Ionic liquid passivated CdSe nanocrystals†

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CdSe nanoparticles have been prepared, using the phosphonium ionic liquid trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentylphosphinate) as a solvent and capping agent.

The organometallic-based pathways to high quality cadmium selenide (CdSe) nanoparticles, the prototypical material for investigations into size quantization effects, have improved noticeably since their genesis in 1993.[1] A range of metal salts and single-source precursors (instead of metal alkyls), non-coordinating solvent and differing passivating ligands are now routinely employed to prepare nanoparticles of the desired size and shape. The most common surfactant, tri-*n*-octylphosphine oxide (TOPO) is used as a passivating agent and solvent for a wide variety of materials, from semiconductors, to metals and metal oxides. The long alkyl chains on the molecule ensure the particle's solubility in a range of non-polar solvents, whilst the Lewis-base phosphine oxide unit coordinates to the nanoparticles surface *via* dative bonds, in the case of CdSe, to the cadmium sites. During the synthesis of CdSe nanoparticles, the selenium is often delivered in the form of a tri-*n*-octylphosphine selenide (TOPSe) solution, which has also been identified as a passivating agent as well as the selenium precursor, whilst TOP has been found to coordinate to selenium sites on the particle surface. The use of TOPO as a surfactant is somewhat limited, as evidence has shown the ligand decomposes into an as yet unidentified luminescent product at elevated temperatures, an undesirable property for a capping agent.[2] The surfactant has also been identified as a toxic material which exhibits remedial effects in biological systems.[3] As nanoparticles used in biological imaging often retain residual ligands, alternatives must be considered.

We have investigated a phosphonium ionic liquid as a replacement for TOPO, the benefit being the potential to bind to both anionic (selenium) and cationic (cadmium) surface sites whilst still maintaining the solubility in organic solvents (see ESI† for diagram/cartoon). The use of an ionic liquid should provide a more complete, well defined surface passivation. The ionic liquid chosen, trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentylphosphinate), was selected for numerous reasons; long alkyl chains, obvious points of coordination with the particle surface, commercial availability, thermal stability at temperatures associated with nanoparticles synthesis, low bioactivity and the potential for recycling.

To date, a variety of nanomaterials have been prepared using ionic liquids; metal fluorides,[4] silver and platinum nanoparticles,[5] aluminium antimonide[6] and cobalt platinum alloys[7] have all been reported, although little mention has been made as to the nature of the interaction of the particle with the ionic liquid. Notably, phase transfer of CdTe has also been achieved using an ionic liquid.[8] Here, we investigate a specific ionic liquid as a surfactant due to its similarities with existing capping agents.

The absorption spectrum of ionic liquid/TOP capped CdSe (Fig. 1) showed a clear excitonic feature at *ca.* 588 nm (2.10 eV), consistent with the $1S_e$–$1S_h$ transition in CdSe and a slight feature at *ca.* 500 nm (2.47 eV) which can be assigned to the $1S_e$–$2S_h$ state.[9] The effective mass approximation estimated a particle diameter of 4.98 nm when considering a shift in the band gap of 0.43 eV, the dielectric constant of 6.1 and effective masses of electrons and holes as 0.13 and 0.45, respectively. The emission spectrum (Fig. 1) was symmetrical and near-band edge, with no evidence of emission from low energy surface traps or defects, even after being stored in ambient conditions for weeks. The X-ray diffraction pattern (Fig. 2) displayed reflection consistent with wurtzite structured CdSe particles, *ca.* 4 nm in diameter. Electron microscopy (Fig. 3) revealed approximately spherical particles with

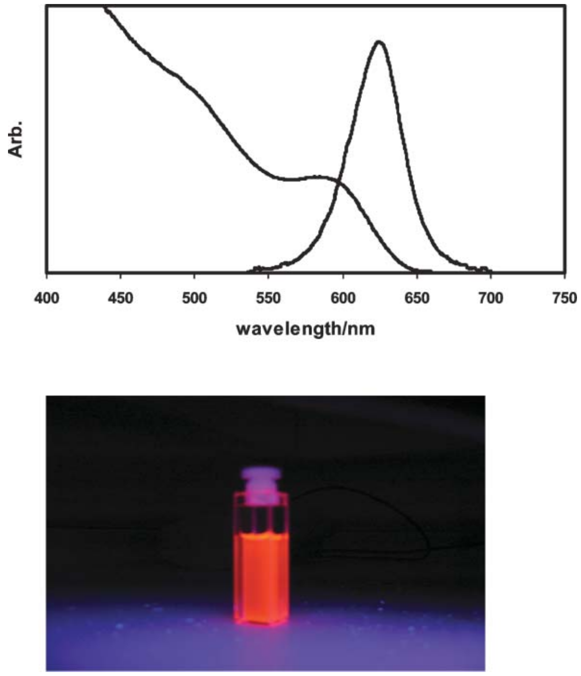

Fig. 1 Top: the absorption and emission spectra of ionic liquid/TOP capped CdSe. Bottom: emission from ionic liquid/TOP capped CdSe (λ_{exc} = 365 nm).

