JOURNAL OF Materials Communication CHEMISTRY

# Synthesis of CdS nanocrystals using cadmium dichloride and trioctylphosphine sulfide

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***Received 10th March 1999, Accepted 5th May 1999***

**The synthesis of CdS nanocrystals has been carried out by the thermolysis of cadmium dichloride with trioctylphosphine sulfide as the sulfur source, in tri-*n*-octylphosphine oxide at 250 °C. The material shows quantum size effects in the optical spectrum. The onset of absorption for CdS is at ≈480 nm (bulk CdS, 515 nm), a blue shift in the absorption edge. The spectrum also shows a second excitonic peak at 379 nm (S. Modes and P. Lianos, *J. Phys. Chem.*, 1989, 93, 5854). The sample is composed of particles of diameter *ca.* 4.5 nm.**

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 due 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; for example, light-emitting diodes,[7,8] photocatalysts[9,10] and electrochemical cells[1,6,11] have been reported.

Nanocrystallites have been prepared by several different synthetic methods,[1–6,11] many involving aqueous solutions. However, for the majority of technologically important semiconductors, *e.g.* CdS, such methods have some limitations, in particular especially the use of noxious compounds, *e.g.* $H_2S$. There is also the potential for oxide or hydroxide incorporation from aqueous solution. In organic systems the use of bis(trimethylsilyl)sulfide[4,12] has been documented, but again this compound is pungent and air/moisture sensitive. 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.[13–15] However, the use of trioctylphosphine sulfide (TOPS) as a sulfide precursor has not, surprisingly, been reported. We now detail the successful use of TOPS, an odourless, air/moisture stable compound, in reaction with the simple salt cadmium dichloride, to give nanocrystalline cadmium sulfide.

The thermolysis of TOPS and $CdCl_2$ in tri-*n*-octylphosphine oxide (TOPO) yielded yellow CdS as a nanocrystalline material.† The electronic spectrum of CdS shows quantum size effects which are characteristic of nanodispersed semiconductor particles. The bulk band gap for hexagonal macrocrystalline CdS is 515 nm (2.41 eV). The CdS synthesised shows a blue shift in the absorption edge to 480 nm (2.58 eV). Using the Brus equation the particle size was estimated at 5.4 nm. Beyond the onset of absorption there is a clear shoulder at 480 nm. The UV spectrum shows a second peak at 379 nm (3.27 eV) (Fig. 1). Such observations are sometimes[16] taken to suggest a highly monodispersed sample of quantum dots in which evidence for excitonic recombination is observed for the first (close to band edge) and second higher energy exciton. The presence of well defined material is confirmed by the TEM of a typical sample (Fig. 2). It should be noted that, to our knowledge, this is the first time a second excitonic peak has been observed in the electronic spectrum of CdS and that this relatively monodispersed sample of CdS was obtained without any size fractionation of the synthesised material. EDAX confirmed the presence of TOPO and CdS in the methanol washed sample. X-Ray powder diffraction also confirmed the presence of hexagonal CdS crystalline nanoparticles.

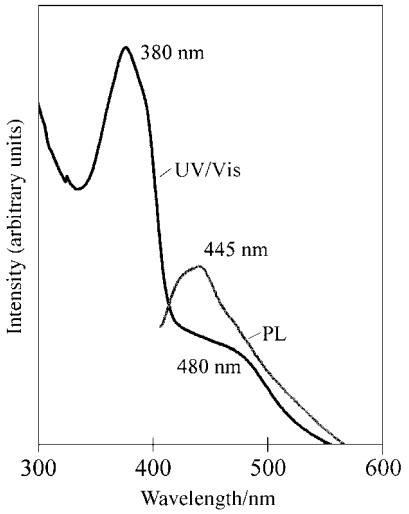


**Fig. 1** UV-Vis and PL spectra of CdS nanocrystals in toluene.

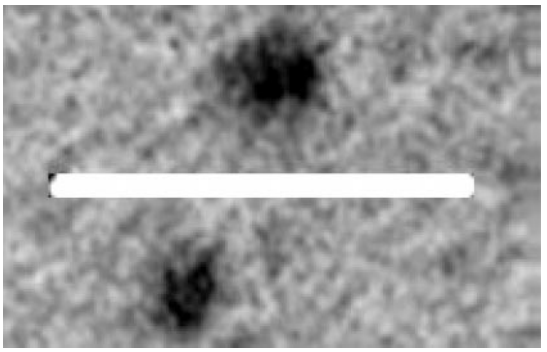

**Fig. 2** TEM of CdS nanoparticles (bar = 20 nm).

The infra-red spectrum of CdS shows peaks at 1465 and 1377 $cm^{-1}$ which are characteristic of TOPO ($\nu(CH_2)$). The peak for $\nu_{sym}$(P=O) at 1140 $cm^{-1}$ [17] has moved and broadened to 1105 $cm^{-1}$, a shift of 35 $cm^{-1}$. This shift is, according to Alivisatos and coworkers,[17] is due to Cd binding to the P=O. This result combined with the EDAX results confirms that TOPO is the capping group. A preliminary photoluminescence measurement ($\lambda_{exc}$ = 390 nm) on these nanoparticles, in toluene, can also been seen in Fig. 1. This shows a broad, close to band edge emission ($\lambda_{max}$) at 445 nm (2.78 eV).

We have demonstrated the synthesis of nanodispersed CdS from the reaction of two air stable precursors.

This work has been funded by an EPSRC grant to P.O.B. We would like to thank Mr. Keith Pell (QMW) for EDAX, SEM and TEM, Mr. Richard Sweeney (IC) for XRD. P.O.B is the Sumitomo/STS Professor of Materials.

## Notes and references

† *Experimental*: TOPO (20 g) was taken and degassed at 100 °C for 30 min. The temperature was then elevated until a steady 250 °C was achieved under nitrogen. Equimolar amounts of cadmium dichloride (*ca.* 1 g) and TOPS were mixed in trioctylphosphine (5 ml) and stirred. This resulting solution was then steadily injected into the hot TOPO. The temperature dropped by 20–30 °C on addition. The temperature of the solution was allowed to restabilise at 250 °C and then heated at this temperature for 30 min. A yellow–orange solution resulted. The heat was then removed and the solution allowed to cool to 60 °C. Methanol (40 ml) was then added and a flocculate formed. The solid was collected by centrifugation and then redispersed in toluene and centrifuged. The solution was decanted to give a clear yellow solution. The solvent was then removed to give TOPO capped CdS nanoparticles. The particles were washed with methanol to remove excess TOPO.

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*Communication 9/01901D*