Novel single molecule precursor routes for the direct synthesis of highly monodispersed quantum dots of cadmium or zinc sulfide or selenide

B. Ludolph, M. A. Malik, P. O'Brien* and N. Revaprasadu

Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, SW7 2AY UK.
E-mail: p.obrien@ic.ac.uk

Good quality highly mono-dispersed nanoparticles of II–VI binary chalcogenides ME ($M = Zn$ or Cd, $E = S$ or Se) have been prepared in a 'one-pot' synthesis by the thermolysis in tri-*n*-octylphosphine oxide (TOPO, *e.g.* at 200 °C for 45 min, *ca.* 50 Å ± 2.5 Å diameter) of the corresponding bis[methyl(*n*-hexyl)di-thio or -seleno]carbamato {$M[E_2CNMe(C_6H_{13})]_2$, $E = S$ or Se} complexes; the CdS, CdSe and ZnSe particles have been characterized by electronic spectroscopy, photoluminiscence, X-ray diffraction and electron microscopy (SAED, SEM and TEM).

Compound semiconductors as isolated quantum dots[1–7] are the subject of considerable interest. Cadmium selenide has been extensively studied and is an attractive material because its band gap can be tuned across the visible region by varying the size of the material in the range 400–800 nm. One particularly useful approach to the synthesis of CdSe is the pyrolysis of metal–organic species in tri-*n*-octylphosphine oxide.[8] We have successfully developed a variation of this method in which single molecule precursors, often based on carbamato complexes, have been used. A wide range of quantum dots have been prepared including CdSe, CdS, PbS, PbSe and ZnSe.[9–11]

However, we have now developed some novel air stable precursors based on bis[methyl(*n*-hexyl)diselenocarbamato]-zinc or -cadmium which decompose cleanly in MOCVD to selenides.[12–14] Here, we have used these compounds in a novel 'one pot' synthesis of quantum dots of the II–VI semiconductors ME ($M = Zn$ or Cd and $E = S$ or Se). Highly monodispersed CdSe, CdS, ZnSe, and ZnS with good optical properties can be prepared.

In a typical synthesis,† 1.0 g of the precursor was dissolved in 15 ml trioctylphosphine (TOP). This solution was then injected into hot trioctylphosphine oxide (TOPO) (200 °C) and kept at this temperature for 30–40 min. The resulting solution was cooled to *ca.* 70 °C and an excess of methanol added and a flocculant precipitate formed. The solid was separated by centrifugation and redispersed in toluene. The toluene was removed under vacuum to give TOPO capped ME nanoparticles. The absorption edge of the nanoparticles were calculated using the direct band gap method.[15]‡ The optical absorption edge for CdSe nanoparticles showed a clear blue shift (614 nm, 2.02 eV, fraction 1 to 599 nm, 2.09 eV, fraction 5) as compared to the bulk band gap (716 nm, 1.73 eV). A similar but smaller shift (498 nm, 2.48 eV, fraction 1 to 493 nm, 2.51 eV, fraction 5) was shown by CdS nanoparticles (bulk 512 nm, 2.42 eV).

Accurate measurement of the absorption edge for ZnS nanoparticles (bulk ZnS 340 nm, 3.65 eV) was difficult owing to the overlap with TOPO absorption (300 nm). Different fractions of ZnSe nanoparticles showed a blue shift in the absorption spectra (362 nm, 3.42 eV to 345 nm, 3.59 eV) as compared to the bulk band gap (480 nm, 2.58 eV). The average size of the particles decreases from fraction 1 to 5. The relatively small shift in the absorption edge from fraction 1 to 5 for both CdS and ZnSe samples reflects the relatively narrow size distribution in these samples.

TEM images show well defined, spherical particles with the size range of 53–59 Å (CdS), 54–59 Å (CdSe) (Fig. 1), and 35–42 Å (ZnSe). The XRD patterns for CdSe, CdS (Fig. 1 and 2) and ZnSe show broad peaks typical of small particles. The SAED pattern exhibits broad diffuse rings owing to the small size of the crystallites. The indexing of the lattice parameters patterns of XRD and SAED for CdSe, CdS and ZnSe indicate the formation of the hexagonal phase.§ The EDAX pattern clearly confirmed the presence of the corresponding elements for ME nanoparticles. The strong peak for phosphorus in each case was due to the capping of the particles by TOPO which was further confirmed by shift in the IR band (P=O) for TOPO.

