalline materials have developed. (1) An essentially aqueous approach, as epitomised by the work of Henglein and Weller on colloidal materials, where often a surface active species such as polyphosphate is used to control the growth of particles.[14] (2) The thermolysis of organometallic species, especially in tri-*n*-octylphosphine oxide (TOPO) at elevated temperatures (*e.g.* 200 °C) is proving to be an important and general method. Initially instigated by Bawendi[15] the use of TOPO seems particularly effective and the method has been widely used.[16–19] The original process involved the reaction of tri-*n*-octylphosphine selenide with dimethylcadmium in hot TOPO which acts as a dispersing medium and capping agent. Several modifications of the method have been reported, including the preparation of high quality material using single molecule precursors based on dithio- or diseleno-carbamates.[18,19] (3) A third general approach can be defined in which the growth of material is physically limited, *e.g.* within a micelle [20] or a polymer matrix.[21] This however restricts the size of the particle to the dimensions of the reacting vessel, such as the pores of a zeolite.[22]

The types of chemical reactions used in the preparation of these materials are summarised in Table 1.

The majority of the successful work has to date involved II–VI materials with the aim of investigating the novel opto-electrical,[23] catalytical,[24] and non-linear properties [25] that result from size quantization effects. The photo-physics of such materials have been investigated thoroughly.[26,27] III–V systems are now also a topic of investigation, however these compound semiconductors are intrinsically harder to prepare than the relatively ionic II–VI materials. Bare metal atoms or ions are unstable as precursors, so complexes such as In–TOPO[28] are utilised. Decomposition of such compounds is

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Table 1 Some typical reactions used in the synthesis of nanodispersed compound semiconductors

Reaction	Conditions
$Cd^{2+} + H_2S \rightarrow CdS_{nano} + 2H^+$	0 °C, polyphosphate,[14] aqueous solution or in a micelle[20]
$Pb^{2+} + H_2S \rightarrow PbS_{nano} + 2H^+$	Polymer supported[21]
$Cd^{2+} + H_2Se \rightarrow CdSe_{nano} + 2\ H^+$	Aqueous solution[10]
$(Me)_2Cd + SeP(n\text{-}C_8H_{10})_3 \rightarrow (CdSe)_n/n$TOPO + organic products	*e.g.* 200 °C, in TOPO[15]
$(Me)_2Cd + S(SiMe_3)_2 \rightarrow (CdS)_n/n$TOPO + organic products	*e.g.* 200 °C, in TOPO[15]
$(Me)Cd(E_2CNEt_2) \rightarrow (CdE)_n/n$TOPO + organic products	*e.g.* 200 °C, in TOPO, E = S or Se[18,19]
$InCl_3$ + TOPO → '$InCl_3$·TOPO' (complex) followed by	100 °C 12 h in TOPO
'$InCl_3$·TOPO' + $P(SiMe_3)_3 \rightarrow (InP)_n/n$TOPO (amorphous)	Days at 265 °C, in TOPO, annealing gave a crystalline TOPO coated product[28]

a high energy process, and the nucleation and growth steps are hard to separate.[29]

Other potentially useful, but unusual, systems such as the II–V and III–VI compounds have received relatively little attention, even though compounds such as cadmium phosphide are known to show interesting quantum size effects.[30,31] Only a handful of methods have been published, possibly due to the difficulties associated with compounds less ionic than the II–VI or III–V systems. The difficulties have been described in some depth elsewhere, and include the production of amorphous materials, diffraction pattern problems, and instability in air.[32,33] Cadmium phosphide nanoparticles have previously been synthesised by a colloidal route, and their physical properties investigated.[33] An organometallic, sol–gel like route has also been developed, resulting in capped quantum dots from a silylated single source precursor.[34]

$$Cd[P(SiPh_3)_2]_2 + 4/3\ MeOH \rightarrow Q\text{-}Cd_3P_2 + \text{other products}$$

Diorganophosphides are possible single source precursors to phosphide containing semiconductors and have been known since 1962, when $Zn(PPh_2)_2$ was synthesised.[35] Characterisation proved difficult due to the polymeric nature of the solid, and analysis extended no further than the confirmation of the stoichiometry. Later, Cowley *et al.* synthesised $[Zn_2(Bu^t{}_2P)_2(OH)(\mu\text{-}OH)]_2$ by the serendipitous inclusion of water in an attempt to prepare a crystalline sample of $Zn(PBu^t{}_2)_2$.[36] Cowley also synthesised $M(EBu^t{}_2)_3$,[37] where M = In, Ga, Al, E = P, As. The first cadmium diorganophosphide has also been synthesised, $[MeCd(PBu^t{}_2)]_3$.[38] This work follows our communication in which we reported the synthesis of TOPO capped Cd_3P_2.[31]

