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FEATURE ARTICLE

Recent advances in the preparation of semiconductors as isolated nanometric particles: new routes to quantum dots

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Nanoparticles of semiconductor materials have been the subject of intense research in the last five years owing to the novel electronic, catalytical and optical properties observed in such materials. The unusual properties of these so called quantum dots can be attributed to two main factors: the large surface to volume ratio of atoms and the confinement of charge carriers in a 'quantum mechanical box'. Small particles of semiconductors have been prepared by a number of routes, often using colloidal chemistry methods but more recently using organometallic routes. The recent advances have resulted in high quality nanoparticles which have been incorporated into simple devices. In this article we cover some of the key advances in the preparation of nanometric particles of semiconductors. The cover illustration depicts three sizes of TOPO capped CdSe.

Introduction

Isolated quantum dots are a novel form of semiconductor of theoretical interest and with potential to develop as an important class of materials for the electronics industry of the 21st century. The electronic properties of a bulk semiconductor are determined principally by the band gap of the material and its type. Typically, bulk samples of CdS, irrespective of their size once $>$ *ca.* 20 nm, will absorb all electromagnetic radiation with an energy greater than the band gap ($h\nu > 2.42$ eV); which is classified, in this case, as direct.[1] 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 antibonding levels in the material.[2] The electronic properties of such small particles are hence more like those of a molecule than an extended solid. The electronic, optical and catalytical properties of such small particles will depend on their size and the material of which they are composed.[3]

For a semiconductor such as CdS, these effects were predicted some years ago to become important in the size range from *ca.* 2 to 10 nm and Brus and coworkers published a number of keynote papers.[4–6] 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, or by the controlled decomposition of organometallic or metal organic compounds. 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.

Electronic properties

The 'band gap' of a quantum confined semiconductor is greater than that of the parent bulk material from which it is derived. This is an effect which is a consequence of the confinement of the electron in a three-dimensional 'box' with discrete energy levels rather than in the quasi-continuous band of a bulk material (Fig. 1).[4] The absorption of electromagnetic radiation by quantum dots, of materials such as CdS, is hence relatively easy to appreciate. However, explaining the luminescent

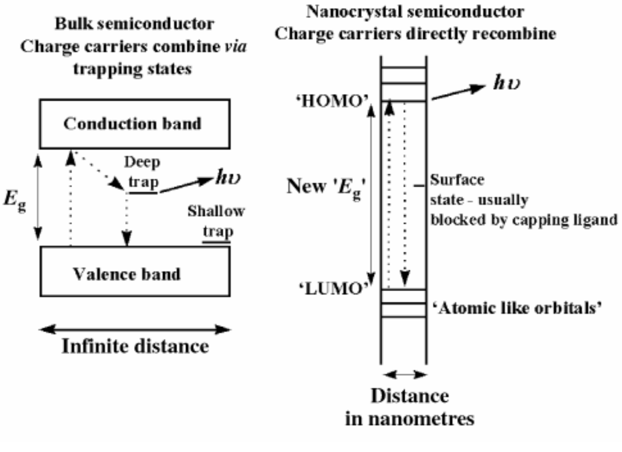

Fig. 1 Spatial electronic state diagram for bulk semiconductor and nanoparticles, after Brus and coworkers.[4]

Dr Mark Green obtained his BSc in chemistry from the Manchester Metropolitan University in 1995. He carried out research for his PhD at Imperial College for Professor Paul O'Brien between 1995 and 1998, studying new routes to nanoparticulate semiconductors. He is currently a post doctoral associate in the O'Brien group looking at nanoparticulate metals and semiconductors.

Professor Paul O'Brien graduated from Liverpool University in 1975, obtained a PhD from the University of Wales, Cardiff in 1978 and was immediately appointed as a lecturer at Chelsea College of Science and Technology. Following the University of London re-structuring, he moved to Queen Mary and Westfield College in 1984 and was promoted to a chair in 1994. In 1995 he moved to Imperial College where he was appointed as a Professor of Inorganic Chemistry and Sumitomo STS Professor of Materials Chemistry (1997–1999) and was Royal Society Amersham fellow (1997–1998). He holds a visiting Professorship at the Georgia Institute of Technology and is also a distinguished scholar at the Molecular Design Institute. In October 1999, he will take up a new position as Professor of Inorganic Materials, a joint appointment between the University of Manchester Chemistry Department and the Manchester Materials Science Centre.

