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Novel single-molecule precursor routes for the direct synthesis of InS and InSe quantum dots

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Nanoparticles of InS and InSe capped with TOPO (tri-*n*-octylphosphine oxide) or nanoparticles of InSe capped with 4-ethylpyridine, which are close to mono-dispersed, have been prepared by a single-source route using tris(diethyldithiocarbamato)indium(III) or tris(diethyldiselenocarbamato)indium(III), respectively. The nanoparticles of InS and InSe both show quantum size effects in their optical spectra and the photoluminescence (PL) spectra show broad emissions due to the surface traps. Substantial blue shifts in the onset of absorption have been observed; 0.44 eV for InS and 1.60 eV for InSe. The X-ray diffraction (XRD) pattern of InS showed co-precipitation with TOPO and the crystalline particles turned powdery when studied by transmission electron microscopy (TEM). Selected area electron diffraction (SAED), X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies of the InSe nanoparticles show the hexagonal phase in the size range 5.8–7.0 nm. The crystallinity of the InSe nanoparticles was also evident from high resolution transmission electron microscopy (HRTEM), which gave well defined images of nanosize particles with clear lattice fringes.

Introduction

Most reports on quantum dots deal with II–VI, III–V or IV–VI materials and there have been few papers concerned with III–VI materials.[1–6] Dimitrijevic and Kamat prepared colloids of In_2Se_3 stabilized with either poly(vinyl alcohol) (PVA) or sodium metaphosphate (SMP).[7] They reported particles with diameters of approximately 2–3 nm (SMP stabilized) and 30 nm (PVA stabilized) with absorption maxima at 375 and 250 nm for the former and an onset of absorption at approximately 550 nm in the latter case. The same authors reported the synthesis of In_2S_3 colloids in acetonitrile, with particle diameters ranging between between 100 and 200 nm.[8] Barron *et al.*[9] have described the preparation of nanoparticles of GaSe and InSe by MOCVD using the cubane precursors $[(^t\mathrm{Bu})\mathrm{GaSe}]_4$ and $[(\mathrm{EtMe_2C})\mathrm{InSe}]_4$. The GaSe particles had a mean diameter of 42(±13) nm whereas the spherical InSe particles were 88(±30) nm in diameter. The particle sizes were determined by TEM and no optical data were reported.

Experimental

Chemicals

Indium chloride, dichloromethane, 4-ethylpyridine (98%), diethylamine, carbon disulfide, tri-*n*-octylphosphine oxide (TOPO) and tri-*n*-octylphosphine (TOP) were purchased from Aldrich Chemical Company Ltd. Methanol, light petroleum (b.p. 40–60 °C) and toluene were from BDH. CSe_2 was prepared by a literature method.[10] TOPO was purified by vacuum distillation at *ca.* 250 °C (0.1 Torr). The solvents used for air sensitive chemistry were distilled, deoxygenated under a nitrogen flow and stored over molecular sieves (type 4 Å, BDH) before use.

Preparation of $In(S_2CNEt_2)_3$ and $In(Se_2CNEt_2)_3$

The single source precursor $[In(S_2CNEt_2)_3]$ was prepared by the literature method.[11] CSe_2 was prepared by the method of Henriksen[10] and immediately added to a solution of diethylamine (excess) in dichloromethane to give a diethylammonium salt[12] which was reacted with indium chloride to give tris(diethyldiselenocarbamato)indium(III).[13]

UV–VIS 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).

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 (XRD)

X-Ray diffraction patterns were measured using a Philips PW 1700 series automated powder diffractometer using Cu-Kα radiation at 40 kV/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.

Electron microscopy

A JEOL 2000 FX MK 1 operated at 200 kV electron microscope with an Oxford Instruments AN 10000 EDS analyzer was used for the conventional transmission electron microscopy (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 the 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. Energy dispersion analytical X-ray (EDAX) studies were performed on samples deposited by evaporation on glass substrates using a JEOL JSM35CF scanning electron microscope. For HRTEM a drop of a dilute solution of the sample was placed on a holey carbon film and left to evaporate, then examined in a JEOL 4000 EX TEM instrument at 400 kV.

Preparation of indium sulfide and indium selenide nanoparticles

A modification of the single source route as described by Trindade and O'Brien[14,15] was used for the preparation of InS and InSe nanoparticles.

