

A Novel Metalorganic Route to Nanocrystallites of Zinc Phosphide

Mark Green[†] and Paul O'Brien^{*‡}

Department of Chemistry, Imperial College of Science, Technology and Medicine,
South Kensington, London SW7 2AY, UK

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Novel chemical routes to high-quality nanodispersed quantum dots of Zn₃P₂ have been developed. The precursors Me₂Zn and HP^tBu₂ were thermolyzed in TOPO (tri-*n*-phosphine oxide) or 4-ethylpyridine, resulting in capped nanomaterial. The nanoparticulates described in this work were capped with either TOPO or 4-ethylpyridine and had optical properties similar to II₃-V₂ compounds prepared by aqueous routes. The as-prepared nanoparticulates were polydispersed (standard deviation of ca. 20%) and appeared to be a mixture of both crystalline and amorphous materials. The nanoparticles were found show quantum confinement effects with band gaps shifted to much higher energies. Luminescence was strong and exhibited large Stokes shifts relative to the absorption edge, probably due to metal vacancies being efficient trapping sites for charge carriers.

Introduction

The preparation and study of nanodimensional semiconductor particles is at present a popular topic for research.^{1–3} These materials have unique optical properties resulting from the three-dimensional confinement of carriers in a quantum well and may be useful in devices such as light-emitting diodes.^{4–6} The majority of research has centered on II–VI materials as they readily form high-quality, crystalline particles.⁷ More recently, despite the greater inherent difficulties in their chemistry, III–V compounds have been prepared.^{8–10}

The most popular routes to quantum dots have involved aqueous colloidal approaches, in which growth is controlled using nucleation kinetics or stabilizers such as polymers.¹¹ Other methods include the use of a restricted reaction space as provided by zeolites or micelles.¹² However, one of the more important, recently

developed, routes involves thermolysis of a metal alkyl and chalcogen source in a hot coordinating solvent, such as tri-*n*-octylphosphine oxide (TOPO).⁷ The method was originally developed to produce organically passivated II–VI quantum dots (especially CdSe) and has been adapted to produce III–V^{8–10} and IV–VI^{13,14} quantum dots. Others semiconductors such as the II₃-V₂ materials have attracted less attention despite having distinct quantum size effects.

Bulk II₃-V₂ compounds have many potential uses including in infrared detectors, lasers, and solar cell technology.^{15–20} Due to the large excitonic radii of these materials, they are expected to exhibit pronounced size quantization effects. An electron in such a compound will become confined in crystals much larger than for the analogous II–VI or III–V materials. However, typical methods employed for the preparation of bulk II₃-V₂ compounds, such as direct combination of stoichiometric amounts of the desired elements in a multi-zone furnace, are not readily adaptable to nanocrystal synthesis.²¹ Nanocrystals of Zn₃P₂ and Cd₃P₂ have been synthesized by the injection of phosphine gas into an aqueous solution of the metal salt.²² Other methods

[†] Present address: Oxonica Ltd., Begbroke Science and Business Park, Sandy Lane, Yarnton, Oxford OX5 1PF, UK.

[‡] Present address: Department of Chemistry and The Manchester Materials Science Centre, University of Manchester, Oxford Rd, Manchester M13 9PL, UK.

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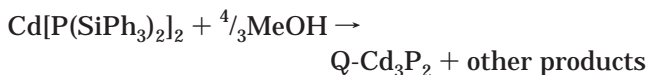
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include the alcoholysis of a silylated single-source precursor.^{23,24}



Cadmium phosphide, Cd_3P_2 , has been the most extensively investigated material in this class, with few reports on Zn_3P_2 . Recently, we have reported an organometallic route to high-quality Cd_3P_2 .^{25,26} In this paper, we report a novel organometallic route to organically passivated nanocrystalline Zn_3P_2 .

Zinc phosphide (Zn_3P_2) is a relatively poorly characterized material, only recently investigated as a novel optoelectronic material.^{27–29} The bulk material is isostructural with Cd_3P_2 and has a band gap of 1.40 eV.^{21,30} Pseudopotential calculations of the electronic structure are complicated by the unusual structure and information on the band structure remains uncertain.³¹

Zinc phosphide nanocrystallites have been briefly reported in the literature. The optical spectrum from a sample prepared by a colloidal route has previously been reported.²² Electron microscopy images of nanoparticulate Zn_3P_2 from the reaction between zinc alkoxide and tris(trimethylsilyl)phosphine have also been reported.³² No experimental details were given in either case.

