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Cadmium ethylxanthate: A novel single-source precursor for the preparation of CdS nanoparticles

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CdS nanoparticles capped with tri-*n*-octylphosphine oxide (TOPO) have been synthesised by a single-source route using cadmium ethylxanthate as a precursor. The nanoparticles obtained show quantum size effects in the optical absorption spectra and the photoluminescence shows an emission maximum that is characteristically red shifted in relation to the band edge. The X-ray diffraction (XRD) pattern shows the material to be hexagonal with a calculated particle size (from the Scherrer equation) of 3.9 nm. The size of the particles is confirmed by the transmission electron microscope (TEM) image, which shows well-defined, spherical particles with an average size of 4.2 nm ± 10%.

Introduction

The synthesis of semiconductor quantum dots has received considerable attention in recent years because of the potential of these materials in many different technological applications and intrinsic interest in the fundamental properties of this form of matter.[1–4] The study of this new class of materials provides an opportunity to investigate properties not generally seen in either the bulk or molecular limits. Quantum dots have discrete, large-molecule-like, electronic states that lead to their 'band-gaps' shifting to higher energy with decreasing particle size. The widening of this HOMO-LUMO gap with the decreasing particle size directly affects the photophysical properties of the material. The synthetic procedures employed generally attempt to control the particle size. In general, nucleation and subsequent growth of the semiconductor material are controlled and the final particle is passivated by a suitable organic molecule.[5–9] There are also reports on the synthesis of nanoparticles in rigid matrices such as that of pores of zeolites,[10] Langmuir–Blodgett films[11]or in polymers.[12,13] Perhaps the most useful general method for the preparation of semiconductor nanocrystallites was initially developed by Murray *et al.*[14] who devised a method to synthesise nearly monodisperse nanometer sized CdE (E = S, Se. Te). The synthesis involves the rapid injection of organometallic reagents into a hot coordinating solvent to produce a homogeneous nucleation followed by growth to give surface derivatised nanocrystallites. In a typical preparation of CdSe, a solution of dimethylcadmium in TOP (tri-*n*-octylphosphine) is prepared and mixed with a solution of TOPSe in TOP and filled into a syringe. TOPO is heated in a reaction vessel to above 300 °C and the solution is injected into it rapidly. The temperature falls rapidly by *ca.* 20 °C and then the contents of the reaction vessel are heated to 230–260 °C. In this synthetic procedure, the nanocrystallites are capped by both TOPO and TOPSe.[15] Single-source precursors, especially thiocarbamates, can also be thermolysed in TOPO to give TOPO capped nanoparticles.[16] We are now involved in systematic studies to develop new single-source precursors to synthesise monodispersed nanoparticles. We have recently published a new method involving the use of a cadmium(II) complex of *N,N′*-bis(thiocarbamoyl)hydrazine as an efficient single-source precursor for the synthesis of CdS nanoparticles.[17] Metal xanthates have been known since 1815 when Zeise prepared xanthates of potassium, barium, lead and copper.[18] These compounds are formed by the reaction between a metal alkoxide and carbon disulfide. In this paper we report the use of a cadmium complex of ethylxanthate as an efficient single-source precursor for the synthesis of CdS nanoparticles

Experimental

Methanol, toluene, cadmium chloride, and potassium ethylxanthate used in the present study were analytical grade reagents. TOP (Aldrich) was used as supplied. TOPO was purified by the method described in the literature.[19] Cadmium ethylxanthate was synthesised by the method of Iimura *et al.*[20]

UV-vis, IR, mass spectroscopy

A PerkinElmer Lamda 20 UV-vis spectrophotometer was used to carry out optical measurements. Samples were placed in quartz cuvettes (1 cm pathlength). IR spectra were taken on PerkinElmer Paragon 1000 FT-IR spectrometer, as KBr pellets. Electrospray mass spectra were recorded on a Micromass platform mass spectrometer.

Thermogravimetric analysis

Thermogravimetric analysis of the precursor was carried out with a PerkinElmer Pyris 6 TGA in nitrogen atmosphere, at a heating rate of 10 °C min^{-1}.

Photoluminescence spectroscopy

A Jobin Yvon–Spex Fluorolog-3 spectrofluorimeter with xenon lamp was used to measure the photoluminescence of the nanocrystallites. The samples were placed in quartz cuvettes (1 cm pathlength)

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X-Ray diffraction (XRD)

The wide-angle X-ray diffraction pattern was recorded using a Philips X'Pert materials research diffractometer. Measurements were taken using a glancing angle incidence detector at an angle 3° for 2θ values over 5–60° in steps of 0.04° with a count time of 2 s.