Indium sulfide

Thermolysis in TOPO. TOPO (30 g) was heated under nitrogen in a three-necked flask fitted with condenser and thermometer to a temperature of 100 °C, the system was degassed and flushed with nitrogen three times. The temperature was then raised to 250 °C and stabilized at this temperature. $[In(S_2CNEt_2)_3]$ (0.28 g) was dispersed under stirring in TOP (10 ml) and injected into the TOPO solution through a septum. The reaction proceeded for 30 min at 250 °C. An excess of methanol was then added to the cooled solution (70 °C), forming a white flocculent precipitate. The solid was separated by centrifugation and re-dispersed in toluene. The colourless solution of InS nanoparticles was evaporated to dryness under vacuum at room temperature. The residue was washed three times with methanol to remove free TOPO, followed by re-dispersion in toluene. A process of size selective precipitation by the addition of a non-solvent (methanol) was attempted to narrow the size distribution.[16] This, however, was unsuccessful because of the instability of the material.

Thermolysis in 4-ethylpyridine. A solution of $[In(S_2CNEt_2)_3]$ (1.0 g) in 4-ethylpyridine (25 ml) was heated to 100 °C for 1 h and then refluxed (167 °C) for 24 h. A solid crystalline material was obtained on overnight cooling, analysis of which showed it to be the starting material.

Indium selenide

Thermolysis in TOPO. $[In(Se_2CNEt_2)_3]$ (1.0 g) was dispersed in TOP (12 ml) and this solution was injected into TOPO (25 g) at 250 °C. After an initial drop in temperature the reaction was stabilized at 240 °C and heated for 30 min. The pale yellow solution was cooled to 70 °C and an excess of methanol added, forming a flocculent precipitate. The white solid was then centrifuged and re-dispersed in toluene. Any undissolved decomposition products were separated by centrifugation. The toluene was removed under vacuum to give a fine white precipitate of InSe nanoparticles.

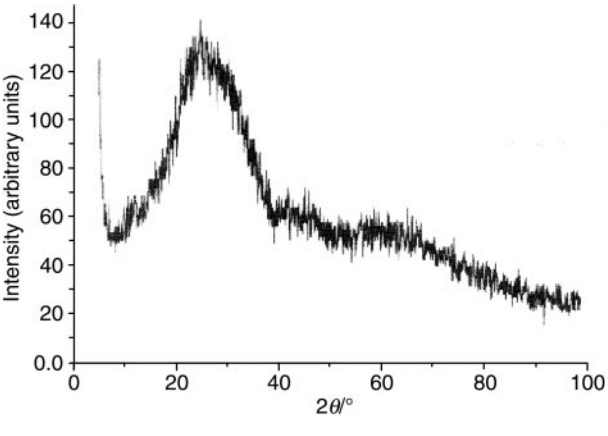

Fig. 1 XRD pattern of TOPO capped InSe nanoparticles.

Thermolysis in 4-ethylpyridine. A solution of $[In(Se_2CNEt_2)_3]$ (0.5 g) in 4-ethylpyridine (15 ml) was heated to 100 °C. The reaction was stabilized at this temperature for 1 h and then heated to 167 °C, at which temperature it was refluxed for 24 h. Excess light petroleum was added to the pale yellow solution on cooling, resulting in a flocculent precipitate. The white precipitate was then centrifuged and re-dispersed in 4-ethylpyridine to give an optically clear solution of InSe nanoparticles.

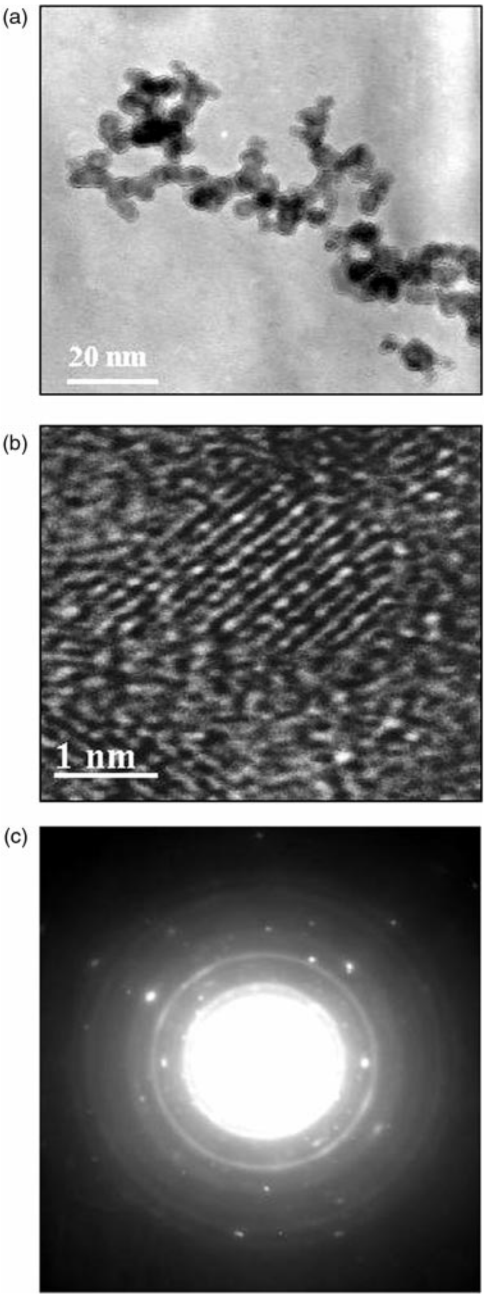

Fig. 2 TOPO capped InSe nanoparticles: (a) TEM image, (b) HRTEM image of a single dot, (c) SAED pattern.