Experimental Section

Dimethylzinc (99.99%) was obtained from Epichem, $\text{HP}(\text{Bu}^t)_2$ (99%), tri-*n*-octylphosphine (TOP) (90%), methanol (99.9+%), toluene (99.9+%), light petroleum (99.9+%), and pyridine (99.9+%) were all obtained from Aldrich and used as received. Tri-*n*-octylphosphine oxide (TOPO) (90%) was obtained from Aldrich and purified as described in the literature.³³ 4-Ethylpyridine (99%) was obtained from Aldrich, degassed, and stored under nitrogen over 4 Å molecular sieves.

Instrumentation. ¹H NMR and ³¹P NMR spectra were obtained using a JEOL ESX 270 instrument in either deuterated chloroform or pyridine. IR spectra were obtained from samples as pressed disks (1% in CsI) using a Perkin-Elmer 1720X machine. Photoluminescence spectra of toluene/4-ethylpyridine solutions were recorded on a Spex fluorometer at room temperature, and electronic spectra were recorded using a Philips PU 8710 spectrophotometer. High-resolution transmission electron microscopy (HRTEM) (400 kV) was carried out at the University of Oxford using a JEOL 4000EX on samples deposited on carbon-coated copper grids. Inductively coupled plasma atomic emission spectroscopy (ICPAES) was carried out on an ARL machine. The samples were acid digested (Nitric/Perchloric) and taken to dryness prior to leaching to give a final matrix of 1 M HCl. Multielement

analysis by ICPAES was obtained using conventional nebulization under standard instrumental conditions.

Synthesis of TOPO-Capped Zn_3P_2 . In a typical experiment, 1.00 g (10.0 mmol) of Me_2Zn was mixed with 0.97 g (6.00 mmol) of HP^tBu_2 in 5 mL of tri-*n*-octylphosphine (TOP). The TOP solution was injected into 25 g of degassed tri-*n*-octylphosphine oxide at either 150 or 250 °C. After growth for 3 h, the heating was discontinued and the solution allowed to cool to 60 °C. Dry methanol (50 mL) was then added and the mixture allowed to cool to room temperature. Centrifugation of the suspension yielded a dark solid, which was then dispersed in toluene. Further centrifugation yielded solid waste products, which were discarded. Size selective precipitation of TOPO-capped particles was not attempted.⁷

Synthesis of 4-Ethylpyridine-Capped Zn_3P_2 . In a typical experiment, 1.00 g (10.0 mmol) of Me_2Zn was mixed with 0.97 g (6.00 mmol) of HP^tBu_2 in 20 mL of dry 4-ethylpyridine. The ethylpyridine solution was then heated to 167 °C for up to 30 h. The nanoparticles were isolated as a powder by allowing the reaction mixture to cool to room temperature followed by the addition of dry petroleum ether (40 mL). The resulting precipitate was isolated by centrifugation and could be redispersed in 4-ethylpyridine or pyridine. Further centrifugation removed solid waste products. Allowing the precipitated quantum dots to dry resulted in reduced solubility. This suggests the labile pyridine species desorbs from the surface on prolonged drying.

Size fractionation of 4-ethylpyridine-capped Q- Zn_3P_2 was achieved by addition of a small amount of nonsolvent (light petroleum ether) to a 4-ethylpyridine solution until turbidity was observed. The solution was then centrifuged to separate the solid. This procedure was carried out with the same solution a number of times, giving fractions containing increasingly smaller sized particles.