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behaviour of such materials is much more complicated but crucially important in identifying materials of sufficient quality for potential practical application. The ideas that have emerged for explaining such phenomena illustrate an interesting interplay between experiment and theory. Brus explained, on the basis of theoretical considerations and studies of excited state lifetimes, the main features expected in the luminescence spectra of quantum confined semiconductors and successfully anticipated the results of subsequent experiments.[4] Emission from passivated semiconductor quantum dots is often found to be 'band-edge' referring to the direct recombination of charge carriers from the atomic like orbitals (Fig. 1). Charge carriers in bulk semiconductors recombine from deep and shallow traps (crystal and surface defects) giving emission at different wavelengths from the band edge.

An alternative view of such structures, which has some conceptual appeal, is that they may be viewed as 'super atoms'. Electrons within the solids are confined within an approximately spherical particle (the diameter of the quantum dot). The solutions of the Schroedinger equation for this three-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.[7] 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'.

Methods of preparation

Many synthetic methods for nanoparticles have been reported in the literature. Many use methods based on colloid chemistry, decomposition of organometallic compounds or growth in a restricted reaction space. An ideal route should result in pure, monodispersed, crystalline particles which are stable, *i.e.* they have robust surface passivation. Nanoparticles of metals, metal oxides, carbides, borides and nitrides have also been produced and have been reviewed elsewhere.[8–10]

Elemental semiconductors have also been studied. For instance, germanium nanoparticles have been produced by the reaction of $GeCl_4$ and lithium naphthalide in tetrahydrofuran.[11] The quantum dots formed were between 60 and 200 Å in diameter. Laser illumination of a hexane solution resulted in further growth and increased crystallinity. Similarly oxide coated silicon nanoparticles have been produced by the combustion of silane.[12]

Problems with nanoparticles grown by colloidal or restricted growth routes, centre around their air sensitivity and poor crystallinity. Nanoparticles prepared in structured media also have their dimensions dictated by the restricting material. The removal of the matrix or the effect of its removal also needs to be considered when developing strategies for materials of practical importance.

Colloidal routes

The first reported routes to such small particles involved the controlled precipitation of dilute colloidal solutions and the cessation of growth soon after nucleation. The synthesis of highly monodispersed colloids was explained in the 1940's by La Mer *et al.*[13–15] who suggested that if seeds (nuclei) could be made to grow in concert into larger particles, monodispersed sols could be formed. In this early work the particles were typically micrometric. However, if nucleation and growth are properly controlled, particles with dimensions of the order of nanometres can be reproducibly synthesized. Small crystals, which are less stable, dissolve and then re-crystallise on larger more stable crystals; a process known as Ostwald ripening. For such methods to be effective, the quantum dots in question must have low solubility, which can be achieved by the correct choice of solvent, pH, temperature and passivating agent. Highly monodispersed samples are obtained if the processes of nucleation and growth are distinctly separated, *i.e.* fast nucleation and slow growth. The colloidal stability of these crystals has been improved by using solvents with low dielectric constants or by using stabilisers such as a styrene/maleic acid copolymer. Henglein,[16] Brus and coworkers[17,18] and Weller[19] have made significant contributions to this field, especially in studies of CdS.

A typical example involved the reaction between aqueous solutions of $CdSO_4$ and $(NH_4)_2S$. Control of the size of nanocrystalline CdS was achieved by altering nucleation kinetics using pH.[17] Although these methods can be efficient, some important semiconductors cannot easily be synthesised, *e.g.* CdSe, GaAs, InP and InAs. Annealing of amorphous colloidal particles is also a problem as these tend to be low temperature processes producing poorly crystalline material. Such aqueously prepared nanoparticles are not sufficiently stable at higher temperatures for annealing without agglomeration. CdS and ZnS have also been produced from methanolic media without the use of an organic ligand for stabilisation, using the repulsion of the electrostatic double layer to stop agglomeration.[18]

Zn_3P_2 and Cd_3P_2 have both been produced by aqueous methods, by the injection of phosphine gas into a solution of the relevant metal perchlorate.[20,21] The quantum dots obtained were coloured, from white for small Cd_3P_2, to brown for the larger particles. The white particles were reported to have band gaps of up to 4.0 eV. Luminescence was reported to be strong at short wavelength, but little attention was paid to crystal morphology. Murphy and coworkers have produced manganese activated (Mn occupying surface sites) and manganese doped (Mn occupying lattice sites) ZnS dots by aqueous routes, displaying increased quantum yields and orange emissions respectively.[22]

Synthesis in confined matrices

Materials which provide distinct defined cavities have been used to synthesise quantum dots. These well defined zones have been used as nanometre sized reaction chambers. Zeolites,[23] micelles,[24] molecular sieves[25] and polymers[26] have all been used to restrict growth. The matrix may also play a role in determining the final properties of the particle, for example, micelles are labile. CdSe and ZnS nanoparticles have been produced in inverse micelle solutions.[27,28] A microemulsion containing the metal ion was reacted with a silylchalcogenide, resulting in nanoparticles. The surface was then capped by phenyl groups or another semiconductor. The surface composition of the crystals were interesting owing to their ability to react further with other silyl groups owing to the excess Cd^{2+} sites, effectively growing larger and developing a different surface capping.