The photoluminescence spectra for CdS nanoparticles show a broad band edge emission from 589 to 504 nm for excitation at 370 nm depending upon the concentration of samples. A shift in luminescence maxima at higher concentration was observed which is due to filtering effects which became important at such concentrations. Near band edge luminescence was observed for CdSe for a excitation wavelength at 465 nm which indicates a fluorescence activation by surface derivation. The maximum of the emission band is gradually blue shifted as the size distribution become weighted with particles of the smaller dimensions. Fig. 3(a) and (b) show the photoluminescence and band edges for CdSe and CdS nanoparticles. The luminescence spectrum of ZnSe nanoparticles showed a broad emission at 440

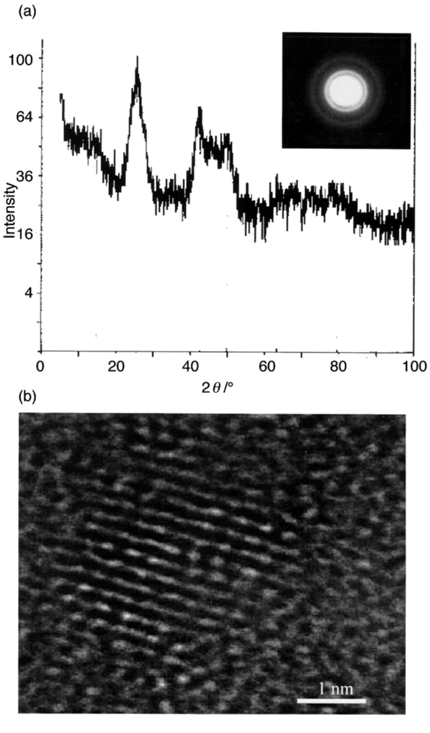

Fig. 1 (a) XRD and SAED pattern for CdSe nanoparticles and (b) HRTEM image of a CdSe Q-dot (diameter: 5 nm)

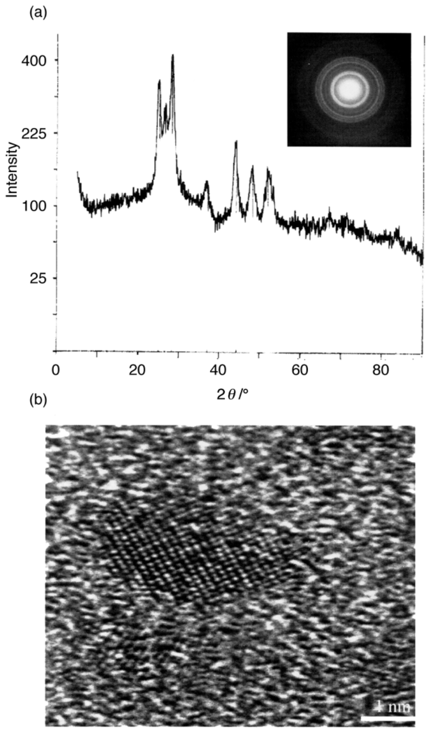

Fig. 2 (a) XRD and SAED pattern for CdS nanoparticles and (b) HRTEM image of a CdS Q-dot (diameter: 5 nm)

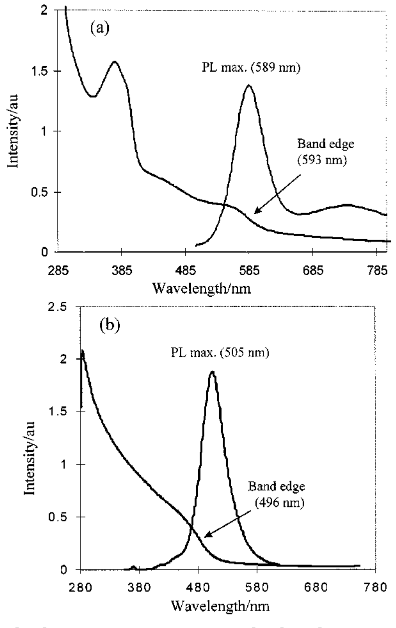

Fig. 3 Optical absorption spectrum and photoluminescence spectrum showing the band edge and emission maximum of (a) CdSe (fraction 3) and (b) CdS (fraction 3)

