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Single-source molecular precursors for the deposition of zinc selenide quantum dots

Neerish Revaprasadu,[ab] M. Azad Malik,[a] Paul O'Brien,*†[a] (the late) Macpherson M. Zulu[b] and Gareth Wakefield[c]

[a] *Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AZ*

[b] *Department of Chemistry, University of Zululand, Private Bag X1001, Kwadlangezwa-3886, South Africa*

[c] *Department of Engineering Science, University of Oxford, Parks Road, Oxford, UK OX1 3PJ*

TOPO (tri-*n*-octylphosphine oxide)-capped ZnSe (in the form of close to mono-dispersed nanoparticles) has been prepared by a single source route using ethyl(diethyldiselenocarbamato)zinc(II) as a precursor. The nanoparticles obtained show quantum size effects in their optical spectra and exhibit near band-edge luminescence. A blue shift of 0.25 eV in relation to the bulk material is observed. The selected area electron diffraction (SAED) and X-ray diffraction (XRD) patterns show the material to be hexagonal. The crystallinity of the material was also evident from high-resolution transmission electron microscopy (HRTEM) which gave well defined images of nanosize particles with clear lattice fringes.

The unique optical properties of semiconductor nanoparticles (quantum dots) have made these materials the subject of intense research in recent years.[1–6] Such properties include a marked blue shift in the absorption band edge and increase in luminescence intensity at the band edge. These effects are due to the influence of the crystallite size on electronic structure quantum size effects. Such materials may be useful for optoelectronic and non-linear optical applications. Several methods have been employed to prepare ZnSe nanoparticles including: the nucleation and growth from a supersaturated glass solution,[7] from non-aqueous solution,[8] and by a sol–gel process.[9] The ZnSe nanoparticles can be potentially useful for blue light lasers.

We report the preparation of isolated tri-*n*-octylphosphine oxide (TOPO)-coated ZnSe nanoparticles from a novel method of using a single source approach as employed previously for CdSe, CdS[10] and PbS.[11] To our knowledge the present study is the first report of well defined isolated ZnSe nanoparticles.

Experimental

Chemicals

Diethylzinc, dichloromethane, diethylamine, selenium, 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. TOPO was purified using the literature method.[12] 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.

UV–VIS 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). Infrared spectra were carried out using a Matteson Polaris FT-IR spectrometer as Nujol mulls.

Photoluminescence spectroscopy

A Spex FluoroMax instrument with a xenon lamp (150 W) and a 152 P photomultiplier tube as a detector were 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 electron microscope operating 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 operating 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 dispersive analysis by X-rays) was performed on the sample deposited by evaporation on glass substrates by using a JEOL JSM35CF scanning electron microscope. For high-resolution TEM (HRTEM) a drop of the dilute solution of sample was placed on a holey carbon film and left to evaporate and then examined under a JEOL 4000EX TEM at 400 kV.

Syntheses

Bis(diethyldiselenocarbamato)zinc(II). CSe_2 was prepared by the method of Henrikson[13] and immediately added to a

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†E-mail: p.obrien@ic.ac.uk

solution of diethylamine (excess) in dichloromethane to give a diethylammonium salt[14] which was reacted with zinc sulfate to give bis(diethyldiselenocarbamato)zinc(II).[15]

Ethyl(diethyldiselenocarbamato)zinc(II). Ethyl(diethyldiselenocarbamato)zinc(II) was prepared from the reaction of diethylzinc with bis(diethyldiselenocarbamato)zinc(II) in toluene as described previously.[16]

Method of preparation of quantum dots

A modification of the single-source route as described by Trindade and O'Brien was used for the preparation of the ZnSe nanoparticles.[10,11] Typically 1.0 g of $EtZnSe_2CNEt_2$ was dissolved in 25 ml TOP. This solution was then injected into hot TOPO (250 °C). A decrease in temperature of 20–30 °C was observed. The solution was then allowed to stabilize at 250 °C and heated for 30 min at this temperature. The pale yellow solution was cooled to approximately 70 °C and an excess of methanol added, a flocculent precipitate formed. The solid was separated by centrifugation and redispersed in toluene. The toluene was removed under vacuum to give pale yellow TOPO-capped ZnSe nanoparticles. The particles were washed three times with methanol and redissolved in toluene. Size-selective precipitation was carried out as described in the literature.[17] Briefly, this procedure involved the dropwise addition of methanol to the toluene solution containing the nanoparticles until the solution became turbid. The precipitate was separated by centrifugation to give the first fraction of nanoparticles. The second and subsequent fractions were obtained by repeating the same process with the supernatant.