Growing particles in the internal cavities of zeolites also limits the particle size of materials, usually no larger than 20 nm. CdS has been synthesised in two different zeolites by ion exchange from the sodium cationic form to the cadmium cationic form, followed by exposure to H_2S gas. Depending upon the amount of cadmium utilised, different sized particles were obtained.[23] Cadmium telluride nanoparticles have also been prepared in a sodium or potassium zeolite. Exchange of the metal with cadmium nitrate followed by reduction by hydrogen at 450 °C prepared the zeolite for vapour phase deposition of tellurium, resulting in CdTe clusters. The size of the clusters could be controlled by using either the potassium or sodium resin, which altered pore diameters.[29]

Q-GaP has also been synthesised in the pores of zeolite Y.[30] The vapour transfer of Me_3Ga into a dry Na^+/H^+ exchange zeolite resulted in methane evolution and the formation of

$Me_{3-x}Ga$ sites. Exposure of this to an excess of PH_3 at various temperatures (200–400 °C) resulted in the growth of particles with a size range of 10–12 Å. The nanocrystals formed were analysed by EXAFS and solid state NMR spectroscopy.

Q-PbS was obtained by exchanging Pb^{2+} into ethylene/methacrylic acid copolymer, followed by exposure to H_2S.[26] The size of the particles was again controlled by Pb^{2+} concentration, with sizes ranging from 13 to 125 Å. A similar technique was used to grow in the interlamellar regions of a layered host, $Zr(O_3PCH_2CH_2CO_2H)_2$. Conversion of the host to $M^{II}[Zr(O_3PCH_2CH_2CO_2)_2]$ (M = Pb, Cd, Zn) followed by treatment with H_2E (E = S, Se) resulted in growth of ME nanoparticles.[31]

An organometallic route to polymeric composites of CdSe and ZnSe has been developed by Cole-Hamilton and coworkers.[32–34] The polymer 2-pyridyl-polybutadiene was reacted with a group IIb metal alkyl, to give an adduct. A toluene solution of the polypyridine bound metal alkyl was exposed to H_2Se gas to give a coloured precipitate. The size of the nanoparticles was determined by both the solvent and the reaction temperature (−76 to 60 °C); quantum dots synthesised at lower temperatures were smaller. Hexagonal CdSe was obtained in the size regime 1–6 nm, with the use of light petroleum instead of toluene giving larger particles. The particles were characterised by HRTEM, powder XRD, UV and photo-acoustic spectroscopy (PAS).

Metal–organic routes

A popular method for the preparation of high quality, crystalline, monodispersed nanoparticles was first described by Murray *et al.* in 1993.[35] In this method, a volatile metal alkyl (dimethylcadmium) and a chalcogen source TOPSe (tri-*n*-octylphosphine selenide) were mixed in tri-*n*-octylphosphine (TOP) and injected into hot TOPO (tri-*n*-octylphosphine oxide), a polar coordinating Lewis base solvent. Nucleation of nanoparticulate CdSe was achieved by the sudden introduction of the concentrated reagents resulting in abrupt supersaturation and the formation of nuclei, followed by slower growth and annealing, consistent with an Ostwald ripening process. The nanoparticles were passivated by a monolayer of the solvent ligands and hence could be isolated by solvent/non-solvent interactions. The particles produced by this method were highly monodispersed (±5%, Fig. 2) and crystalline. By varying the temperature of synthesis the diameter can be controlled in the size range 24–230 Å. The organic surface cap can be replaced by other organic groups such as pyridine, 4-picoline, tris(2-ethylhexyl)phosphate, and 4-(trifluoromethyl)thiophenol.[36] Computer modelling of XRD patterns suggests that Q-CdSe prepared at temperatures of up to 300 °C have around one defect per nanocrystal.[35]

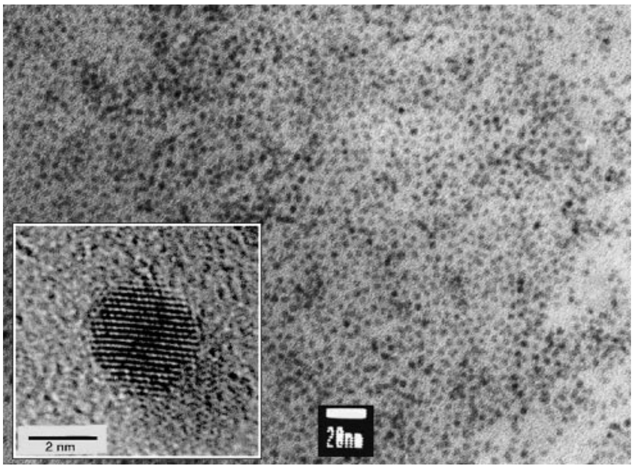

Fig. 2 TEM image of TOPO capped CdSe nanoparticles prepared as described in ref. 38 (scale bar = 20 nm); inset, HRTEM image, scale bar = 2 nm.