Experimental

Dimethylcadmium (99.99%) was obtained from Epichem, $HP(Ph)_2$ (99%) was obtained from Strem, $HP(Bu^t)_2$ (99%), tri-*n*-octylphosphine (90%), methanol (99.9+%), toluene (99.9+%), anhydrous hexane (99.9+%), anhydrous THF (99.9+%), light petroleum (bp 40–60 °C) (99.9+%) and pyridine (99.9+%) were all obtained from Aldrich and used as received. Tri-*n*-octylphosphine oxide (90%) was obtained from Aldrich and purified as described in the literature.[39] 4-Ethylpyridine (99%) was obtained from Aldrich, degassed and stored under nitrogen over 4 Å molecular sieves.

Synthesis of $[MeCd(PBu^t{}_2)]_3$

A typical synthesis follows, standard Schlenk line techniques were used.

Me_2Cd (0.96 g, 67 mmol) was reacted with 2.5 ml $HPBu^t{}_2$ (1.97 g, 134 mmol) in dry hexane (10 ml). Effervescence occurred, and after 20 minutes of reaction, the flask was wrapped in foil and placed in a freezer. After a matter of hours, colourless crystals formed. This reaction was also carried out in tri-*n*-octylphosphine, 4-ethylpyridine, and with no solvent producing a white powder. Once the crystals were removed from the solvent, or upon agitation, the crystals effloresce, and produce a powder.

$[MeCd(PBu^t{}_2)]_3$. ^1H NMR (C_6D_6, 25 °C, 400 MHz), δ 0.13 (s, CH_3, 9H), 1.15 (d, $Bu^t{}_2$, 54H, $^3J_{PH} = 11.2$ Hz), 1.30 (satellites $^{111}Cd/^{113}Cd$); ^{31}P NMR, δ 20.39 (s, $PBu^t{}_2$); $^{13}C\{^1H\}$ NMR (100 MHz), δ 31.91 [$C(CH_3)_3$], 34.21 [$C(CH_3)_3$]; IR bands ν/cm^{-1} (w = weak, s = strong, b = broad) 1620 (w), 1261 (w), 1169 (s), 1100 (s), 1029 (s), 923 (s), 822 (s), 814 (s), 721 (w), 669 (s), 286 (vb,vs).

Owing to the insoluble nature of the compound, the NMR sample was prepared using the method previously described by Beachley *et al.*[40] The ^1H and ^{31}P NMR results correlate with previous reports. $^{13}C\{^1H\}$ NMR spectra were not previously reported, and no resonance corresponding to the methyl group was observed.[38]

Synthesis of $[MeCd(\mu\text{-}PPh_2)]_3(HPPh_2)_2$

A typical synthesis follows, standard Schlenk line techniques were used.

Me_2Cd (0.51 g, 3.58 mmol) was reacted with $HPPh_2$ (1.2 ml, 6.98 mmol) in dry hexane (10 ml), forming a green solid. Removal of the solvent and volatiles *in vacuo*, followed by washing with dry methanol left a white solid. Attempted recrystallisation from a number of solvents failed. The reaction was also carried out in tri-*n*-octylphosphine, 4-ethylpyridine, and THF giving the same results.

$[MeCd(\mu\text{-}PPh_2)]_3(HPPh_2)_2$. ^1H NMR (C_6D_6, 25 °C, 400 MHz), δ 0.54 (s, CH_3, 9H), 5.19 (d, $HPPh_2$, 2H, $^1J_{PH} = 215.51$ Hz), 7.0–7.6 (m, PPh, 50H); ^{31}P NMR, δ −39.93 (s, H-PPh_2), 17.78 (s, μ-PPh_2); ^{13}C NMR (100 MHz), δ 134.28 (d, *ortho*-C), 128.78 (d, *meta*-C), 128.54 (s, *para*-C). IR bands (ν/cm^{-1}) (w = weak, b = broad, s = strong) 2935 (aryl C–H) (s), 2332 (P–H) (w), 1911, 1726, 1261, 721.

