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# A novel single source precursor route to self capping CdS quantum dots

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**The synthesis of CdS nanocrystals has been carried out from the thermolysis in a dynamic vacuum, between 150 and 300 °C, of the novel asymmetric cadmium dithiocarbamate [$Cd\{S_2CNMe(C_{18}H_{37})\}_2$]; the particles 'self cap' during preparation; different size nanocrystals were synthesised, at different temperatures, and there was a change in phase from cubic to hexagonal CdS at a decomposition temperature of 300 °C.**

Nanocrystalline semiconductors have electronic properties intermediate between those of molecular entities and macrocrystalline solids and are at present the subject of intense research.[1–6] Nanometric semiconductor particles exhibit novel properties owing to the large number of surface atoms (and resultant states) and/or the three-dimensional confinement of electrons. Altering the size of the particle alters the degree of confinement of the electrons, and affects the electronic structure of the solid, in particular 'band edges', which are tunable with particle size. Nanoparticles of semiconductors have many potential applications and demonstration devices including light-emitting diodes,[7,8] photocatalysts[9,10] and electrochemical cells[1,6,11] have been reported.

We are interested in developing novel routes to these materials and have previously reported the use of single source precursors to prepare several II–VI chalcogenides.[12–14] These nanocrystals are organically capped with tri-*n*-octylphosphine oxide (TOPO). Other capping groups such as 4-ethylpyridine have also been used to solubilise nanocrystals, for example, InP.[15] We have also recently reported the use of trioctylphosphine sulfide as an air/moisture stable sulfiding precursor[16] for cadmium or zinc sulfide. However, to date there has only been one paper[17] describing the synthesis of nanocrystals in a process in which the particle is capped by a ligand transferred from the precursor; as a single parent molecule is involved, we term this process 'self-capping'. Finely divided silver has been prepared from the salts of fatty acids by a bulk pyrolysis. Here we report the first synthesis of self-capped CdS nanocrystals *via* thermolysis at 150–300 °C, in a dynamic vacuum, of the novel asymmetric cadmium dithiocarbamate, [$Cd\{S_2CNMe(C_{18}H_{37})\}_2$].

The cadmium dithiocarbamate precursor, [$Cd\{S_2CNMe(C_{18}H_{37})\}_2$] was prepared from the amine $HNMe(C_{18}H_{37})$, using a method described elsewhere.[14] The precursor was thermolysed *in vacuo* at temperatures ranging between 150 and 300 °C‡. The resulting solid was readily redispersed in pyridine. The absorption edges of the nanoparticles were calculated using the direct band gap method. The onset of absorption for all the samples showed a clear blue shift: 150 °C, *ca.* 430 nm (2.88 eV), 200 °C, 449 nm (2.76 eV), 250 °C, 465 nm (2.66 eV) as compared to that of bulk CdS, 515 nm (2.41 eV) [Fig. 1(*a*)]. The CdS samples all showed Stokes shifts in their photoluminescence spectra [Fig. 1(*b*)]. However, the observed Stokes shift decreases as the particle size increases: 150 °C, absorption maxima, $A_{\max}$, at 454 nm (2.73 eV) ($\lambda_{exc}$ = 370 nm) a Stokes shift, (SS), of 0.15 eV; 200 °C, $A_{\max}$ = 472 nm (2.63 eV) ($\lambda_{exc}$ = 400 nm), SS = 0.13 eV; 250 °C, $A_{\max}$ = 482 nm (2.57 eV) ($\lambda_{exc}$ = 390 nm), SS = 0.09 eV. This trend in the shifts of the absorption maxima in the PL spectra is as expected.