Alivisatos and coworkers produced similar quantum dots with fewer crystal defects by using a higher temperature synthesis (350 °C) and tributylphosphine instead of tri-*n*-octylphosphine.[37] Replacing the metal alkyl with an adduct of the metal alkyl produces similar quality quantum dots whilst reducing the risks of using pyrophoric precursors.[38] The physical chemistry of TOPO capped nanoparticles has been thoroughly investigated.[39–41] Emission from TOPO capped II–VI materials is found to be near band edge with quantum yields of *ca.* 10% (Fig. 3).[35]

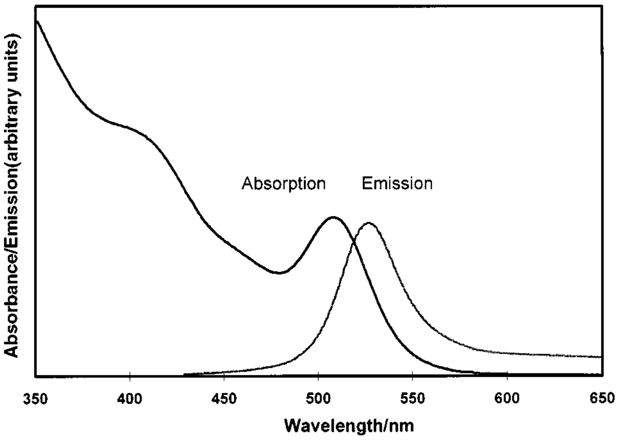

Fig. 3 Electronic and photoluminescence spectra of TOPO capped CdSe nanoparticles prepared as described in ref. 38.

The nanoparticles prepared by this method are of high quality, but the reaction requires harsh/difficult conditions, such as the injection of hazardous metal alkyls at elevated temperatures (*ca.* 350 °C) which is clearly undesirable. One way to avoid such potential problems is the use of a single-molecular precursor in which the metal–chalcogen bond is already in place. Trindade and O'Brien investigated cadmium dithio- and diseleno-carbamate complexes as precursors for the preparation of TOPO capped II–VI materials.[42,43] Thermolysis of the air stable complex $[Cd(S_2CNEt_2)]_2$, in TOPO resulted in high quality nanoparticles of CdS. The thermolysis of the analogous diselenocarbamate complex in TOPO resulted in micrometric particles of selenium. However, compounds of the formula $RCd(E_2CNEt_2)$, (R = neopentyl, Me; E = S, Se) were efficient precursors to CdE nanoparticles on thermolysis in TOPO (reaction scheme shown in Fig. 4). Such compounds eliminate the need for volatile metal alkyls, but are however air-sensitive; air-stable precursors would be preferred. Simple diselenocarbamate complexes of cadmium with unsymmetrical R groups, such as hexyl and methyl $(CdSe_2CNMeHex)_2$, are air stable and are found to be excellent precursors for CdSe.[44] GC–MS studies have suggested the decomposition mechanisms of symmetrical diselenocarbamates, which produce selenium clusters.[45] However, unsymmetrical diselenocarbamates (with alkyl groups longer than hexyl) produce only the metal selenide and organic by-products. Revaprasadu *et al.* have also recently doped nanoparticulate ZnS with Mn, giving emission in the orange region of the visible spectrum rather than the blue.[46]

Hines and Guyot-Sionnest[47] and Revaprasadu *et al.*[48] reported simultaneously the preparation of TOPO capped ZnSe. Hines and Guyot-Sionnest[47] used the same methodology adopted by Bawendi *et al.*,[35] *i.e.* dimethylzinc and tri-*n*-octylphosphine selenide as precursors. However, the use of TOPO/TOP as capping agents failed and a mixture of hexadecylamine and TOPO was used instead. Revaprasadu *et al.*[48] used the single source complex $[EtZn(E_2CNEt_2)]_2$ (E = S, Se) in TOPO to prepare crystalline capped nanoparticles of ZnE. Comparison of Hines' metal alkyl route and the single source route suggests there may be surface differences in the as-