The NMR data suggest a structure similar to $\{[EtZn(\mu\text{-}PPh_2)]_3(HPPh_2)_2{\cdot}thf\}$,[41] previously reported by Wright *et al.*, with $HPPh_2$ bound to the metal *via* the P atom. No *ipso*-carbon resonance was observed. NMR studies on metal salts of diphenylphosphine show a major shift in the *ipso*-carbon resonance of up to 30 ppm with small metals.[42] In our structure, a large metal such as cadmium is expected to attenuate such a shift. No methyl resonance was observed. As with previous diorganophosphides,[41] elemental analysis is hampered by the presence of co-ordinating solvent molecules, giving irreproducible results. Mass spectrometry studies show a species with a mass of *ca.* 1300 mass units, confirming the trimeric structure.

Synthesis of nanoparticles

All manipulations were carried out in an inert atmosphere, using standard Schlenk line techniques.

Owing to the relative insolubility of the isolated precursor, $[MeCd(PBu^t{}_2)]_3$ (1 g) was synthesised *in situ* with TOP

(10 ml), producing a pale green solution. The solution was then injected into degassed TOPO (25 g) at the desired temperature (100 °C or 250 °C). After 30 min of growth, the heating was discontinued and the solution allowed to cool to 60 °C. Dry methanol (50 ml) was then added and the mixture stirred until room temperature was reached. Centrifugation of the suspension yielded a dark solid which was then dispersed in dry toluene. Further centrifugation yielded solid waste products, which were discarded. The toluene solutions resulting from the pyrolysis varied in colour, from bright yellow (100 °C) to dark brown (250 °C).

For 4-ethylpyridine capped nanoparticles, 1 g of precursor was synthesised in the solvent, and was then heated to reflux temperature (167 °C). After 2 h, heating was discontinued and the reaction vessel allowed to cool to room temperature. Addition of light petroleum resulted in a flocculant, which could be re-dispersed in either pyridine or 4-ethylpyridine. Further centrifugation yielded solid waste products which were discarded. The final solution was deep red in colour. Size selective precipitation was carried out as previously described[15] giving gradually smaller fractions which were characterised by UV spectroscopy.

Instrumentation and physical measurements

^{1}H NMR, ^{31}P NMR, ^{13}C{^{1}H} NMR spectra were obtained using a JEOL ESX 270 NMR machine, using either $CDCl_3$ or C_5D_5N. IR spectra were recorded on samples as pressed discs (1% in CsI) on a Perkin Elmer 1720X machine. Photoluminescence spectra of toluene/4-ethylpyridine solutions were recorded on a Spex fluorometer spectrophotometer at room temperature, and UV–VIS optical spectra were recorded using a Philips PU 8710 spectrophotometer. High resolution transmission electron microscopy (HRTEM; 400 KV) was carried out on at the University of Oxford using a JEOL 4000EX on samples deposited on carbon coated copper grids. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was carried out on an ARL machine. The samples were acid digested (nitric and perchloric acids) and taken to dryness prior to leaching to give a final matrix of 1 M HCl. Multi-element analysis by ICP-AES was obtained using conventional nebulisation under standard instrumental conditions.

Results and discussion

Thermolysis of $[MeCd(\mu\text{-}PPh_2)]_3(HPPh_2)_2$ and $[MeCd(PBu^t_2)]_3$

Thermolysis of $[MeCd(PBu^t_2)]_3$ resulted in different products, depending upon the reaction conditions. In 4-ethylpyridine at 100 °C for 30 min a nanodispersed product was formed with a Cd : P ratio of 1.6 : 1 (*ca.* Cd_3P_2 as determined by ICP-AES). High temperatures (above 100 °C) resulted in a higher cadmium content with a ratio up to 7 : 1. Stoichiometries from TOPO capped nanoparticles are invalid as the capping group itself contains phosphorus. The observed Cd : P ratio can be explained if we assume that two different temperature dependent mechanisms are operating: (1) a process involving β-hydrogen elimination may dominate at lower temperatures (under 100 °C); (2) and reductive elimination at higher temperatures (over 100 °C).

This hypothesis is supported by a related study of the thermolysis of $[MeCd(\mu\text{-}PPh_2)]_3(HPPh_2)_2$, in which there are no β-hydrogens. Upon prolonged heating, the only reaction product was bulk elemental cadmium. These observations highlight the importance of the decomposition mechanism of the precursor in determining reaction products.

