JOURNAL OF
Materials
Communication
CHEMISTRY

Preparation of CdS nanoparticles using the cadmium(II) complex of *N*,*N*′-bis(thiocarbamoyl)hydrazine as a simple single-source precursor

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Received 18th January 2001, Accepted 6th April 2001
First published as an Advance Article on the web 19th April 2001

CdS nanoparticles have been synthesised by thermolysing $Cd(SCNHNH_2)_2Cl_2$ in tri-*n*-octylphosphine oxide (TOPO) at 230 °C. The optical properties and structural characteristics of the particles are reported.

Semiconductor nanoparticles have been identified as useful materials due to their unique size dependent optical and electronic properties. Much current work has focused on harnessing these unique properties in the fabrication of electronic devices such as light emitting diodes (LEDs),[1,2] quantum dot lasers,[3] or single electron transistors.[4] For their effective use in such applications, the nanoparticles have to be uniform in size, shape, and crystallinity. There have been many reports on routes to CdS nanoparticles, the most common being a colloidal route, based on controlled precipitation reactions yielding highly dilute suspensions of colloidal particles. Brus, Henglein and Weller have carried out pioneering work in the studies of the photophysical properties of nanocrystalline CdS.[5–9] The thermolysis of dimethylcadmium and a chalcogen source, *e.g.* bis(trimethylsilyl)sulfide for CdS, in tri-*n*-octylphosphine oxide (TOPO) at high temperatures (120–300 °C) has proven to be a useful route to nanoparticles.[10] The use of highly hazardous and volatile compounds such as dimethylcadmium and noxious compounds such as H_2S in some routes has justified the need for the development of efficient and safer routes to high quality nanoparticles.

We report here the synthesis of tri-*n*-octylphosphine oxide (TOPO) capped CdS nanoparticles using *N*,*N*′-bis(thiocarbamoyl)hydrazinecadmium(II) chloride, a novel single-source precursor.† O'Brien *et al.* have reported the use of dithiocarbamates of divalent metals as efficient single-source precursors for the deposition of high quality, monodispersed nanoparticles.[11–13] In the present work $Cd(SCNHNH_2)_2Cl_2$ is dispersed in tri-*n*-octylphosphine (TOP) and injected into TOPO at 150 °C. The resulting grey solution turned yellow after heating, to give TOPO capped CdS nanoparticles. The particles were isolated according to the method reported in the literature.[10]

Particles in the nanosize regime exhibit quantum confinement effects, the evidence of which is a blue shift in the optical spectrum. The optical spectrum for the TOPO capped CdS is typical of CdS particles smaller than the excitonic diameter (40 Å) for bulk CdS. The absorption edge of CdS, as calculated by the direct band gap method,[14] is 478 nm (2.59 eV) (Fig. 1a). This is a blue shift of 37 nm in relation to that of the bulk material (515 nm). The UV spectrum also shows a sharp excitonic feature at 450 nm which could be indicative of a highly monodispersed sample.[10] Bulk CdS is reported to have a broad emission with the emission maximum in the 500 to 700 nm region of the luminescence spectrum. The emission is due to recombination from surface defects (predominantly sulfur vacancies).[15] The photoluminescence spectrum (Fig. 1b) of CdS shows close to band edge emission, with the maximum at 450 nm (λ_{exc} = 380 nm). There is no evidence of any emission from surface defects confirming the passivation of the surface by TOPO. The EDAX spectrum shows strong peaks for cadmium, sulfur and phosphorus. The presence of TOPO is also confirmed by IR spectroscopy. A shift of 18 cm^{-1} to lower wavenumbers from the characteristic stretch of TOPO (ν_{sym},P=O = 1466 cm^{-1}) is observed. This shift has been observed previously for TOPO capped nanoparticles.[16,17]

The TEM micrograph (Fig. 2a) of the sample shows small particles with an average diameter of 5.05 nm (±8%). The calculation of the CdS diameter using the effective mass approximation (EMA) model[18,19] gives a value of 5.35 nm. The selected area electron diffraction (SAED) shows broad diffuse rings, indicative of the small particle size (Fig. 2b). The indexing of the diffraction rings confirms the (100), (103) and (112) planes of the wurtzite phase.

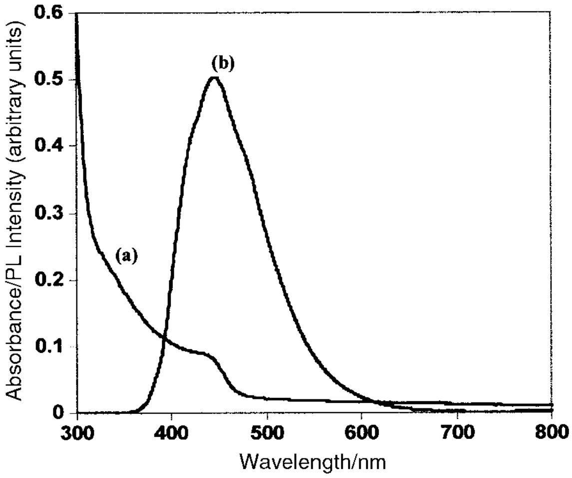

Fig. 1 (a) Optical absorption and (b) photoluminescence spectra of TOPO capped CdS nanoparticles.

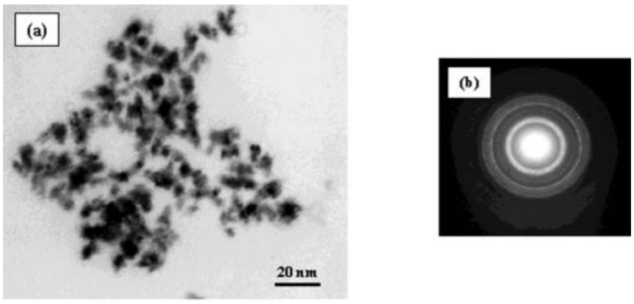

Fig. 2 CdS nanoparticles: (a) TEM micrograph and (b) SAED pattern.

We have hence demonstrated the preparation of nanoparticles of CdS from a very simple, effectively inorganic single-molecule precursor, the cadmium(II) complex of *N*,*N*′-bis(thiocarbamoyl)-hydrazine.

Acknowledgements

This work has been funded by the National Research Foundation (NRF) of South Africa. The authors would also like to thank Keith Pell (QMW, UK) for the TEM and SAED.

Notes and references

†**Experimental:**
Synthesis of N,N′-bis(thiocarbamoyl)hydrazinecadmium(II) chloride: $Cd(SCNHNH_2)_2Cl_2$ was synthesized by dissolving $CdCl_2\cdot H_2O$ (0.201 g) in water (50 ml). The resulting solution is then added to a hot solution of *N*,*N*′-bis(thiocarbamoyl)hydrazine (0.15 g) in water (50 ml). The precipitate was then digested over a water bath, filtered, washed thoroughly with distilled water and dried at room temperature.

Synthesis of CdS nanoparticles: In a typical procedure $Cd(SCNHNH_2)_2Cl_2$ (1.10 g) was dispersed in TOP (10 ml). This mixture was then injected into TOPO (30 g) at 150 °C. The resulting solution was grey and turbid. After heating (15 min) to 250 °C, the solution turned yellow. The temperature was maintained at 230 °C for three hours. The mixture was then cooled to 70 °C and excess methanol was then added. A yellow precipitate formed upon addition of methanol. The precipitate was isolated through centrifugation and redissolved in toluene for further analysis.

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