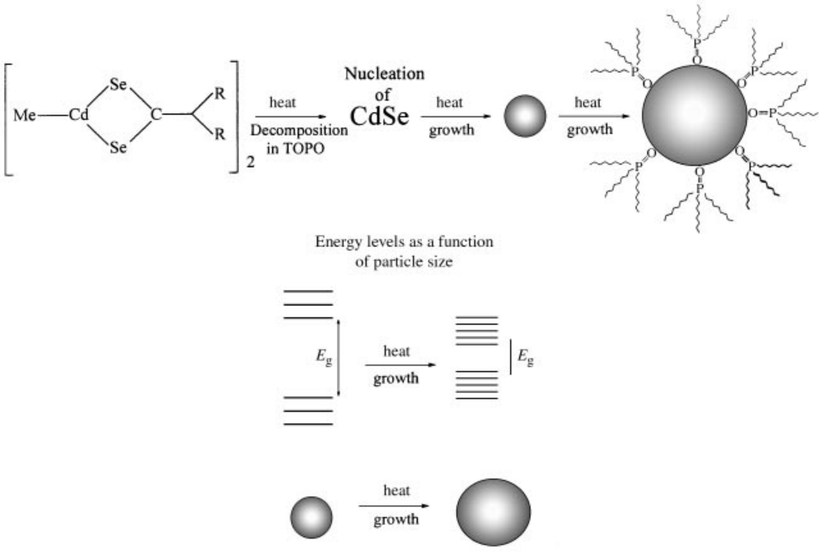

Fig. 4 Theoretical decomposition schematic for the preparation of TOPO capped CdSe using a single source precursor.

prepared materials. Comparisons of CdSe nanoparticles prepared by single source precursors and the metal alkyl by IR spectroscopy again suggest different surface environments which are currently under investigation by our group.

The preparation of lead chalcogenide nanocrystals has also been achieved using various lead dithio- and diseleno-carbamates.[49] Group IV–VI semiconductors are a prime example of materials where precursors such as highly toxic lead alkyls are undesirable. The nanoparticles of lead chalcogenides have a cubic shape inherent in PbS materials (Fig. 5). Nanoparticles of PbE and CdE (E = Se, S) have been linked using bridging ligands such as 2,2′-bipyrimidine.[43]

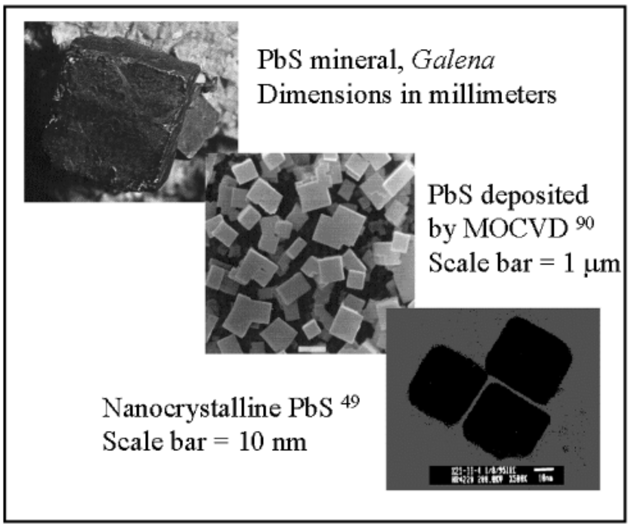

Fig. 5 Photo, SEM and TEM of PbS of various sizes.

Nanoparticles of TOPO capped II–VI materials are found to degrade in the presence of light and oxygen, forming unstable chalcogen oxide species which leave surface defects.[50] One significant recent advance is the preparation of quantum dot–quantum wells, where one nanoparticle is capped by a layer of another semiconductor.[51,52] The surface is then protected and photoluminescence of the core semiconductor is enhanced, with quantum yields of up to 50%. Experiments have also indicated that upon excitation, the hole is confined to the core whilst the electron is delocalised through the entire structure. Precursors for such core–shell structures are generally metal alkyls and bis(trimethylsilyl)sulfide, but core–shell structures of CdSe–CdS have also been grown using single molecular precursors.[53] Thin films of CdSe nanoparticles in a ZnSe matrix, grown by electrospray-organometallic chemical vapour deposition, have also been reported.[54]