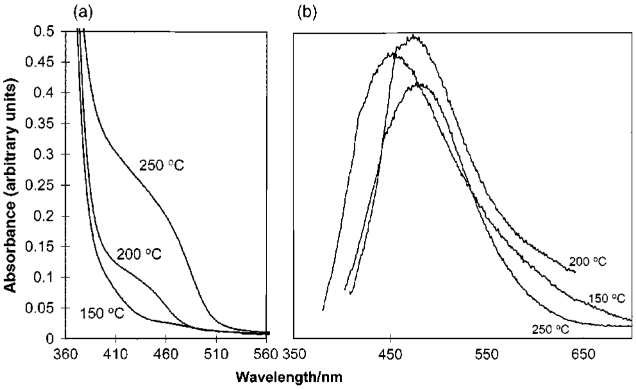

**Fig. 1** (a) UV and (b) PL spectra for CdS samples.

XRD of the powdered samples showed an interesting feature in the as-prepared CdS nanoparticles (Fig. 2). The CdS samples prepared at temperatures of 150–250 °C could be indexed to the standard patterns of the cubic phase.§ The largest particles of CdS from the thermolysis at 300 °C, were clearly of the hexagonal phase. There is no evidence that there is a mixing of phases as described by Bawendi *et al.* for CdSe nanocrystals prepared from inverse micelles.[18] The broadening of the peaks in the XRD patterns for all samples is typical of nanoparticles.

The nanoparticles were analysed by IR spectroscopy to establish the nature of the capping group. The capping agent of the nanocrystals could presumably be HNR′R″ or $S_2CNR'R''$. The IR showed no stretches associated with a C–N bond from the CdS nanocrystal samples (a typical C–N bond stretch was seen in the precursor sample). This suggests that the CdS nanocrystals are capped by $HNMe(C_{18}H_{37})$. $^1H$ and $^{13}C$ NMR spectroscopy show resonances associated with the amine. This taken with the IR data, is good evidence that the capping group is $HNMe(C_{18}H_{37})$. X-Ray photoelectron spectroscopy was used to analyse the CdS samples prepared at 200 and 300 °C. The analysis shows the presence of Cd, S, N and C. The ratio of C

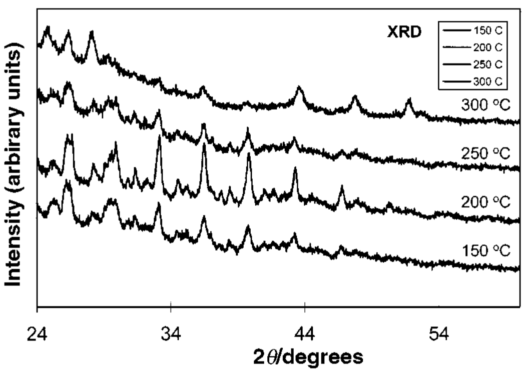

**Fig. 2** XRD patterns for the as-prepared CdS samples.

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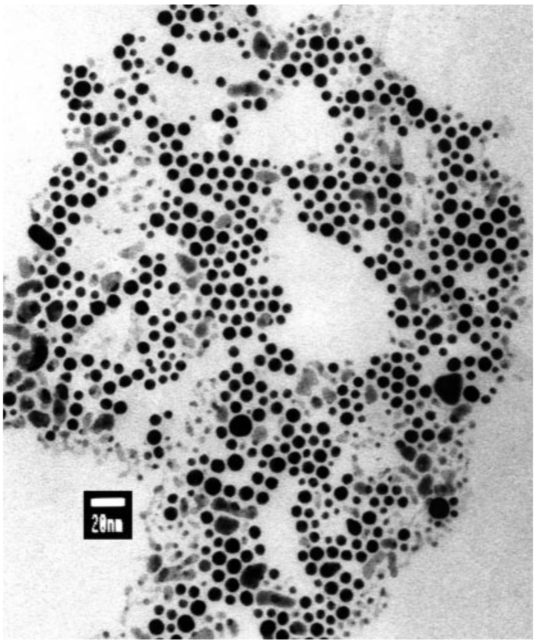