Results and Discussion

Organically passivated Zn_3P_2 was prepared from the thermolysis of Me_2Zn and HP^tBu_2 in polar Lewis base solvents. The two compounds were mixed in TOP and injected into TOPO (at various temperatures) to prepare the TOPO-capped nanoparticles. Nanoparticles of Zn_3P_2 capped with 4-ethylpyridine were prepared by mixing the precursors in 4-ethylpyridine followed by heating to reflux. The use of a related precursor, the primary phosphine $\text{H}_2\text{P}^t\text{Bu}$, as an alternative phosphorus source to the usual precursor (PH_3) in low-pressure metalorganic chemical vapor deposition (MOCVD) has proved successful, and several phosphorus-containing semiconductors have been synthesized.^{34,35} Other alkylphosphines such as cyclopentylphosphine show prereaction in MOCVD and are considered less useful as precursors.^{36,37}

Optical Properties of Q- Zn_3P_2 . Thermolysis of Me_2Zn and HP^tBu_2 in hot TOPO or 4-ethylpyridine gave colloidal suspensions of nanoparticulates. Isolation of the particles by the addition of a nonsolvent (methanol/TOP, light petroleum/4-ethylpyridine) resulted in the production of a white powder for TOPO-capped particles and an orange powder for 4-ethylpyridine-capped particles. These observations suggest that particles capped with 4-ethylpyridine are larger; however, size quantiza-

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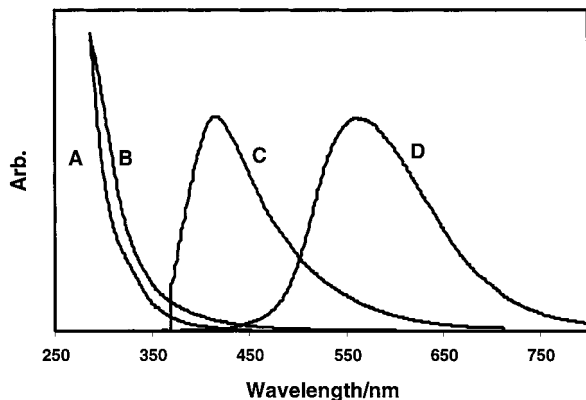


Figure 1. Optical spectra of different samples of TOPO-capped Q-Zn₃P₂: (a) absorption (synthesized at 150 °C); (b) absorption (synthesized at 250 °C); (c) emission (synthesized at 150 °C); (d) emission (synthesized at 250 °C).

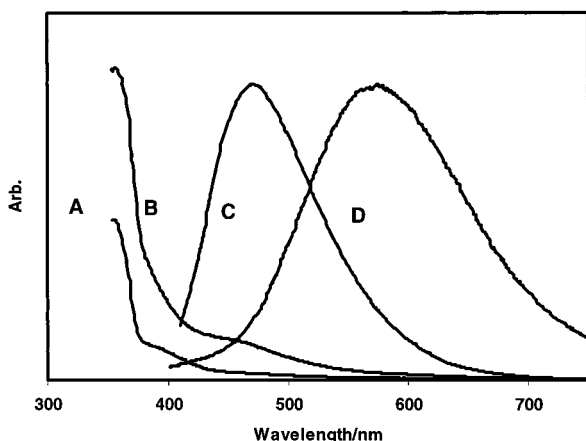


Figure 2. Optical spectra of different samples of 4-ethylpyridine-capped Q-Zn₃P₂: (a) absorption (synthesized at 167 °C for 4 h); (b) absorption (synthesized at 167 °C for 30 h); (c) emission (synthesized at 167 °C for 4 h); (d) emission (synthesized at 167 °C for 30 h).

tion effects for II₃-V₂ compounds are very sensitive to small changes in particle size.

Bulk Zn₃P₂ has a band gap of 1.4 eV (885 nm),³⁰ which is increased in nanoparticles due to quantum confinement. The UV spectra of nanoparticulate Zn₃P₂ revealed a distinct blue shift (Figures 1 and 2). Using the direct band gap method, Zn₃P₂ (HP^tBu₂ and Me₂Zn, TOPO, 150 °C, 3 h) was found to have a band edge at 3.55 eV (349 nm) (Figure 1). Materials synthesized at 250 °C for 3 h were found to have a band edge of 3.30 eV (375 nm) (Figure 1). The band edge position for both sets of particles indicates growth to similar sizes with, as expected, the lower temperature of synthesis producing slightly smaller particles (Figure 1). These observations are similar to those made for TOPO-capped Q-Cd₃P₂, for which temperature did not greatly affect the size of the particles produced.²⁵ In contrast, for II-VI materials, size is found to be markedly temperature dependent.^{7,38} TOPO-capped Zn₃P₂ is comparable to the smallest reported particles of colloidal Cd₃P₂, which are also white and are reported to have a band gap at ca. 4.0 eV (309 nm).¹¹