The preparation of III–V materials is significantly more difficult to achieve. The increased covalent character results in the routes to crystal formation being hampered by large energetic barriers. There is, therefore, no discrete nucleation step and separation of nucleation and growth is difficult. Precursors for III–V materials, such as $InCl_3$ coordinate to the reaction solvent inhibiting direct reaction between the reagents, which is often suggested as a key step in the nucleation and growth steps.[55] Nozik and coworkers[56] and Alivisatos and coworkers[57] have developed the dehalosilylation reaction as first reported by Wells *et al.*,[58] and Barron and coworkers,[59] to prepare III–V quantum dots capped with TOPO or TOP. In these reactions, $InCl_3$ is complexed to either TOPO or TOP, followed by the injection of $E(SiMe_3)_3$ (E = As, P). Growth and annealing take up to 7 days at *ca.* 265 °C. The size distribution is large (*ca.* 20%) and the final product is contaminated by oxide side products. Photoluminescence from the final material is near to band edge and dependent upon surface oxidation. InP dots are reported not to luminesce until the surface is oxidised, highlighting the importance of the surface state whilst emission from InAs dots is insensitive to oxidation.[57,60] The formation of stable surface species is reported to hinder size fractionation procedures, but is reversible using hydrogen fluoride etching processes.[61]

We have recently developed a single molecular precursor route to InP and GaP using metal diorganophosphides as precursors.[62,63] The compounds $M(PBu^t{}_2)_3$, (M = Ga, In) are dissolved in 4-ethylpyridine and heated at reflux for up to 7 days. Nanoparticles of *ca.* 8 nm diameter (±20%) could be isolated by solvent/non-solvent interaction and a glass formed upon prolonged evacuation. These single source routes avoid the need for volatile precursors such as silylated pnictides. The use of diorganophosphides has been extended to the preparation of high quality TOPO and 4-ethylpyridine capped Cd_3P_2 using the precursor $[MeCdP(Bu^t)_2]_3$.[64,65] Cadmium phosphide is reported to have a large excitonic diameter (*ca.* 36 nm, *cf.* CdS *ca.* 3 nm) which means the band edge can be shifted over a wide spectral range upon quantum confinement of the charge carriers. Nanometer sized Cd_3P_2 prepared by conventional colloidal chemistry can have band gaps between 0.5 and 4.0 eV. Colloidally prepared Cd_3P_2 is air-sensitive and decomposes upon illumination, whilst TOPO capped Cd_3P_2 appears more resistant to photodegradation. The organic substituent on the diorganophosphide appears to control reactions, changing the *tert*-butyl group for a phenyl or cyclohexyl group results in bulk cadmium with an extremely small amount of nanometric material. GC–MS and TGA analysis were used to deduce two competing mechanisms; reductive elimination, which leads to elemental cadmium and β-hydrogen elimination (for $[MeCdP(Bu^t)_2]_3$) resulting in nanoparticles of Cd_3P_2. The mechanisms were found to be temperature dependent, with β-hydrogen elimination predominating at lower ($<$ 150 °C) temperatures giving purer Cd_3P_2.

Zinc phosphide quantum dots have also been prepared by using dimethylzinc and di-*tert*-butylphosphine in either TOPO or 4-ethylpyridine. The nanocrystals are *ca.* 4 nm in diameter, with band gaps shifted up to 3.5 eV depending upon the capping agent and reaction conditions.[66]

TOPO is not the only Lewis base to be utilised in nanocrystal preparation. Nanoparticles of GaP and GaAs have been synthesised by refluxing $GaCl_3$ with either $P(Na/K)_3$ or $As(Na/K)_3$ in toluene/glyme to give crystalline glyme capped quantum dots.[67] The same reaction in aromatic solvents alone again yields nanoparticles which are capped with methanol upon extraction. Nanoparticulate GaP has also been produced through the thermolysis of a single source precursor $[X_2GaP(SiMe_3)_2]_2$ (X = Br, I) and $(Cl_3Ga_2P)_n$ with both decomposing at relatively low temperatures whilst under vacuum to yield crystalline Q-GaP.[68] Q-GaP and Q-GaAs have also been produced by thermolysis of $[H_2GaE(SiMe_3)_2]_3$ (E = P, As) at 450 °C in xylenes, giving nanoparticles *ca.* 5 nm in diameter. The capping agent was not discussed.[69]

The groups of Alivisatos[70] and Nozik[71] used a similar method to Bawendi's[35] to produce GaAs nanoparticles, by refluxing $GaCl_3$ and tris(trimethylsilyl)arsine in quinolene at 240 °C for 3 days. Flame annealing at 450 °C was used to improve crystallinity, but resulted in a slight loss of solubility. Crystalline InAs nanoparticles of size 1–8 nm have been synthesised by the reaction of $In(acac)_3$ with tris(trimethylsilyl)arsine in triglyme at 216 °C for 70 h. Investigations were also carried out into the non-linear optical properties of the resulting materials.[72] The same method was applied successfully to GaAs using $Ga(acac)_3$.[73] These methods are attractive because they present routes that do not use hazardous precursors, *e.g.*, phosphine or arsine.