**Fig. 3** TEM image of CdS nanoparticles prepared at 150 °C.

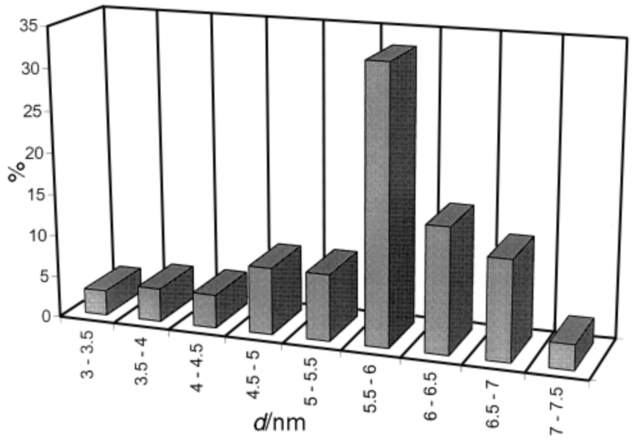

**Fig. 4** Size distribution of CdS nanoparticles.

to Cd in the 200 °C sample was significantly higher than in the sample prepared at 300 °C. This observation suggests that there is less capping agent on the sample prepared at 300 °C than that prepared at 200 °C. Hence, the CdS samples prepared at 150–250 °C are very soluble in pyridine while the sample prepared at 300 °C is only partially soluble. TEM images (Fig. 3) show quantum dots of CdS synthesised at 150 °C, which are not agglomerated. The size distribution of the dots is shown in Fig. 4. The dots are predominately of size 5.5–6 nm. The dots synthesised at 250 °C appear to have a halo-like tail structure. This could be the capping group emanating from the CdS nanoparticle. The estimated diameters of the dots are between 5 and 7 nm (Table 1); as calculated using the Scherrer equation and the direct band gap method from the onset of absorption in the UV spectra. These values compare well with those obtained from the TEM images.

**Table 1** UV and PL data and calculated diameters of particles using the direct bandgap method (onset of absorption from UV spectra) and the Scherrer equation (XRD data).

| Sample[a] | Onset of abs./eV | Abs. max./eV | Av. size/nm (Calc. from UV) | Calc. size/nm (Scherrer eqn.) |
|---|---|---|---|---|
| 150 | 2.88 | 2.73 | 4.5 | 5 |
| 200 | 2.76 | 2.63 | 5 | 5.5 |
| 250 | 2.66 | 2.57 | 6 | 6 |

[a] Preparation temperature/°C.

In conclusion, good quality, self capped CdS nanoparticles have been synthesised from the vapour phase thermolysis of the novel cadmium dithiocarbamate, $[Cd\{S_2CNMe(C_{18}H_{37})\}_2]$. The CdS nanoparticles are cubic in nature when prepared at 150–250 °C and hexagonal at 300 °C. The CdS samples were characterised by UV–VIS, IR, PL, XRD, XPS, NMR and TEM. Studies into other metal sulfide precursors are ongoing.

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## Notes and references

‡ Into a quartz vessel was put *ca.* 0.5 g of $[Cd\{S_2CNMe(C_{18}H_{37})\}_2]$. The decomposition apparatus was then put into a carbolite tube furnace. The apparatus was opened to a dynamic vacuum, *ca.* 0.01 mm Hg, there was also a liquid nitrogen trap to condense any volatiles from the thermolysis. The decomposition apparatus was heated at a range of temperatures, 150–300 °C, for 1 h (timed from temperature stabilisation). The vessel was allowed to cool and the contents, varying from off-white-yellow (150 °C) to dark orange (300 °C), were removed.

§ Optical measurements of the nanoparticles were carried out on a Philips PU 8710 spectrophotometer. The sample solutions were placed in silica cuvettes (path length = 1 cm). The samples were in pyridine solutions and pyridine was used as the reference. IR spectra were carried out using a Matteson Polaris FT-IR spectrometer with Nujol mulls. $^1H$ and $^{13}C$ solution NMR spectra were recorded on a Bruker AM 500 or a DRX 400 in $CDCl_3$. XRD patterns were measured using a Siemens D500 series automated powder diffractometer using Cu-Kα radiation at 40 kV/40 mA with a secondary graphite crystal monochromator. Samples were supported on glass slides (5 cm$^2$). PL measurements were obtained using a Spex FluoroMax instrument with a xenon lamp (150 W) and a 152 P photomultiplier tube as a detector. Silica cuvettes of 1 cm path length were used. Solutions were made using pyridine. A JOEL 2000 FX MK1 electron microscope operating at 200 kV with an Oxford Instruments AN 10000 EDS analyser was used for the conventional TEM micrographs. The samples for TEM were prepared by placing a drop of a dilute solution of sample in toluene on a copper grid (400 mesh, Agar). The excess solvent was wicked away with a paper tip and the sample allowed to dry completely at room temperature. The XPS measurements were performed in the ultra-high vacuum chamber (base pressure $10^{-8}$ Pa) of a VG ESCALAB-Mk II (VG Scientific) using Al-Kα excitation (analyser pass energy of 50 eV). The energy scale was calibrated using C 1s (at 284.4 eV) as a reference.

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