Results and Discussion

ZnSe nanoparticles were prepared by the thermolysis of $EtZnSe_2CNEt_2$ in TOPO at 250 °C, a single-source route. The pale yellow precipitate obtained after completion of the reaction was redispersed in toluene followed by size-selective precipitation. The TOPO-capped particles have been characterized by several physical techniques to investigate their structural and optical behavior.

Optical and structural properties

Semiconductor particles of similar dimensions to the de Broglie wavelength of an electron (or hole) contained within them have an absorption edge shifted from the bulk value to higher energy, a quantum size effect.[2–5,18–21] The absorption edge of the ZnSe nanoparticles were calculated using the direct band gap method.[22] Subsequently, five different particle sizes of ZnSe nanoparticles were separated by size fractionation. Fraction 1 with the largest average particle size has an absorption edge at 479 nm (2.59 eV); fraction 2 at 456 nm (2.72 eV), and fraction 3 is smaller with an edge at 451 nm (2.75 eV). Fractions 4 and 5 are similar and smallest with edges at 438 nm (2.83 eV). The band edge of each of the five fractions is blue shifted in relation to bulk ZnSe which is characterized by the absorption edge at 480 nm (2.58 eV). All fractions show a broad excitonic shoulder close to the band edge. The peak at 331 nm for the fractions 1, 2 and 5 is an instrument artifact. The shift of electronic levels with decreasing particle size is shown in Fig. 1.

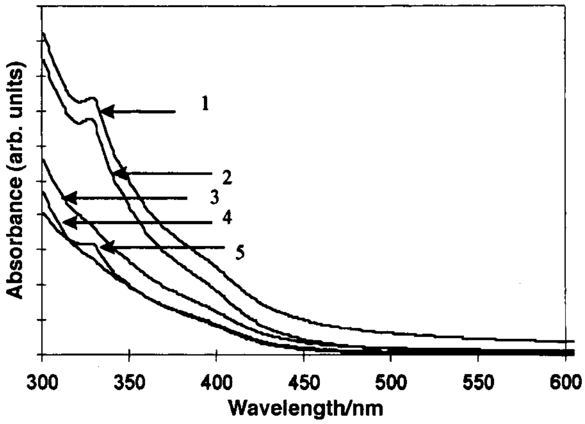

Fig. 1 Optical absorption spectra of fractions 1–5 of ZnSe

Fig. 2 shows the relationship between the absorption spectra and the TEM (images and particle size histograms) for fractions 1, 3 and 5. The TEM images of the selected fractions show well defined, spherical particles with the size range of 55–49 Å [mean diameter (*D*) of particles from fraction 1, 54.8 ± 6.8 Å; fraction 3, 52.5 ± 7.4 Å; fraction 5, 49 ± 8.1 Å]. The average size of the particles decreases from fraction 1 to 5 as seen in the particle size histograms and images. This change corresponds to the shift in the absorption spectra (blue shift for fraction 1, 0.01 eV; fraction 3, 0.17 eV; fraction 5, 0.24 eV). The relatively small shift in the absorption edge from fraction 1 to 5 corresponds to the relatively small difference (6 Å) in particle size from fraction 1–5 showing a narrow size distribution.

The photoluminescence spectrum of fraction 5 shows a broad band edge emission at 446 nm (for an excitation at 350 nm, Fig. 3). 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. Deep trap emission associated with such states is absent in passivated quantum dots. The infrared spectrum of a typical sample showed a broad band at 1078 cm^{-1} (ν_{sym} Zn—O—P), a shift of 62 cm^{-1} from the characteristic stretch for TOPO (ν_{sym} P=O, 1140 cm^{-1}).[23] The IR spectrum together with the EDAX, which shows a strong phosphorus peak, confirm the capping of the particles by TOPO.