Nanoparticles of CdSe has been also been synthesised by pyrolysis of the single source precursors $Cd(SePh)_2$ and $[Cd(SePh)_2]_2[Et_2PCH_2CH_2PEt_2]$ in 4-ethylpyridine.[74] Cd_3P_2 has been produced by the methanolysis of $Cd[P(SiPh_3)_2]_2$.[75]

Manipulation of quantum dots

The organisation of quantum dots into ordered structures presents a significant challenge and lends itself to potential industrial applications. Superlattices of TOPO capped CdSe have been prepared by controlled crystallisation in an octane–octanol mixture under reduced pressure.[76] Alivisatos and coworkers have also prepared dimers of TOPO capped CdSe by linking the nanoparticles with *N*-methyl-4-sulfanylbenzamide followed by size selective precipitation.[77] Alivisatos and coworkers have also investigated the effects of mixing organically capped CdSe with the conjugated polymer poly[2-methoxy,5-(2′-ethyl)hexyloxy-*p*-phenylenevinylene] (MEH-PPV).[78] TOPO capped nanoparticles had the surface ligand exchanged for pyridine. The pyridine capped dots were mixed with a solution of polymer and spin coated onto indium tin oxide (ITO) coated glass. Excitation of the polymer resulted in an electron being transferred onto the nanoparticle. This resulted in quenching of polymer luminescence, consistent with charge separation at the polymer/quantum dot interface. The resulting Q-CdSe/MEH-PPV composite luminescence efficiency was found to be 12% when loaded with high concentrations of quantum dots. TEM demonstrated a distinct interconnected network forming at concentrations of *ca.* 90% CdSe. The incorporation of quantum dots into a conducting medium is an essential step towards device fabrication.

The idea of incorporation was further advanced by the removal of surface TOPO and replacement with a polymer back-bone rather than a simple dispersion.[79,80] In this method, nanoparticles of either CdSe or CdSe coated with ZnSe, were prefabricated by the normal method, and added to a solution of copolymer containing phosphine/phosphine oxide norbornene blocks. The addition of $[MTD]_{300}$ and $[NBE\text{-}CH_2O(CH_2)_5P(Oct)_2]_{26}$ (MTD = methyltetracyclododecene, NBE = 5-norbornen-2-yl) resulted in excellent take up of the quantum dots, and led to increased fluorescence, whilst the addition of $[MTD]_{300}$ alone had negligible results. Further addition of the polymer resulted in an increase of 2% in the quantum yield, indicating passivation of the quantum dots by the polymer bound phosphine. TEM experiments showed networks of nanoparticles segregated by phosphine rich domains. An investigation was also undertaken into the potential competition between TOPO and TOP to passivate the surface of the crystals. Further addition of TOPO resulted in a small increase in luminescence, whilst addition of TOP doubled the emission. This suggests TOP binds to the unpassivated selenium sites, whilst TOPO specifically binds to cadmium.

Thin films have also been prepared by spin-coating TOPO capped nanoparticles onto various substrates such as nano-polished monocrystalline semiconductor wafers.[81] Further layers can be added by various methods such as chemical bath (electroless) deposition or MOCVD. Fig. 6 shows a nano-composite prepared by spin coating TOPO capped CdSe onto a GaAs substrate, followed by deposition of a layer of CdS by chemical bath.

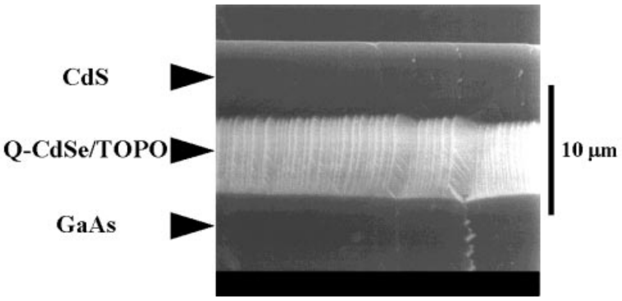

Fig. 6 SEM side profile of a nanocomposite heterostructure. The substrate is nanopolished GaAs. A layer of nanocrystalline CdSe is spin coated on top, followed by a layer of CdS deposited by chemical bath deposition.[81]

Other recent advances of note are the uses of DNA in nanocrystal processing, with possible applications in developing chemical biosensors. Mirkin *et al.* have used thiol capped, non complementary DNA oligonucleotides to assemble 13 nm Au quantum dots into a macroscopic material.[82] In similar work, Alivisatos *et al.* synthesised *ca.* 3 nm Au nanocrystals which were then attached to single strand oligonucleotides, which organised into spatially defined structures on addition of a single complementary DNA strand, due to Watson–Crick interactions.[83]