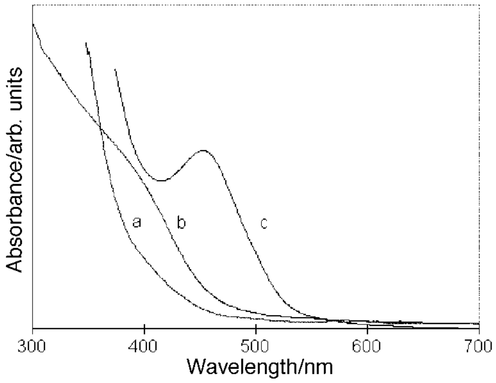

Fig. 1 UV–VIS spectra of different nanoparticle solutions: a) 7th fraction of 4-ethylpyridine capped particles synthesised at 167 °C; b) TOPO capped particles synthesised at 100 °C; c) unfractionated 4-ethylpyridine capped particles synthesised at 167 °C.

Optical properties of Cd_3P_2 nanoparticles

The size quantization of Cd_3P_2 is pronounced.[30,31] This effect can be attributed to the large bulk exciton diameter which is found to be 361 Å when taking the reduced exciton mass as 0.454 (units of the free electron mass) and the relative permittivity as 15.5.[43] The diameter is large when compared to InP (150 Å) and CdSe (80 Å) and the resulting properties are best illustrated by optical spectroscopy. UV spectra of the solutions of Cd_3P_2 in toluene/4-ethylpyridine showed the typical blue shift in the bandgap associated with nanoparticulate semiconductors. TOPO capped particles show a band edge around 2.60 eV (475 nm), (Fig. 1) irrespective of the synthesis temperature. Samples synthesised at low temperatures (100 °C) showed distinct shoulders in the spectrum, whilst higher temperature samples (250 °C) show a similar spectrum without the sharp features. 4-Ethylpyridine capped nanoparticles showed a smaller shift in the absorption spectrum with an excitonic peak at about 456 nm, and a band edge at 2.44 eV (507 nm) as determined by the direct band gap method.[44] Size selective precipitation gave smaller particles and showed a decrease in the intensity of the excitonic feature. The seventh fraction resembled that of TOPO capped particles, indicating that the 4-ethylpyridine particles are larger in size. This hypothesis is endorsed by the colour of the samples, indicating that TOPO capped particles are smaller. The optical spectra are similar to those reported for Cd_3P_2 prepared by colloidal routes.[33]

Photo-luminescence of various solutions gave emissions of varying intensity which depended upon the conditions of synthesis. TOPO capped nanocrystals synthesised by injection into hot solvent above 100 °C showed a weak emission between 525 and 675 nm. Smaller nanoparticles are expected to have an increased emission due to the increase oscillator strength (Fig. 2). Samples prepared below 100 °C show strong luminescence (Fig. 2). Samples synthesised by injection at low temperature (100 °C), followed by slow growth displayed strong luminescence at higher wavelengths, with no loss of peak intensity. Samples prepared in 4-ethylpyridine show similar luminescent properties. Emission spectra taken from the initial sample and selected smaller size fractions show increase luminescence from particles with a smaller diameter (Fig. 3). All luminescence spectra have a substantial Stokes' shifts, previously attributed to the systematic metal vacancies being effective trapping sites.[30]

NMR, IR and HRTEM studies on Cd_3P_2 nanoparticles

Room temperature solution and solid state MAS ^{31}P NMR experiments on TOPO capped nanocrystals showed only a resonance at 50 ppm which can be attributed to the TOPO

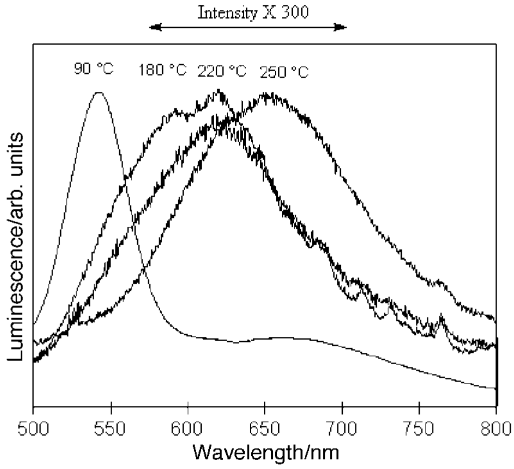

Fig. 2 Luminescence spectra of TOPO capped Q-Cd_3P_2, synthesised at different temperatures.