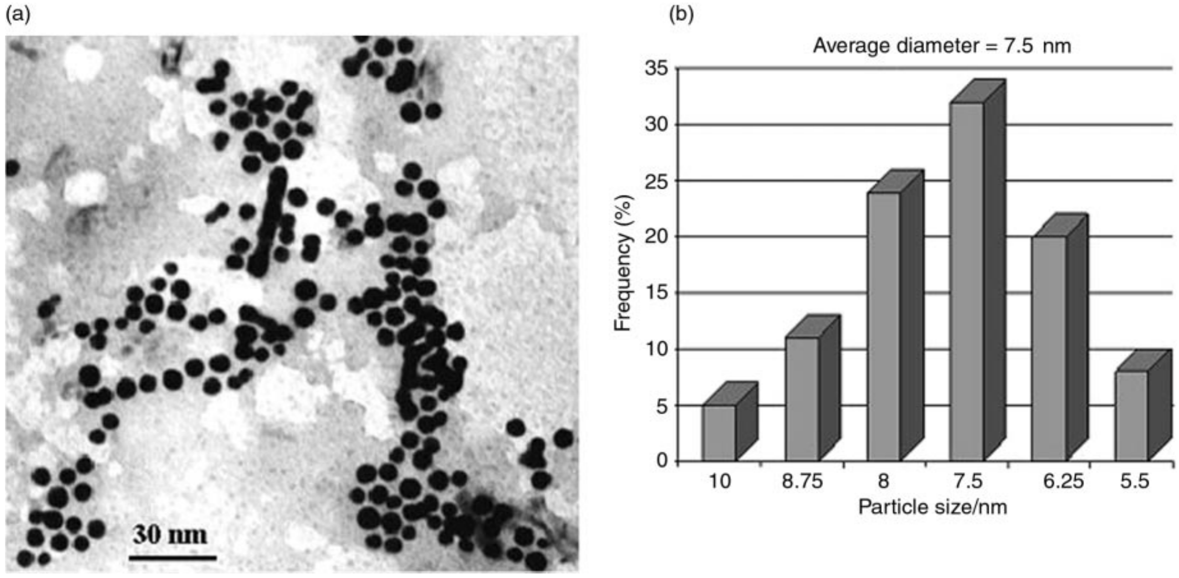

Fig. 3 4-Ethylpyridine capped InSe nanoparticles: (a) TEM micrograph, (b) size distribution histogram.

Results and discussion

Indium sulfide and indium selenide nanoparticles were prepared from tris(diethyldithio/selenocarbamato)indium(III) precursors in TOPO. Attempts at size fractionation for both types of nanocrystals were unsuccessful. No precipitate was obtained on addition of methanol. The inability to narrow the size distribution is probably due to the formation of a stable oxide layer on the particle surface, preventing any interaction with the non-solvent.[17] Moreover the particles started to coagulate in toluene solution at room temperature after a period of four days. The indium sulfide nanoparticles also turned powdery when studied by TEM.

Attempts were made to prepare more stable nanoparticles of indium sulfide and indium selenide in 4-ethylpyridine. Only the starting materials were recovered from attempted preparations of indium sulfide nanocrystals in 4-ethylpyridine. However, thermolysis of tris(diethyldiselenocarbamato)indium(III) gave well defined mono-dispersed nanoparticles under similar conditions.

