A simple route to synthesise nanodimensional CdSe–CdS core–shell structures from single molecule precursors

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Highly mono-dispersed CdSe–CdS core–shell nanoparticles have been prepared by a novel method in which $[Cd\{Se_2CNMe(^nHex)\}_2]$ (250 °C for 30 min) and $[Cd\{S_2CNMe(^nHex)\}_2]$ (250 °C for a further 30 min) are thermolysed in tri-*n*-octylphosphine oxide (TOPO) in a 'one pot' synthesis; the core–shell structure has been characterized by electronic spectroscopy, photoluminescence, X-ray diffraction and electron microscopy (SAED, SEM and TEM).

Unique physical and chemical properties due to quantum confinement effects have been reported for a wide range of semiconductor nanoparticles.[1–6] Whilst many studies have focused on the relationship between particle size and optical behavior, the control of the surface chemistry is still a challenge to chemists. The presence of localized surface trap sites (defects) due to the high surface-to-volume ratio has made surface modification a necessity. Passivation of the surface has been achieved by organic ligands such as thiopyridine,[7] thiolates,[8] and 2,2′-bypyrimidine.[9] Core–shell structures such as Si–SiO_2,[10] CdS–Cd(OH)_2,[11] CdSe–ZnS,[12] CdSe–ZnSe,[13,14] CdS–HgS–CdS[15] and CdSe–CdS[16–18] are examples of inorganic passivation. These systems normally show an increase in photoluminescence efficiency and reduced fluorescence lifetimes.

We report the synthesis of a CdSe–CdS core–shell structure using the precursors $[Cd\{Se_2CNMe(Hex)\}_2]$ and $[Cd\{S_2CNMe(Hex)\}_2]$ for the CdSe core and CdS shell, respectively.† In a typical synthesis, $[Cd\{Se_2CNMe(Hex)\}_2]$ (0.8 g) was dissolved in tri-*n*-octylphosphine (TOP) (15 ml). This solution was then injected into hot (250 °C) tri-*n*-octylphosphine oxide (TOPO) (20 g) and kept at this temperature for 30 min to give CdSe. To prepare the core–shell structure a solution of $[Cd\{S_2CNMe(Hex)\}_2]$ (0.5 g) in TOP (10 ml) was injected into the deep red reaction mixture. The reaction was allowed to proceed for a further 30 min and the resulting solution was cooled to *ca.* 70 °C. Methanol was then added and a flocculant precipitate formed which was separated by centrifugation. CdS and CdSe nanocrystals were also synthesized as described previously.[19]

The absorption spectra for CdS, CdSe and CdSe–CdS nanoparticles are shown in Fig. 1.‡ The band edge (652 nm; 1.90 eV) of the CdSe–CdS structure is red shifted (22 nm, 0.02 eV) as compared to the CdSe nanocrystals (630 nm; 1.96 eV). This red shift is indicative of the formation of the core–shell structure. The overall shape of the spectrum is similar to that of CdSe, however a slight sharpening of the features at 535 and 613 nm is observed which may suggest a narrower size distribution. Photoluminescence (PL, λ_{ex} = 400 nm) shows an emission maximum close to the absorption band edge in both CdSe (585 nm) and the core–shell (622 nm) nanocrystals (Fig. 1), an observation consistent with the observed absorption spectra. The intensity of the emission maximum is considerably increased in the core–shell structure as compared to the parent materials.[10–17]

The X-ray diffraction pattern‡ of CdSe–CdS shows broad peaks along the (110), (103) and (112) planes which are assigned to the hexagonal phase of CdSe (Fig. 2) suggesting that the diffraction is predominantly due to the CdSe core. The sharp X-ray pattern§ indicates epitaxial growth of the shell. This also accounts for the slight shift in the peaks to higher 2θ values in the core–shell structure since the epitaxy requires that the lattice parameters are the same for both core and shell and hence will be between those for CdS and CdSe, as is observed. Similarly, in the SAED,‡ a pattern intermediate between that for CdS and that for CdSe was observed, as expected (Fig. 2). The reflections for the (002), (100) and (101) planes shown in the hexagonal CdS diffraction pattern are not visible in the CdSe and CdSe–CdS patterns owing to broadening of the peak in the region 2θ
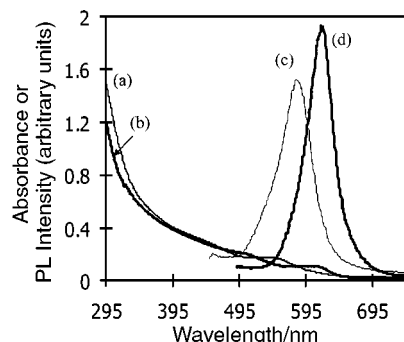

Fig. 1 Absorption spectra of (a) CdSe–CdS, (b) CdSe and photoluminescence spectra (λ_{ex} = 400 nm) of (c) CdSe, (d) CdSe–CdS.
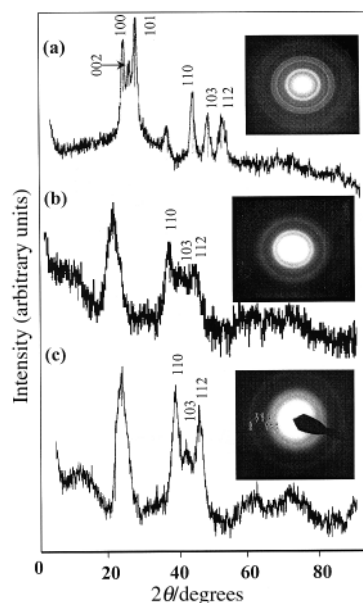