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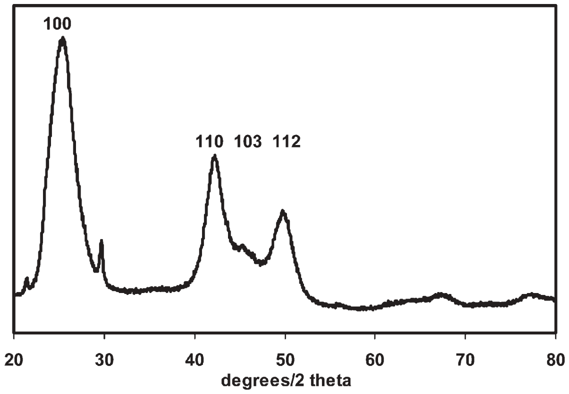

Fig. 2 X-Ray diffraction pattern and Miller indices for ionic liquid/TOP capped CdSe.

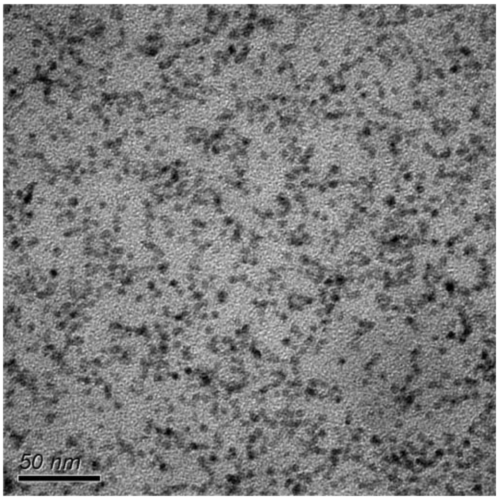

Fig. 3 Electron microscope image of ionic liquid/TOP capped CdSe. Scale bar = 50 nm.

an average diameter of 4.4 nm diameter ±7%. High resolution microscopy showed crystalline particles, some of which had a slight aspect ratio (supplementary material).

Nuclear magnetic resonance (NMR) of ionic liquid/TOP capped CdSe particles confirmed the presence of the ionic liquid species on the particle surface (ESI†). The proton NMR spectra of the particles showed clear resonances attributable to both the ionic liquid and trioctylphosphine. A number of multiplets between 0.9 and 1.5 ppm cannot be assigned to either the ionic liquid or TOP and appears to be numerous overlapping resonances consistent with both species, whilst a small, broad feature at 2.45 ppm is clearly associated with the ionic liquid.

Solution ^{31}P NMR of TOP/ionic liquid capped particles displayed a number of resonances, attributable to numerous phosphorus environments on the particle surface. The resonance at 32.8 ppm can be assigned as the ionic liquid free in solution (as references, free trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentylphosphinate) in $CDCl_3$ displayed a resonance at 32.71 ppm, as compared to 33.39 ppm as described in the literature.[10] A small amount of impurity was also detected at 44.85 ppm, and found in subsequent spectra). The resonances at *ca.* 36.5 and 48 ppm were assigned as ionic liquid species bound to the particle surface. The shift in the resonance downfield upon coordination to the Lewis acid Cd^{2+} is consistent with the surface deshielding the phosphorus nuclei, as previously found in cadmium complexes of triphenylphosphine oxide and in contrast to TOPO capped CdSe.[11]

We also examined CdSe prepared in the ionic liquid alone, the absorption spectra of which is included in the ESI.† The absorption spectrum suggests slightly larger particles than those prepared in the ionic liquid/TOP. We obtained essentially the same NMR spectra apart from two new features; the absence of a resonance at 34 ppm, and the presence of a new resonance at *ca.* 60 ppm. Thus the resonance observed in ionic liquid/TOP capped particles at 34 ppm was attributed to the presence of TOP in the reaction. We found no signal at −20 ppm previously attributed to TOP bound at a particle surface,[11] although it is worth noting that free TOPSe in solution exhibits a resonance at *ca.* 36 ppm. The new downfield signal suggests either an unknown mode of coordination, such as the entire molecule bound to the particle or a decomposition product, such as a novel phosphine selenide species obtained from the reaction between the trihexyl(tetradecyl)phosphonium cation and selenium. Although we cannot as yet attribute either of the two resonances to either the cationic or anionic species, it is clear there are (at least) two separate and distinct species (no evidence of coupling was observed) on the particle surface. Electron microscopy of CdSe capped with just the ionic liquid showed some particles with an increased aspect ratio (Fig. 4 and ESI†) which displayed a tendency to cluster (attributed to drying on the grid).

Fourier-transform IR spectroscopy of the ionic liquid revealed a number of sharp bends and stretches consistent with previous reports.[10] Similar spectroscopic investigations on the ionic liquid/TOP capped nanoparticles revealed a distinct single feature (ESI†) consistent with a (P=O) stretch at 1385 cm^{-1}, shifted from the other bends and stretches. This suggests that the 2,4,4-trimethylpentylphosphate species is present, bound to the surface cadmium much in the same way as phosphinic acids coordinate.[12]

An unusual effect observed with TOP/ionic liquid capped CdSe particles was the gradual evolution of the band edge emission.