4-Ethylpyridine-capped particles of Zn₃P₂ (167 °C for up to 30 h) have a smaller band gap, indicating slightly

larger particles than the TOPO-capped Q-Zn₃P₂ (Figure 2). The particles were orange/brown in color. An aliquot taken after 4 h at 167 °C had a band edge at 2.87 eV (431 nm), and an aliquot after 30 h shows a band edge at 2.33 eV (531 nm) (Figure 2). Fractionation of the 30 h sample gave a gradual blue shift for the later size fractions, indicating the larger particles precipitate first. Fraction 10 produced a pale yellow solid with an excitonic peak at ca. 450 nm (2.74 eV), consistent with a more monodispersed sample.

Luminescence of Q-Zn₃P₂. There are no reports in the literature regarding the luminescence of Q-Zn₃P₂. A sizable Stokes shift is observed in the photoluminescence from the band edge in all samples, similar to the emission observed from Q-Cd₃P₂.³⁹ This effect may be explained by systematic metal vacancies in the lattice being efficient trapping sites for electrons. The polycrystalline material reported here may also exhibit a high degree of trapping at glide planes mismatches. The TOPO-capped sample synthesized at 250 °C had a relatively broad emission at 563 nm (2.20 eV), with the smaller particles synthesized at 150 °C having a narrower emission at 418 nm (2.95 eV) (Figure 1). In all cases there was no low-energy emission as commonly associated with surface defects. The samples were excited between 300 and 400 nm. The narrow emission profile for nanoparticles synthesized at 150 °C can be attributed to the narrower size distribution expected from lower temperature synthesis. Stokes shifts observed for the samples synthesized at lower temperatures (150 °C) were on the order of ca. 0.6 eV (70 nm), while the particles synthesized at higher temperatures (250 °C) had Stokes shifts of up to 1.1 eV (180 nm). Nanoparticles of Zn₃P₂ capped with TOPO exhibit strong luminescence at all wavelengths investigated as expected for small nanoparticles of II₃-V₂ compounds.³⁹

4-Ethylpyridine-capped nanoparticles also exhibit strong luminescence (Figure 2) with no evidence of deep traps. Samples prepared at 167 °C for 30 h were found to have a band edge of 531 nm (2.33 eV) and displayed emission maximum at 575 nm (2.15 eV) and a Stokes shift of 0.18 eV (44 nm).

The eighth size fraction sample (with a band edge of 410 nm, 3.02 eV) produced emissions at 474 nm (2.61 eV) and a Stokes shift of 0.41 eV (64 nm). Emission from fractionated samples had narrower profiles, indicating a narrower size distribution. In all cases, strong luminescence was observed, even with the longest wavelength emission (575 nm). In comparison, Q-Cd₃P₂ displays strong emission profiles in this region (cf. TOPO capped, synthesized at 100 °C) but exhibits weak emission above 600 nm.^{25,26} Quantum yields were not calculated for any samples.

Structural Characterization of Q-Zn₃P₂. Zn₃P₂ is isostructural with Cd₃P₂, which is an anti-flourite (Zn₃P₂, *a* = 8.09 Å, *c* = 11.45 Å; Cd₃P₂, *a* = 8.75 Å, *c* = 12.26 Å).³⁰ However, powder X-ray diffraction showed no evidence of crystallinity in any as-prepared samples of nanometer-sized Zn₃P₂. The composition of the material was confirmed by ICPAES. Analysis of an aliquot taken after 4 h (167 °C, 4-ethylpyridine) gave a Zn:P ratio of 1.7:1 (Zn_{3.4}P₂) but no X-ray powder diffraction