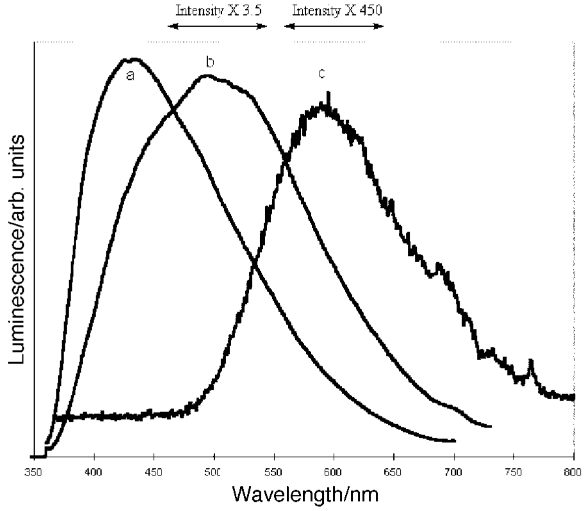

Fig. 3 Luminescence spectra of various 4-ethylpyridine capped Q-Cd_3P_2: a) 7th fraction; b) 4th fraction; c) initial solution prior to fractionation.

capping agent. No phosphorus resonance attributed to the Cd_3P_2 core could be observed.

^{31}P MAS experiments on 4-ethylpyridine capped particles display a multiplet of resonances at 37.8, 47.1 and 64.1 ppm. Bulk Cd_3P_2 has resonances at -140, -162, -178 ppm.[45] An upfield shift of this type has been observed in GaP.[46] Buhro's route to Cd_3P_2 reports a solid state NMR with one broad peak at -220 ppm.[32] The origin of resonances in nanocrystal NMR is uncertain, and is the subject of current research. ^1H solution NMR showed the capping group for both TOPO and 4-ethylpyridine capped quantum dots.

IR spectroscopy on TOPO passivated samples shows a shift in the ν(P=O) peak normally found at 1147 cm^{-1}, to 1126 cm^{-1}, indicating P=O complexing to surface cadmium.[17] IR bands at 227, 255 and 303 cm^{-1} were found as predicted for Cd_3P_2.[47] IR on 4-ethylpyridine capped particles show all stretches and bends associated with 4-ethylpyridine, with no shift in peaks associated with hindrance in ring stretching as previously described.[48] Peaks were also observed at 231, 246 and 314 cm^{-1}, again attributable to Cd_3P_2 except the 314 cm^{-1} feature which can be assigned to the ring nitrogen binding to surface cadmium.

HRTEM images of 4-ethylpyridine capped nanoparticles show crystalline nanoparticles approximately 4 nm in diameter. Particles were found to be slightly prolate, with aspect ratios around 1.3. Dark images were also observed and assumed to be amorphous material. The 4-ethylpyridine capped particles show a hexagonal structure (Fig. 4). Using the Brus equation[49] to estimate the size of nanoparticles with a band gap of 2.44 eV gave a prediction of 4.04 nm; this is found to be in good agreement with experimental data (Fig. 5). A TOPO capped nanocrystal synthesised at 100 °C (Fig. 6), approximately 5 nm in size, shows a lattice spacing of 0.92 Å attributed to the 226 plane of Cd_3P_2 (literature value 0.91 Å).[50] The Brus equation for such a sample predicts a diameter of 3.72 nm, however the approximation for particles is known to fail at such dimen-

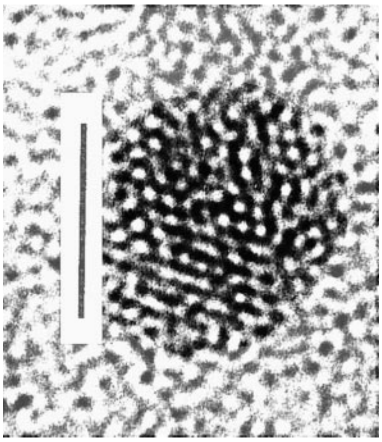

Fig. 4 HRTEM image of a 4-ethylpyridine capped Cd_3P_2 quantum dot, synthesised at 167 °C. Bar = 3 nm.