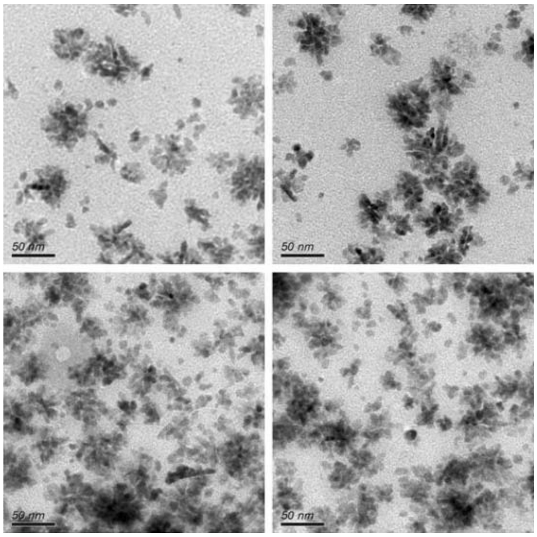

Fig. 4 Electron microscope images of CdSe nanoparticles capped with the ionic liquid alone. Scale bars = 50 nm.

Immediately after synthesis, no emission was observed when the sample was illuminated with a UV lamp (λ_{exc} = 365 nm).

In comparison, TOPO capped and notably amine capped CdSe particles exhibit band edge emission immediately after isolation. In some cases, when TOPO or amine capped particles are exposed to ambient condition, water and/or oxygen adsorb to the surface providing surface protection, hence the emission increases slightly (photobrightening).[13–20]

In comparison, prolonged exposure of TOPO capped CdSe nanoparticles to ambient conditions results in oxidation, releasing SeO_2 from the surface, leaving surface defects which may trap charge carriers and provide non-emissive recombination pathways. With TOPO capped CdSe quantum dots, the oxidation can be readily observed over a two day period, whilst amine capped CdSe dots can be stable for months, although all particle appear to oxidise eventually. In a report by Cordero *et al.*,[13] a thin film of TOPO capped CdSe particles in ambient conditions exhibited photobrightening, peaking at *ca.* 200 seconds followed by a gradual decrease in emission over the following 1.5 h. Importantly, Asami *et al.* have examined the photobrightening of TOPO capped CdSe films, and found ligand rearrangements (specifically the formation of a TOPO–Se complex not present in the initial material) are the key to the photobrightening process.[14]

The emission from the TOP/ionic liquid capped CdSe reported here emerged gradually over a matter of days, eventually becoming significantly bright in a matter of weeks (Fig. 1, bottom image); this photobrightening appeared to be distinct due to its slow development. Isolation of the particles with dry solvents, followed by manipulation under an inert atmosphere, dissolution in dry toluene and storage under nitrogen showed a slower evolution of the band edge emission. Although the onset of emission was still clearly observed, the photoluminescence was not as bright as emission from samples isolated with reagent grade solvent and stored in ambient conditions. This strongly suggests a species, such as water or oxygen protected the surface, although no evidence of oxidation (such as the eventual deep trap emission due to the oxide desorbing from the surface) was found in the nanoparticles spectra taken over a period of weeks. It is worth noting that particle exhibited the brightening effect only after being isolated with methanol. Particles dispersed directly in toluene did not show the effect to the same degree as samples isolated by precipitation induced by a non-solvent (methanol) This suggests the excess ionic liquid protected the particle surface, or that methanol was capable of coordinating to the particle surface and blocking surface defects. Importantly, the photobrightening process (and hence the generation of noticeable emission) does not occur in samples prepared solely in the ionic liquid, and it appears the presence of trioctylphosphine is essential. We suggest, whilst referring to the NMR spectra, that in the ionic liquid/TOP system, TOP also binds to the selenium sites, whilst in the pure ionic liquid system, both anion and cation species coordinates. We therefore suggest photobrightening is in fact a complex process dependent upon both ligand chemistry and environment.

The slow evolution of the emitting state in a dry, inert atmosphere leads us to suggest that the emission is not solely based on the absorption of other species to the particle surface. Gradual surface reconstructions are a key element in the development of luminescent particles,[21] and the absence of emission in solely ionic liquid capped particles leads us to suggest that the tight binding of both the cationic and anionic species may not allow surface reconstruction. Ionic species have been found to bind aggressively to all crystal facets in CdSe, even to cadmium atoms in underlying crystal planes (*i.e.*, not at the surface) when the surface is selenium rich.[22] The presence of trioctylphosphine as a less strongly bound capping agent may accommodate the surface reconstruction in selenium rich nanoparticles. In fact, this process closely resembles the photoluminescence enhancement described by Myung *et al.* in which oxygen provided a surface passivation for CdSe particles over a two week period.[23] Further experiments and modelling investigations are underway to understand this phenomenon better.

In conclusion, we have reported the use of a commercially available ionic liquid, as a convenient capping agent for passivating nanoparticles. The particles produced emitted bright, band edge emission and were stable in ambient conditions for months.

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