Applications

Alivisatos and coworkers have produced an electroluminescence device using TOPO capped CdSe nanocrystals with sizes between 3 and 5 nm, and a semiconducting polymer, poly(*p*-phenylene–vinylene) (PPV).[84] The device was fabricated by multiple exposures of a indium tin oxide (ITO) plate or ITO/PPV plate, pre-treated with hexane thiol, to a toluene solution of nanocrystals. For stability, the layer is built up to 1000 Å. Electrical contact is made by silver coated magnesium. The colour of the emission can be controlled by the particle sizes giving red to yellow emissions. At increased voltage, green luminescence from the polymer layer is predominant. This was then improved upon by fabrication of a LED using CdSe nanocrystals capped with CdS instead of the organic ligand.[85] The device was produced by using the same basic techniques but using a pre-PPV polymer precursor deposited on ITO coated glass. This film was then annealed at 300 °C for 3 h before having CdSe/CdS spin deposited onto the PPV. The use of CdSe/CdS instead of CdSe/TOPO results in an increase in efficiency by a factor of eight and a factor of ten increase in lifetime. This is attributed to the inorganically capped particles being resistant to photo-oxidation.

Electroluminescence has been reported from TOPO capped CdSe when incorporated into thin films of poly(vinylcarbazole) (PVK) and an oxadiazole derivative.[86] The film was then sandwiched between ITO and Al electrodes. The device was tuneable from *ca.* 530 to 650 nm by varying the size of the dots. Low temperature studies (77 K) also indicated that only the nanocrystals luminesced at low voltage, whilst at higher voltages both the dots and the PVK matrix electroluminesce. Electroluminescence efficiency was also found to increase at 77 K.

The anaerobic conditions employed to manufacture TOPO capped quantum dots used in device fabrication have the advantage of avoiding potential doping with oxygen. For this reason, aqueous routes to nanocrystals were often assumed to be unfavourable. However, Gao *et al.* fabricated a device using CdSe nanocrystals synthesised using a Cd salt and H_2Se in aqueous solution with thiolactic acid, at pH 11.[87] The thiolactic acid acted as a capping agent, effectively giving the particle a negatively charged surface, which facilitates adsorption onto the substrate. The size of the particles was controlled by altering the molar ratios between Cd^{2+} and H_2Se, with intense fluorescence obtained by adding an excess of Cd^{2+} shortly after synthesis. Optical glass and ITO coated glass which had been coated with PEI [poly-(ethyleneimine)] to give a positively charged surface, were used as substrates. The next step involved the exposure of the substrate to a solution of the nanoparticles for a defined time giving a monolayer of quantum dots. Positively charged PAH [poly(allylamine hydrochloride)] or a precursor for poly(*p*-phenylene–vinylene) (pre-PPV) were then adsorbed on top. The application of a number of inorganic and organic layers was repeated until 20 double layers had been applied. The CdSe/PPV multilayer film was then obtained by heating the CdSe/pre-PPV at 130 °C *in vacuo* for 11 h. The device was finished by the evaporation of an aluminium electrode on the top layer. The device produced almost white light electroluminescence (500–850 nm) under a forward bias of 3.5–5 V with the positive pole on the ITO electrode. Such a broad emission, similar to that of the CdSe solution, was attributed to deep traps, surface defects and a large size distribution. It is interesting to note that a device incorporating aqueous derived nanocrystals has a broad emission, which may be attributable to doping with oxygen. The device is reported to have a longer lifetime than similar simple organic devices.

Single electron transistors have also been reported in devices in which a single nanoparticle is trapped between two gold electrodes by dithiols.[88] Biological applications are now being explored such as water soluble semiconductor nanoparticle fluorophores used to examine mouse fibroplasts.[89] Other potential uses include amplification of electromagnetic radiation in fibre optic communication systems and non-linear optical effects in the region of absorption edges.

Advances in the preparation of highly luminescent, nearly monodispersed nanocrystals have led to materials which now have the potential for use in optoelectronic applications. The use of oxide nanoparticles in photovoltaic devices is well documented, however, a wide range of other applications are now being investigated. The reproducible preparation and easy manipulation of organically passivated quantum dots offers simple routes to practical devices. The widening of the 'band gap' in a semiconductor quantum dot can be controlled by careful alteration of the particle's dimensions (often referred to as band gap engineering) and has opened up possible new areas of electronic research with a wide range of applications such as tunable diodes and lasers. The degree of control over small particles is exhibited in the preparation of single electron transistors, where the particle can be specifically placed between two electrodes. The preparation and manipulation of semiconductor nanoparticles is an interesting and exciting area of current research.

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