The XRD pattern of ZnSe nanoparticles shows broad peaks typical of such small particles. The SAED pattern [Fig. 4(a)] exhibits broad diffuse rings due to the small size of the ZnSe crystallites. The indexing of the lattice parameter patterns of XRD and SAED indicates the formation of the hexagonal phase (Table 1). The EDAX pattern clearly confirms the presence of zinc and selenium. The strong peak for phosphorus is due to the capping of the particles by TOPO. Other low intensity peaks for potassium, calcium and silicon are due to the glass substrate.

The HRTEM [Fig. 4(b)] shows a single quantum dot of 4 nm in diameter. Visible lattice fringes correspond to the (101) lattice planes of the hexagonal phase as confirmed by the SAED pattern. The predicted diameter of the ZnSe nanoparticles of fraction 5 using the effective mass approximation model gives a value of 3.52 nm. This value is smaller than that observed by TEM (4.90 nm). However such deviations are expected for smaller particles using this model.[20,21,24]

Conclusions

Good quality ZnSe mono-dispersed nanoparticles have been prepared for the first time by thermolysis in TOPO using

Table 1 SAED and XRD data for ZnSe (hexagonal)

observed values		
SAED	XRD [*I*(%)]	ASTM[a] values *d*/Å [*I*(%)]
2.96	2.99 (70)	3.05 (70)
1.98	2.00 (100)	1.99 (100)
1.24	1.23 (40)	1.22 (40)
1.10	1.10 (40)	1.09 (40)

[a] American Society for Testing and Materials.