Electron microscopy

A JEOL JEM-1200EXII transmission electron microscope using a JEOL EM-ACD10 anti-contamination device was used for the conventional TEM measurements. The operating voltage was 80–100 kV. The EDAX spectra were obtained using the LINK QX2000 energy dispersive analysis system operating at 25 kV at a tilt angle of 30°. The samples were deposited on to carbon-filmed grids using a fine pipette, air-dried and immediately examined by the microscope.

Synthesis of cadmium ethylxanthate: $Cd(C_2H_5OCS_2)_2$

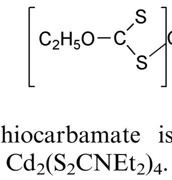
Cadmium chloride 1.0 g (0.005 mol) was dissolved in 20 mL distilled water. A solution of potassium ethylxanthate 1.6 g (0.02 mol) in 20 mL distilled water was added to it. A pale yellow precipitate was formed, which was filtered, washed with distilled water and dried under vacuum. mp 165 °C, yield 1.32 g (74.6%), CHS analyses (%), experimental (theoretical): C, 20.9 (20.3); H, 2.85 (2.82); S, 36.1. Mass spectra (electrospray) highest molecular ion, 710, corresponding to $[Cd(C_3H_5OS_2)_2]_2$.. IR (cm^{-1}) and tentative assignments: 1195, C–O; 1035, C–S; and 346, Cd–S.[21]

Synthesis of CdS nanoparticles

The TOPO-capped nanoparticles were synthesised by the general method outlined in ref. 16 using standard Schlenck techniques. TOPO (20 g) was dried and degassed in a three-necked flask fitted with a thermometer, condenser and rubber septum. The TOPO was then heated to about 160 °C under an atmosphere of nitrogen. Cadmium ethylxanthate (1 g) dispersed in 10 mL TOP was injected into the hot TOPO through the rubber septum. The temperature of the reaction mixture was observed to drop by 15–20 °C. Heating was continued to raise the temperature to 180 °C. The precursor decomposed at this temperature to give a yellow solution. The temperature was then raised to 280 °C, which was maintained for 1 h. The solution was then cooled to *ca.* 70 °C and excess methanol was added. The flocculant precipitate formed was centrifuged and washed with methanol. The isolated solid was dispersed in toluene for further analysis. The growth of the CdS nanoparticles was monitored as a function of time by withdrawing aliquots from the reaction mixture (2 mL) with a syringe at various time intervals. Measurement of the optical absorption spectrum of the isolated particles as a dispersion in toluene followed.

Results and discussion

Metal xanthates have been known since 1815, however detailed structural studies have only been carried out in the last three decades.[20] Xanthates are expected to resemble dithiocarbamates in their bonding mode. In the solid state the 1 : 2 complex of cadmium



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with *N,N*-diethyldithiocarbamate is built from essentially molecular dimers of $Cd_2(S_2CNEt_2)_4$. Two of the dithiocarbamate groups act as bidentate chelating ligands, and the other two as bridging ligands. The cadmium atom is five-coordinate, the coordination polyhedron being intermediate between a tetragonal pyramid and a trigonal pyramid.[22] In contrast, in the case of cadmium ethylxanthate each cadmium atom is surrounded by four sulfur atoms arranged almost tetrahedrally around it. A major structural difference from the dithiocarbamates is that each sulfur atom is attached to a different xanthate group, which in turn, bridges two adjacent cadmium atoms resulting in a two-dimensional network consisting of the cadmium atoms and xanthate groups.[20]

The synthesis of CdS nanoparticles *via* the organometallic route reported by Murray *et al.*[14] involves the use of dimethylcadmium, which is extremely toxic, pyrophoric, expensive and unstable at room temperature. However, there are reports on a modification of the above synthetic procedure by using simple cadmium salts as the cadmium precursor. But the choice of the cadmium salt is critical as the anion of the salt plays a crucial role in deciding the quality of the nanocrystals synthesised.[23] The use of single-molecule precursors has the advantage of avoiding the toxic cadmium precursors and eliminating the undesired effects of the anions of the cadmium salt during the synthesis. When the precursor dispersed in TOP is injected into TOPO, well above the decomposition temperature of the precursor, sudden decomposition takes place which results in a burst of homogeneous nucleation. The sudden drop in temperature prevents further nucleation and on gentle heating controlled growth and annealing of the naocrystallites occurs. It is well established that group II–VI materials form defects and interdiffuse at temperatures above 500 °C and hence the use of single-source precursors are of great advantage in synthesising good quality nanocrystals as they need to be heated to only moderately high temperatures.[24]

In the present study, $Cd(C_2H_5OCS_2)_2$ has proven to be an efficient single-molecule precursor for the deposition of CdS nanocrystallites. This precursor is easy to synthesise, air stable and pyrolyses cleanly to give good yields.