nm for an excitation wavelength of 345 nm. The emission spectrum is red shifted in relation to the band edge by *ca.* 0.04 eV. As the particle size decreases the surface/volume ratio increases thereby increasing the number of surface traps. These surface states or defects normally associated with semiconductor nanoparticles are passivated by TOPO. Therefore the deep trap emission associated with these states are absent.

In conclusion, good quality highly mono-dispersed nanoparticles of ME have been prepared for the first time by thermolysis in TOPO using $M[E_2CNMe(C_6H_{13})]_2$ type single molecule precursors in a one pot synthesis. These are the first stable, non-air sensitive single molecule precursors which can easily be used to give high yields of TOPO capped quantum dots. The CdS, CdSe and ZnSe particles have been characterized by UV–VIS, PL, EDAX, XRD, SAED and TEM whereas the ZnS particles were characterized by UV–VIS, PL and EDAX only and are being investigated for other properties.

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Notes and References

† The compounds were prepared by adaptations of the literature methods[15,16] and fully characterised by NMR, mass spectrometry, microanalysis and IR spectroscopy.

‡ A Philips PU 8710 spectrophotometer was used to carry out the optical measurements, the samples were placed in silica cuvettes (1 cm path length). For photoluminescence spectroscopy a Spex FluoroMax instrument with a xenon lamp (150 W) and a 152 P photomultiplier tube as a detector was used to measure the photoluminescence of the particles. Good spectra were obtained with the slits set at 2 nm and an integration time of 1 s. The samples were placed in quartz cuvettes (1 cm path length). The wavelength of excitation is indicated in the text and was shorter than the onset of absorption of the particular sample being studied. X-Ray diffraction patterns were measured using a Philips PW 1700 series automated powder diffractometer using Cu-Kα radiation at 40 kV and 40 mA with a secondary graphite crystal monochromator. Samples were supported on glass slides (5 cm). A concentrated toluene solution was slowly evaporated at room temperature onto a glass slide to obtain a sample for analysis. A JOEL 2000 FX MK 1 electron microscope operating at 200 kV with an Oxford Instrument AN 10000 EDS analyser was used for the conventional TEM images. Selected area electron diffraction (SAED) patterns were obtained using a JEOL 2000 FX MK2 electron microscope operated at 200 kV. The samples for TEM and SAED were prepared by placing a drop of a dilute solution of sample in toluene on a copper grid (400 mesh, agar). The excess of solvent was wicked away with a paper tip and the sample allowed to dry completely at room temperature. EDAX (energy dispersion analytical X-ray spectroscopy) was performed on the sample deposited by evaporation on glass substrates by using a JEOL JSM35CF scanning electron microscope.

§ The X-ray diffraction pattern of the CdS particles gave peaks with the following observed *d*/Å values (% relative intensity, *hkl*): 3.55 (76, 100), 3.35 (52, 002), 3.16 (100, 101), 2.06 (43, 110) and 1.90 (26, 103) corresponding to hexagonal cadmium sulfide; 3.57 (62, 100), 3.36 (91, 002), 3.16 (100, 101), 2.45 (29, 102), 2.07 (48, 110) and 1.90 (50, 103) (ASTM). CdSe: 3.50 (100, 002), 2.13 (80, 110), 1.84 (50, 112) and 1.48 (10, 211) corresponding to hexagonal phase; 3.51 Å (70, 002), 2.15 (85, 110), 1.83 (50, 112) and 1.38 Å (8, 211) {ASTM}. ZnSe: 3.06 (70, 101), 1.99 (100, 110), 1.24 (35, 105), 1.10 (40, 302) corresponding to hexagonal phase; 3.05 (70, 101), 1.99 (100, 110), 1.22 (40, 105), 1.09 (40, 302){ASTM}.

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