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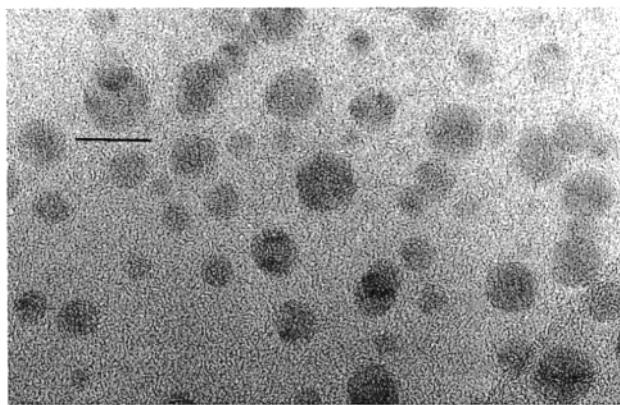


Figure 3. HRTEM of Zn_3P_2 capped with 4-ethylpyridine obtained from Me_2Zn and HP^tBu_2 in 4-ethylpyridine for 30 h; bar = 10 nm.

pattern. After heating at 167 °C for 30 h, the ratio had risen to 7.7:1, and a powder diffraction pattern for ZnO was observed. ICPAES of TOPO-capped Zn_3P_2 gave Zn:P ratios of 1:1, consistent with the excess phosphorus expected due to the TOPO capping ligand. It may be useful to consider the material as a “ZnP nanomaterial” rather than Zn_3P_2 as no distinct crystalline phase can be determined. The ICPAES results suggest a Zn_3P_2 stoichiometry so for convenience we refer to the material as Zn_3P_2 . Annealing of the samples at 600 °C resulted in decomposition of the product, with no improvement in either crystallinity or optical properties. Selected area electron diffraction did not give any patterns that could be indexed.

The HRTEM of 4-ethylpyridine-capped Zn_3P_2 (167 °C, 30 h) showed a crystalline product with a strong hexagonal pattern of zinc metal together with spherical, poorly crystalline Zn_3P_2 quantum dots. Reaction byproducts isolated during the purification of the nanoparticles were also identified by XRD as bulk zinc⁴⁰ and zinc oxide.⁴¹ HRTEM images of the 4-ethylpyridine-capped Q- Zn_3P_2 suggested a mixture of amorphous, crystalline, and poorly crystalline particles. HRTEM also revealed faceted particles with lattice distortions and disordered plane orientations (Figures 3 and 4). Measurement of the lattice fringes does not agree with any known crystal planes of Zn_3P_2 ,⁴² Zn,⁴⁰ or ZnO.⁴¹ The particles of sizes between 3.5 and 13 nm in diameter were slightly prolate, with aspect ratios up to 1.25. The relevant size distribution and optical spectra of fractions 2, 5, and 8 for 4-ethylpyridine-capped Q- Zn_3P_2 are shown in Figure 5.

The second size fraction consists of quantum dots with an average diameter of 4.32 ± 0.77 nm (17.8%). The fifth fraction has an average diameter of 3.82 ± 0.62 nm (16.2%), while the eighth fraction has an average diameter of 3.59 ± 0.57 nm (15.8%). This observation demonstrated that size fractionation results in larger particles precipitating from solution first, followed by smaller particles. The size distribution also narrows with fractionation, explaining the evolution of an excitonic feature in the electronic spectra (Figure 5).

TEM of TOPO-capped nanoparticles, synthesized at 150 °C for 4 h, showed particles with an average diameter of 4.09 ± 0.89 nm (21%) (Figure 6). This observation is consistent with the optical spectra, which suggests that TOPO-capped nanoparticles of Q- Zn_3P_2 were on average smaller than 4-ethylpyridine-capped nanoparticles. The large standard deviation in diameter is comparable to those of TOPO-capped Cd_3P_2 ²⁵ and TOPO-capped III–V materials reported by Alivisatos et al.⁸ Comparison of optical spectra and electron microscopy of 4-ethylpyridine and TOPO-capped particles presents an apparent discrepancy. Particles capped with 4-ethylpyridine are larger than TOPO-capped particles, despite 4-ethylpyridine having a lower boiling point which tends to favor the formation of smaller particles. However, pyridine is a relatively labile passivating agent and can be easily removed. If it were assumed that the growth of quantum dots involves the exchange of the capping agent with further crystallite material (Ostwald ripening) at the surface of a small cluster, pyridine would be expected to exchange more readily than strongly bound TOPO. Pyridine is also less sterically demanding, which could affect exchange processes. This could explain the formation of larger particles despite the lower temperature of synthesis.