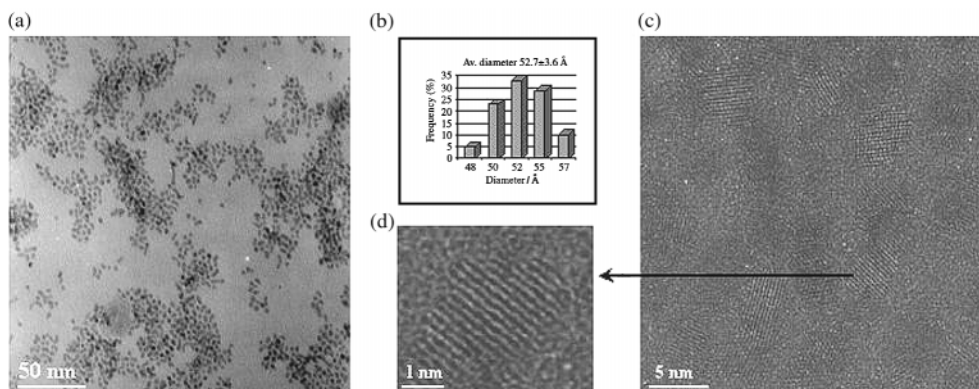**Fig. 2** XRD and SAED patterns showing the hexagonal phase for (a) CdS, (b), CdSe and (c) CdSe–CdS.

Fig. 3 CdSe–CdS core–shell nanocrystals: (a) TEM image, (b) particle size histogram, (c) HRTEM image, (d) HRTEM image of a single quantum dot (*ca.* 5.3 nm in diameter).

$\approx$ 20–25°. The X-ray data may be consistent with a core–shell structure or with the formation of a composite but the composite would give blue shifts in the emission and absorption maxima. A red shift clearly shows the presence of the core–shell structure.

TEM images‡ show well defined, spherical CdSe–CdS particles (Fig. 3) with an average size of 53 ± 3.6 Å. The average size of the bare CdSe nanoparticles is 45 Å which indicates an increase of 8 Å due to the CdS shell in the core–shell nanoparticles. The crystallinity of the core–shell structure is confirmed by an HRTEM image (Fig. 3) which shows clear lattice fringes for the CdSe core (hexagonal phase).

HRTEM‡ showed lattice spacings intermediate between those for CdSe and CdS as is observed by SAED and X-ray patterns. As expected, no interface can be observed by HRTEM between the CdSe core and the CdS shell. The EDAX pattern and ICP analysis‡ confirmed the presence of Cd, Se and S in the CdSe–CdS nanoparticles. The peak for phosphorus in each case was due to the capping of the particles by TOPO which was further confirmed by a shift in the IR band (from 1146 to 1120 cm^{-1}, P=O) for TOPO.

Highly monodispersed CdSe–CdS core–shell nanoparticles have been prepared by a novel route involving thermolysis in TOPO using [Cd{Se$_2$CNMe(^{n}Hex)}$_2$] and Cd{S$_2$CNMe-(^{n}Hex)}$_2$] as single molecule precursors in a one-pot synthesis. This route is a simple and convenient route to produce reasonable quantities of high quality, monodispersed core–shell nanoparticles. The precursors are easy to synthesize and store and give high yields of TOPO capped quantum dots.

Notes and references

† The compounds were prepared by adaptations of the literature method[20,21] and fully characterised by NMR, mass spectometry, microanalysis and IR spectroscopy.

‡ A Philips PU 8710 spectrophotometer was used to perform the optical measurements for which 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. Measurements were carried out on samples with an optical density of 0.1 at 400 nm, also the excitation wavelength. 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). X-Ray diffraction studies were performed using secondary graphite-monochromated Cu-Kα radiation (40 kV) on a Philips X'Pert Materials Research Diffractometer (MRD, R. Sweeney, IC). Measurements were taken using a glancing angle incidence detector at an angle of 3°, for 2θ values in the range 20–60° in steps of 0.04° with a count time of 1 s. For electron microscopy a JEOL 2000 FX MK 1 electron microscope operated at 200 kV with an Oxford Instrument AN 10000 EDS analyser was used for the conventional TEM (transmission

electron microscopy) 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 solvent was wicked away with a paper tip and the sample allowed to dry completely at room temperature. EDAX (energy dispersion analytical X-rays) was performed on samples deposited by evaporation on glass substrates using a JEOL JSM35CF scanning electron microscope. ICPAES analyses (Cd, Se, S) were recorded on an ARL instrument, Geology Department, Imperial College.

§ The X-ray diffraction pattern of the CdS particles gave peaks with the following observed *d* values (% relative intensity, *hkl*): of 3.55 Å (76, 100), 3.35 Å (52, 002), 3.16 Å (100, 101), 2.06 Å (43, 110) and 1.90 Å (26, 103) corresponding to the hexagonal cadmium sulfide *cf.* 3.57 Å (62, 100), 3.36 Å (91, 002), 3.16 Å (100, 101), 2.45 Å (29, 102), 2.07 Å (48, 110) and 1.90 Å (50, 103) {ASTM}. For CdSe: 3.50 Å (100, 002), 2.13 Å (80, 110), 1.84 Å (50, 112) and 1.96 Å (48, 103) corresponding to the hexagonal phase *cf.* 3.51 Å (70, 002), 2.15 Å (85, 110), 1.83 Å (50, 112) and 1.98 Å (70, 103) {ASTM}. For the CdSe–CdS core–shell: 3.50 Å (100, 002), 2.15 Å (85, 110), 1.83 Å (66, 112), 1.98 Å (60, 103) corresponding to the hexagonal phase *cf.* 3.51 Å (70, 002), 2.15 Å (85, 110), 1.83 Å (50, 112) and 1.98 Å (70, 103) {ASTM}.

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