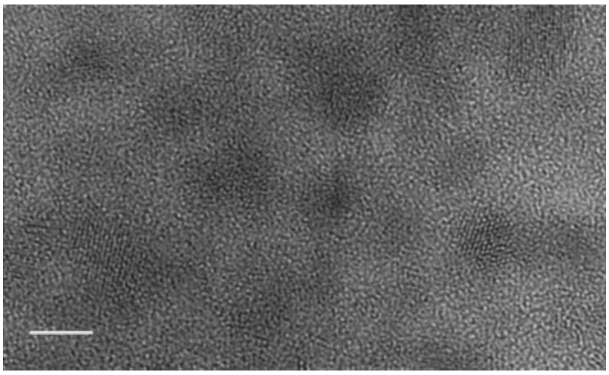

Fig. 5 HRTEM image of an array of 4-ethylpyridine capped Q-Cd_3P_2, synthesised at 167 °C. Bar = 3 nm.

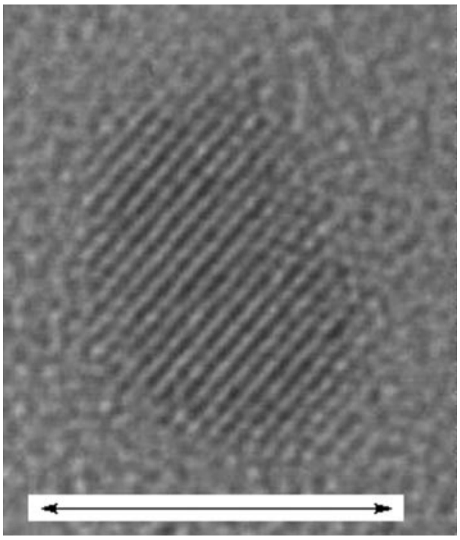

Fig. 6 HRTEM Image of a TOPO capped Cd_3P_2 nanoparticle, synthesised at 100 °C. Bar = 5 nm.

sions.[51] As with other routes to II–V materials, no X-ray diffraction pattern was observed for the quantum dots.[32,34] Samples with high levels of cadmium as determined by ICP-AES were found to have XRD patterns for elemental cadmium and cadmium oxide.

Conclusion

We have demonstrated that a specific single source molecular precursor can be successfully used in a variety of co-ordinating solvents to produce organically passivated cadmium phosphide nanocrystals. Single molecular precursors containing β-hydrogens can be utilised in producing high quality quantum dots, *ca.* 4 nm in diameter, with band gaps up to 2.44 eV. Different Lewis base solvents result in dots with different optical properties, attributable to different sizes of nanoparticles. In systems such as the II–V compounds, pronounced quantum size effects mean small differences in size result in markedly different degrees of confinement, hence the strong differences in optical spectra. Luminescence is found to be strong in the absence of elemental cadmium, a potential byproduct from reductive elimination. We are also investigating other single source routes to II–V and III–V nanoparticles in our laboratories.