Estimates of the particle size by the effective mass approximation described by Brus⁴³ could not be made due to a lack of information on the required physical constants for Zn_3P_2 . There are no values for the effective mass of holes or electrons in Zn_3P_2 . Pseudopotential calculations for nanoparticle dimensions developed by Krishna and Friesner⁴⁴ and employed by Trindade⁴⁵ all depend on an accurate bulk band structure. This method of estimating particle size is not applicable in the present case as there is controversy regarding the validity of the existing pseudopotential model.³¹ For bulk Zn_3P_2 using an approximation modeled on the anti-fluorite lattice, a discrepancy is observed when comparing the theoretical band gap and experimental data. Hence, estimates of diameter based on experimentally derived band gaps are unlikely to be reliable.

Infrared spectroscopy on TOPO-capped Zn_3P_2 shows the characteristic $\nu(\text{C}-\text{H})$ bending mode of CH_3 at 1465 cm^{-1} . The $\nu(\text{P}=\text{O})$ stretch at 1145 cm^{-1} , found to shift to a lower wavenumber (1125 cm^{-1})⁴⁶ in cadmium phosphide, was found to have shifted in a similar manner when complexed to surface zinc. The $\nu(\text{P}=\text{O})$ stretch was found as a broad band at 1097 cm^{-1} , a shift of ca. 40 cm^{-1} . This is in agreement with previous studies on alkylphosphine oxides bonded to zinc salts, in which a shift of 40 cm^{-1} was found.⁴⁷ This suggests TOPO binds in a manner similar to surface sites in Zn_3P_2 and Cd_3P_2 dots. 4-Ethylpyridine-capped Q- Zn_3P_2 shows bending and stretching modes similar to those observed for other quantum dots passivated with 4-ethylpyridine (Table 1). The Zn–N bend is observed as a broad weak feature at 320 cm^{-1} , suggesting bonding through the ring nitrogen.⁴⁸

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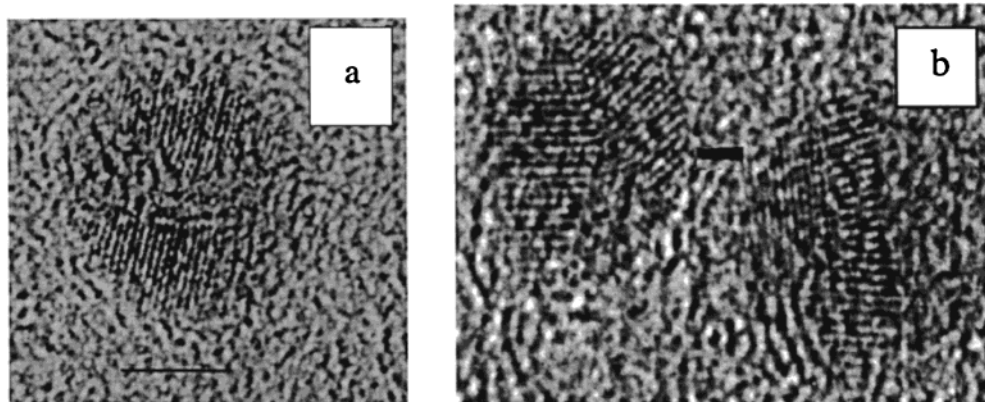


Figure 4. HRTEM of Zn_3P_2 capped with 4-ethylpyridine from Me_2Zn and HP^iBu_2 in 4-ethylpyridine for 30 h. Bar = (a) 5 nm and (b) 1 nm.