Thermogravimetric analysis (TGA) of cadmium ethylxanthate was carried out. The TGA curve shown in Fig. 1 reveals that decomposition occurs around 160 °C, therefore allowing the injection of the precursor into the TOPO at 160 °C.

Optical properties of CdS nanoparticles

The UV-vis absorption spectrum of CdS nanoparticles is shown in Fig. 2. The spectra were recorded in transmission mode and samples were prepared by making a dispersion in toluene. For the bulk crystallites we usually observe the interband absorption spectrum with a band edge around 515 nm. As the crystalline size decreases there is a blue shift of the absorption edge. In the present case the band edge is observed at 418 nm with a further shoulder at *ca.* 380 nm. A similar feature for the UV-vis spectrum of the nanocrystalline CdS has

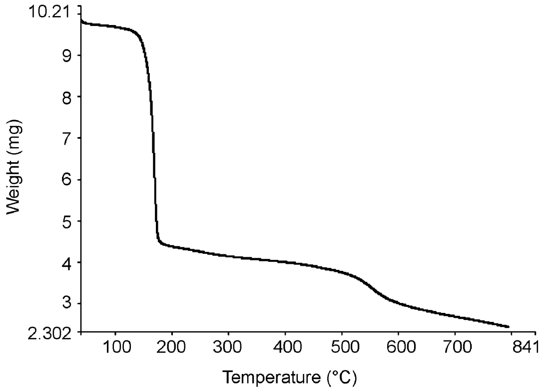

Fig. 1 Thermogravimetric analysis (TGA) curve for the decomposition of $Cd(C_2H_5OCS_2)_2$.

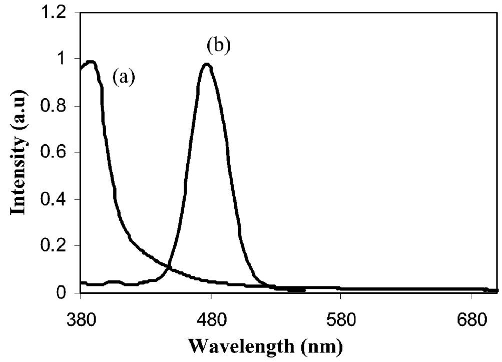

Fig. 2 CdS nanoparticles (a) optical absorption spectrum and (b) photoluminescence spectrum (t = 1 h).

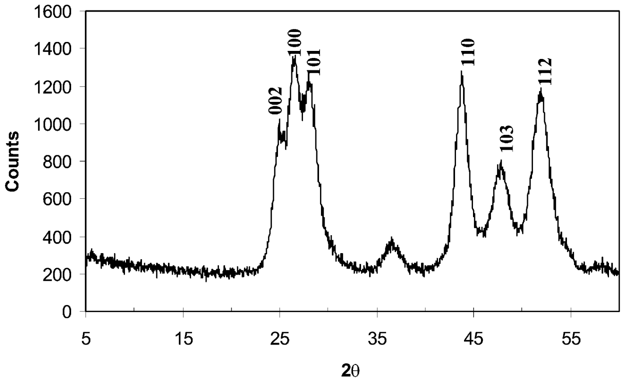

Fig. 4 X-ray diffraction pattern of CdS nanoparticles (t = 1 h).

been reported by Motte[25] and Hoyer *et al.*[26] As the crystallite size increases the shoulder shifts to lower wavelengths and finally disappears in bulk solids. There is a change in the band gap from 2.41 eV (bulk sample) to 2.97 eV, a significant shift in the band gap.

There have been attempts to propose models to explain the change in band gap as a function of particle size.[3] The particle size in the present case was calculated by the Brus equation[27,28] and was found to be 3.4 nm. The particle growth was monitored by measuring the optical absorption spectrum of samples withdrawn at various time intervals from the reaction vessel. The absorption spectra of the samples isolated after 5, 10, 30 min and 1 h are shown in Fig. 3. The band edge of all the samples falls in the 415–425 nm range, a blue shift in relation to bulk CdS (515 nm). The absence of any substantial change in the band gap of the samples at different time intervals is an indication that nucleation and growth takes place very rapidly at the temperature of injection. The particles grow to an optimum size within 5 min of injection.