Structural characteristics

The XRD pattern of the InS nanoparticles provides firm evidence for coprecipitation with TOPO. In the 2θ range 10–25° several sharp peaks can be assigned to TOPO. However, a broad hump seen at 2θ 10–25° may suggest some other amorphous material is present. The EDAX spectrum displays peaks for phosphorus, sulfur and indium, which is consistent with particles of indium sulfide capped with TOPO. The crystalline nanoparticles turned to powder while being studied by TEM. In_2Se_3 exists in the α, β and γ phases with transition temperatures of 200 and 250 °C, respectively, for the α–β and β–γ transitions.[18] The poor crystallinity of the particles, as evident in the XRD pattern, made it difficult to define the phase present. The XRD pattern (Fig. 1) shows a broad peak in the 2θ region 20–30° with a less defined peak in the 45° region. The broad peak corresponds to the (004) plane of hexagonal InSe with the less defined peak corresponding to the (008) plane. Such broad peaks are typical of particles in the nano-size range, as confirmed by the selected area electron diffraction pattern which shows diffuse rings. The faint rings are indexed as corresponding to the *d*-spacing of the (004) and (008) planes of wurtzite InSe [Fig. 2(c)]. The TEM micrograph exhibits spherical, chain-like particles of InSe [Fig. 2(a)] with an average size of *ca.* 6.4 nm. The lattice fringes were visible although accurate indexing of the spacing was not possible. The HRTEM micrograph shows a nanoparticle with an average diameter of *ca.* 5.25 nm [Fig. 2(b)]. The EDAX spectrum shows the presence of indium, selenium and phosphorus. The TEM micrograph of particles capped with 4-ethylpyridine shows well defined mono-dispersed nanoparticles [Fig. 3(a)] with an average diameter of *ca.* 7.5 nm.

Optical properties

The optical spectra of both InS and InSe display quantum size effects. The shape of the absorption spectrum of the TOPO capped InS nanoparticles is typical of a wide size distribution (Fig. 4). The band edge (as determined by the direct band gap method)[19] is at 430 nm (2.88 eV), a blue shift in relation to bulk InS (508 nm; 2.44 eV). The PL spectrum shows a broad peak with an emission maximum at 452 nm which again indicates a large size distribution of nanoparticles. The absorption spectrum (Fig. 5) of the TOPO capped InSe nanoparticles has an excitonic shoulder at 320 nm, with the band edge at 365 nm (3.40 eV), a blue shift in relation to the bulk band gap of InSe (689 nm; 1.80 eV). The 4-ethylpyridine capped InSe nanoparticles exhibit a band edge at 402 nm (3.08 eV), a slightly smaller (0.32 eV) band gap than those capped with TOPO (average diameter 6.4 nm) due to the larger particle size (average diameter 7.5 nm) of the former. The PL spectra of both the TOPO capped and 4-ethylpyridine capped InSe nanoparticles show broad PL peaks with emission maxima at 412 and 450 nm, respectively. The broad shapes of the PL

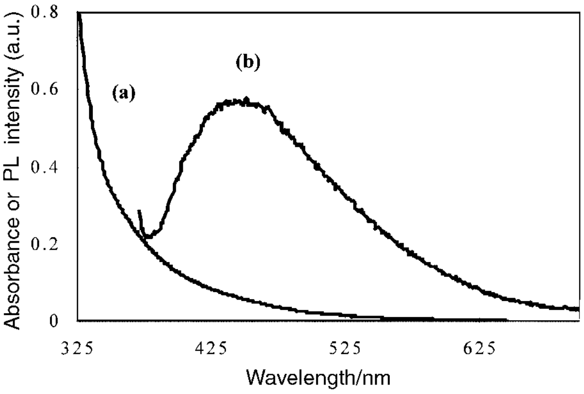

Fig. 4 Optical spectra of TOPO capped InSe: (a) absorption spectrum showing a band edge at 430 nm, (b) PL spectrum showing an emission maximum at 452 nm.

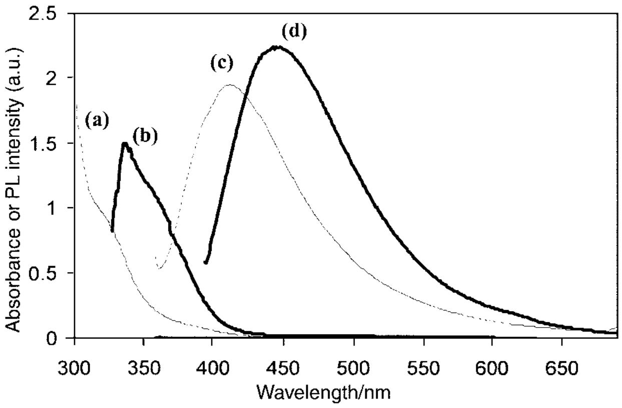

Fig. 5 Optical spectra of indium selenide: (a) absorption spectrum of TOPO capped InSe showing the band edge at 365 nm, (b) absorption spectrum of 4-ethylpyridine capped InSe showing a band edge at 402 nm, (c) PL spectrum of TOPO capped InSe showing an emission maximum at 412 nm, (d) PL spectrum of 4-ethylpyridine capped InSe showing an emission maximum at 450 nm.

peaks are indicative of a large size distribution. The emission maxima are red shifted in relation to the band edges. This red shift is attributed to recombination from surface traps, resulting from inefficient surface passivation.

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