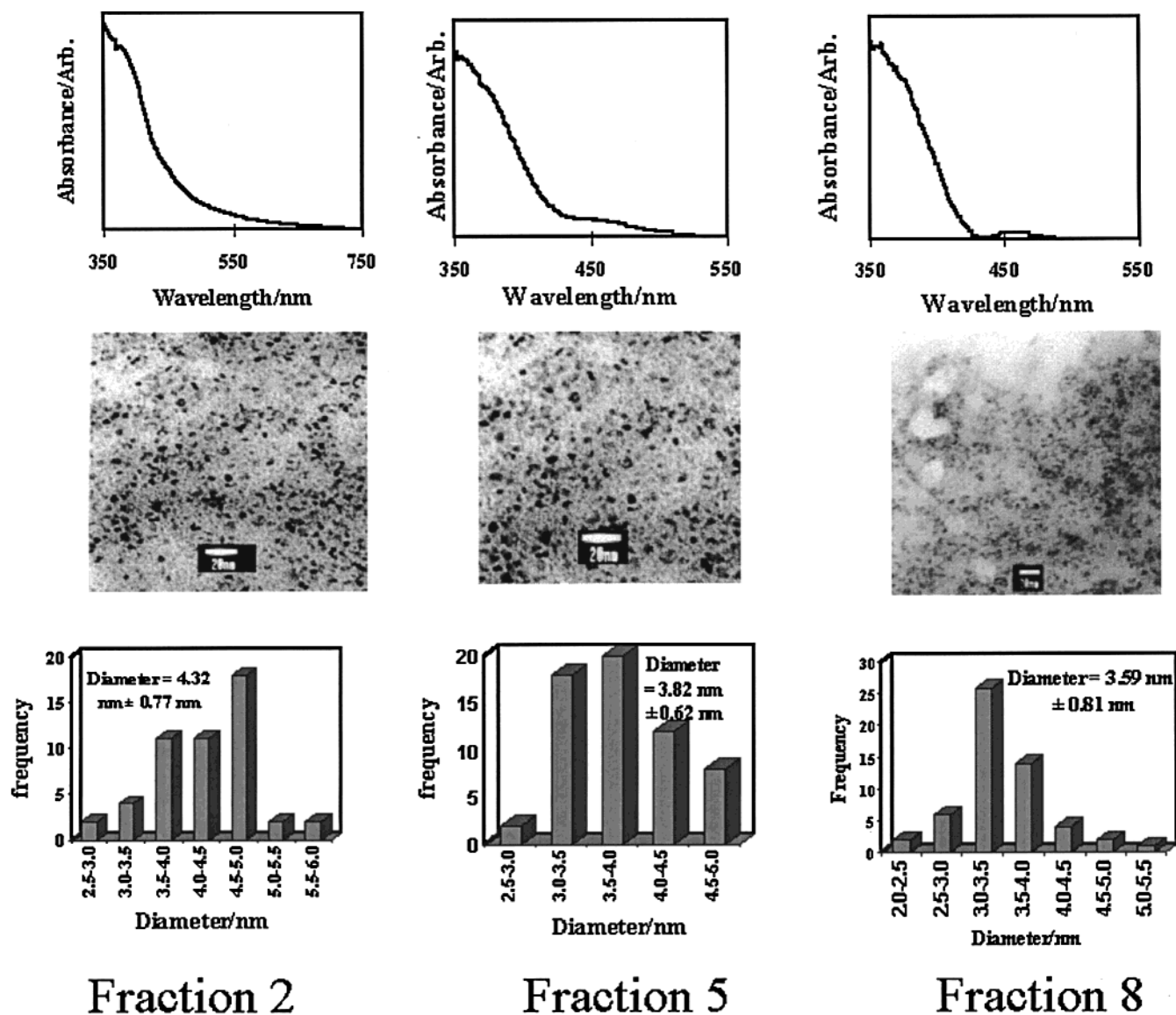


Figure 5. Comparison of optical spectra, size distributions, and TEM of three size fractions of Zn_3P_2 .

Solution ^{31}P NMR of Q- Zn_3P_2 capped with 4-ethylpyridine displayed features similar to those previously observed with Q- Cd_3P_2 . Three distinct broad resonance's were observed, suggesting three phosphorus environ-

ments as predicted for M_3P_2 , with phosphorus atoms arranged in three orientations around lattice vacancies (Table 2).^{49,50} The resonance's are significantly downfield from those observed in the bulk material. The observa-