Bulk CdS has a broad emission with a maximum in the 500–700 nm region of the luminescence spectrum. The emission is believed to be due to recombination from surface defects.[29] The photoluminescence spectrum of CdS in this work has a maximum at 476 nm (λ_{ex} = 308 nm), (Fig. 2). This red shift in relation to the absorption band edge is generally observed in II–VI semiconductor nanoparticles.[30,31] The EDAX spectrum gives strong peaks for cadmium, sulfur and phosphorus. The phosphorus peak arises from the capping agent TOPO. The presence of TOPO is further confirmed by IR spectroscopy. The CdS particle show a band around 1450 cm^{-1}which can be assigned to (ν_{sym}, P=O). Similar shifts in IR frequencies of TOPO-capped nanoparticles are reported in literature.[32]

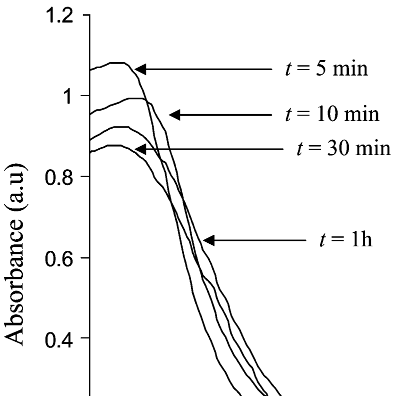

Fig. 3 Optical absorption spectra of CdS nanoparticles taken at different time intervals.

Bulk CdS usually exists in the hexagonal phase from room temperature to the melting point.[33] However, CdS nanocrystallites can exist as either cubic or the hexagonal phase. The wide-angle X-ray diffraction pattern of the nanocrystallites is shown in Fig. 4. The XRD peaks are broadened compared to those of the bulk CdS indicating that the particles are in the nanosize regime. However, the (110), (103), and (112) planes of wurtzite CdS are clearly distinguishable in the diffraction pattern. The mean crystallite diameter, d, can be calculated by the Scherrer formula,[34]

$$d = 0.94\lambda/B\cos\theta \qquad (1)$$

where λ is the X-ray wavelength, and B is the full width at half maximum of the diffraction peak on the 2θ scale. The size of the crystallites was determined using the (110) reflection at 43.786° (2θ) and the calculated value is found to be 3.9 nm.

The TEM image of CdS nanocrystallites (Fig. 5a) shows quite well-defined, spherical particles. The particles have a narrow size distribution with a mean particle size of 4.2 nm (Fig. 5b).

Conclusions

In the present work we have synthesised CdS nanocrystallites with a relatively narrow size distribution by the thermolysis of cadmium ethylxanthate. The average particle size of the crystallites was estimated by three different methods *viz.* optical absorption, XRD and TEM measurements. The values obtained are 4.8, 3.9 and 4.2 nm, respectively, which are in reasonable agreement with each other. X-ray diffraction studies reveal that the CdS nanocrystallites exist as the hexagonal phase. Optical absorption measurements show that the band edge is blue shifted indicating the quantum confinement of the particles. The optical absorption measurements of samples withdrawn from the reaction vessel at various time intervals after the injection of the precursor was used to monitor the growth of the particle with time and it is observed that nucleation and growth of the particles take place rapidly.

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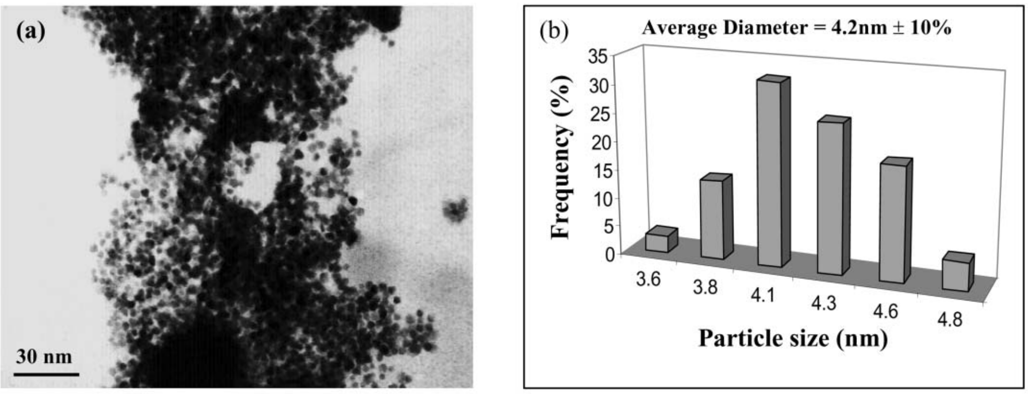

Fig. 5 CdS nanoparticles ($t = 1$ h): (a) TEM image and (b) particle size distribution.

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