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References

1 M. L. Steigerwald and L. E. Brus, *Acc. Chem. Res.*, 1990, **23**, 1834.
2 H. Weller, *Adv. Mater.*, 1993, **5**, 88.
3 A. P. Alivisatos, *Science*, 1996, **271**, 933.
4 D. R. Lide, *CRC Handbook of Chemistry and Physics*, 73rd edition, section 12–82, 1993, CRC Press, Boca Raton.
5 S. Taucha, *MRS Bull.*, 1998, **23**, 49.
6 L. Brus, *J.Phys. Chem.*, 1986, **90**, 2555.
7 R. Rosetti, J. L. Ellison, J. M. Gibson and L. E. Brus, *J. Phys. Chem.*, 1984, **80**, 4464.
8 S. M. Stuczynski, J. G. Brennan and M. L. Steigerwald, *Inorg.Chem.*, 1989, **28**, 4431.
9 E. Matijevic, *Ann. Rev. Mater. Sci*, 1985, **15**, 483.
10 M. Gao, B. Richter and S. Kirstein, *Adv. Mater.*, 1997, **10**, 802.
11 M. Schlamp, X. Peng and A. P. Alivisatos, *J. Appl. Phys.*, 1997, **82**, 5837.
12 V. L. Colvin, M. C. Schlamp and A. P. Alivisatos, *Nature*, 1994, **370**, 354.
13 M. Burt, *Br. Telecommun. Eng.*, 1996, **15**, 230.
14 L. Spanhel, M. Haase, H. Weller and A. Henglein, *J. Am. Chem. Soc.*, 1987, **109**, 5649.
15 C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706.
16 A. A. Guzelian, U. Banin, A. V. Kadavanich, X. Peng and A. P. Alivisatos, *Appl. Phys. Lett.*, 1996, **69**, 1432.
17 J. E. Bowen Katari, V. L. Colvin and A. P. Alivisatos, *J. Phys. Chem.*, 1994, **98**, 4109.
18 T. Trindade and P. O'Brien, *Adv. Mater.*, 1996, **8**, 161.
19 T. Trindade, P. O'Brien, *J. Mater. Chem.*, 1996, **6**, 343.
20 A. R. Kortan, R. Hull, R. L. Opila, M. G. Bawendi, M. L. Steigerwald, P. J. Carrol and L. E. Brus, *J. Am. Chem. Soc.*, 1990, **112**, 1327.
21 W. Mahler, *Inorg. Chem.*, 1988, **112**, 6858.
22 Y. Wang and N. Herron, *J. Phys. Chem.*, 1987, **91**, 257.
23 A. Henglein, *Chem. Rev.*, 1989, **89**, 1861.
24 A. Henglein, *Top. Curr. Chem.*, 1988, **143**, 113.
25 H. Uchida, T. Matsunaga, H. Yoneyama, T. Sakata, H. Mori and T. Sasaki, *Chem. Mater.*, 1993, **5**, 716.
26 M. Nirmal, D. J. Norris, M. Kuno, M. G. Bawendi, A. L. Efros and M. Rosen, *Phys. Rev. Lett.*, 1995, **75**, 3728.
27 M. Nirmal, C. B. Murray, D. J. Norris and M. G. Bawendi, *Z. Phys. D*, 1993, 361.
28 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.
29 J. R. Heath and J. J. Shiang, *Chem. Soc. Rev.*, 1998, **27**, 65.
30 A. Kornowski, R. Eichberger, M. Giersig, H. Weller and A. Eychmuller, *J. Phys. Chem.*, 1996, **10**, 12467.
31 M. Green and P. O'Brien, *Adv. Mater.*, 1998, **10**, 527.
32 W. E. Buhro, *Polyhedron*, 1994, **13**, 1131.
33 H. Weller, A. Fojtik and A. Henglein, *Chem. Phys. Lett.*, 1985, **117**, 485.
34 M. A. Matchett, A. M. Viano, N. L. Adolphi, R. D. Stoddard, W. E. Buhro, M. S. Conradi and P. C. Gibbons, *Chem. Mater.*, 1992, **4**, 508.
35 K. Issleib and H. O. Froelich, *Chem. Ber*, 1962, **95**, 375.
36 A. M. Arif, A. H. Cowley, R. A. Jones and S. U. Koschmieder, *J. Chem. Soc., Chem. Commun.*, 1987, 1319.
37 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.
38 B. L. Benac, A. H. Cowley, R. A. Jones, C. M. Nunn and T. C. Wright, *J. Am. Chem. Soc.*, 1989, **111**, 4986.
39 R. A. Zingaro and J. C. White, *J. Inorg. Nucl. Chem.*, 1960, **12**, 315.
40 O. T. Beachley and J. D. Maloney, *Organometallics*, 1997, **16**, 4016.
41 M. G. Davidson, A. J. Edwards, M. A. Paver, P. R. Raithby, C. A. Russell, A. Steiner, K. L. Verhorevoort and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1995, 1989.
42 Y. Yokoyama and K. Takahashi, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3485.
43 Landolt-Bernstein, *Numerical data and functional relationships in science and technology, new series*, vol. 17f, Springer, Berlin, 1983, pp. 183.
44 J. I. Pankove, *Optical processes in semiconductors,* Dover Publications Inc., New York, 1970, p. 78.
45 N. L. Adolphi, R. D. Stoddard, S. C. Goel, W. E. Buhro, P. C. Gibbons and M. S. Conradi, *J. Phys. Chem. Solids*, 1992, **53**, 1275.
46 J. E. MacDugal, H. Eckert, G. D. Stucky, N. Herron, Y. Wang, K. Moller, T. Bein and D. Cox, *J. Am. Chem. Soc.*, 1989, **111**, 8006.
47 M. J. Gelton, *Lect. Notes. Phys.*, 1982, **152,** 167.
48 T. Trindade, PhD thesis, University of London, 1996.
49 L. E. Brus, *J. Chem. Phys.*, 1983, **79**, 5566.
50 X-Ray powder diffraction file, *ASTM special technical publication 48-j*, 2-1181.
51 H. Weller, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 41.

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