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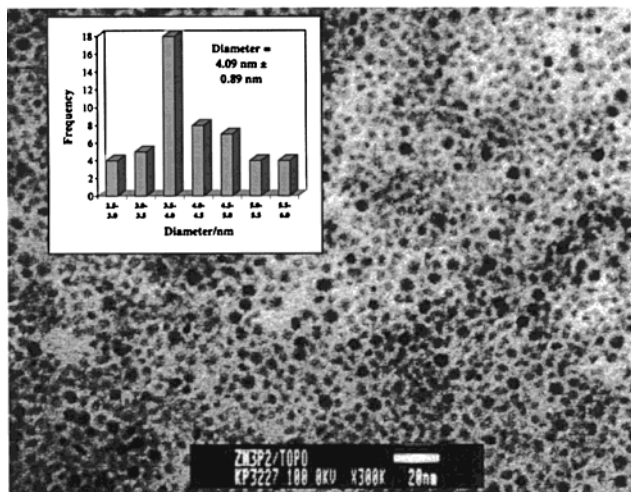


Figure 6. TEM image of Q- Zn_3P_2 capped with TOPO and synthesized at 150 °C for 4 h. Bar = 20 nm.

Table 1. IR Data for 4-Ethylpyridine and 4-Ethylpyridine-Capped Q- Zn_3P_2

free ligand/ cm^{-1}	Zn_3P_2 -4-Etpy/ cm^{-1}	assignment
1606	1619	$\nu(\text{C}-\text{C})$
1417	1409	$\nu(\text{C}-\text{C})$
	1226	$\nu(\text{C}-\text{H})$
1066	1062	$\nu(\text{C}-\text{H})$
777	773	$\nu(\text{C}-\text{H})$
	320	$\nu(\text{Zn}-\text{N})$

Table 2. Solid-State and Solution-State ^{31}P NMR Data for TOPO-Capped Q- Zn_3P_2

solution-state ^{31}P NMR		^{31}P MAS NMR	
δ (ppm)	assignment	δ (ppm)	assignment
35.33	bound TOPO	3.93	
48.93	excess TOPO	30.70	bound TOPO
53.29	TOPO Impurity	52.76	excess TOPO

tion is rather unexpected as MAS NMR on macrocrystalline Zn_3P_2 is reported to show only two of the expected three resonances.⁵⁰ The unusual resonances could be due to phosphorus(V) impurities.

Proton decoupled ^{31}P MAS solid-state NMR of Q- Zn_3P_2 capped with 4-ethylpyridine showed a broad resonance at 32.41 ppm, with weak signals at ca. 1 and 60 ppm. Alteration of the spin speed of the sample confirmed the absence of spinning sidebands. CPMAS showed broad resonances at ca. 15, 33, and 56 ppm. Each broad resonance had a distinct narrow feature at 0.9, 40.18,

and 62.38 ppm, respectively. The narrow resonance's enhanced in CPMAS experiments are hence assigned as phosphorus at the surface and proximate to the capping ligand.

Solution and solid-state ^{31}P NMR on TOPO-capped Zn_3P_2 show the typical resonances for TOPO/TOP species bonded to the surfaces (Table 2). No resonance attributable to core phosphorus was observed in TOPO-capped Zn_3P_2 .²⁵ Solution ^1H NMR of both TOPO and 4-ethylpyridine capped particles show broad resonances consistent with the restricted rotation of the capping group. These unusual results are being further investigated. The effect of atmospheric degradation is also being examined.

Conclusions

Novel chemical routes to nanodispersed quantum dots of Zn_3P_2 have been developed. The precursors Me_2Zn and HP^tBu_2 were thermolyzed in TOPO or 4-ethylpyridine, resulting in organically capped nanomaterial.

All the nanoparticulates described in this work were capped with either TOPO or 4-ethylpyridine and had optical properties similar to $\text{II}_3\text{-V}_2$ compounds prepared by aqueous routes. The as-prepared nanoparticulates were relatively polydispersed (standard deviation of ca. 20%) and appeared to be a mixture of both crystalline and amorphous materials. The nanoparticles were found to show quantum confinement effects with band gaps shifted to much higher energies. Luminescence was strong and exhibited large Stokes shifts relative to the absorption edge, probably due to metal vacancies being efficient trapping sites for charge carriers. The nanoparticles may have advantages over aqueously prepared $\text{II}_3\text{-V}_2$ quantum dots by being air stable, resistant to photodegradation, and organically capped.

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