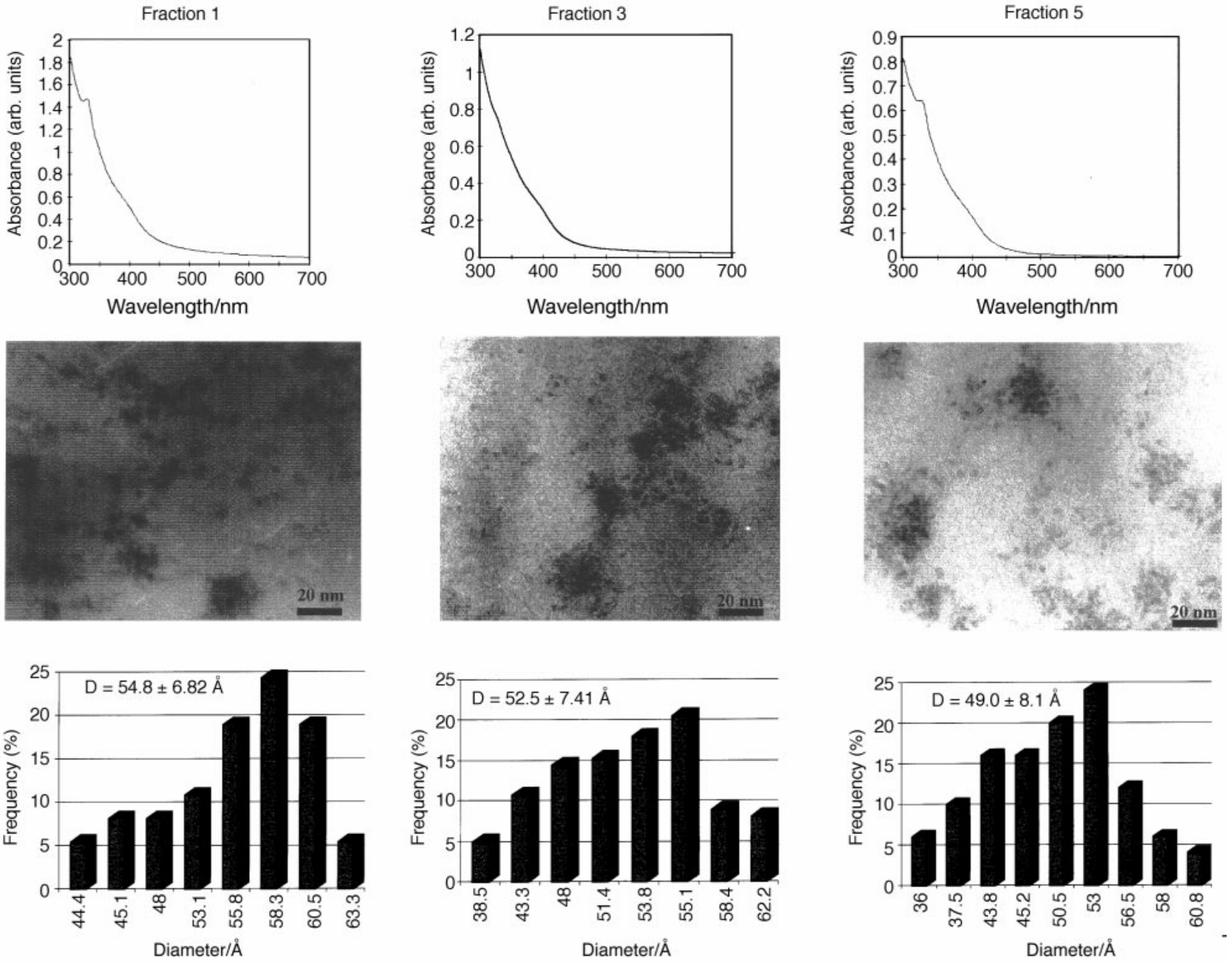

Fig. 2 The relationship between the absorption spectra and the TEM (images and particle size histograms) for fractions 1, 3 and 5

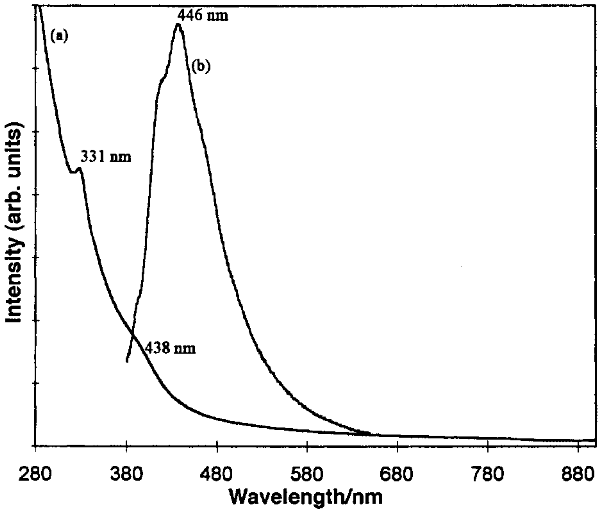

Fig. 3 (*a*) Optical absorption spectrum of ZnSe fraction 5 showing a band edge at 438 nm and an excitonic peak at 331 nm. (*b*) Photoluminescence spectrum of the same fraction showing an emission maximum at 446 nm.

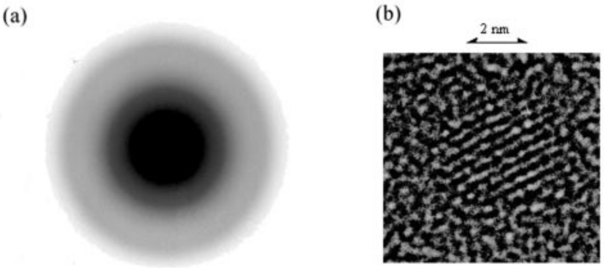

Fig. 4 (*a*) SAED Pattern of ZnSe. (*b*) HRTEM of a single ZnSe quantum dot (*ca.* 4 nm in diameter).

$EtZnSe_2CNEt_2$, a single-source molecular precursor. The particles were characterized by several physical techniques. HRTEM images showed that the particles are close to monodispersed and clear lattice fringes of a single dot confirmed that the nanosize particles are crystalline with sizes in the range 3.6–6.3 nm. The presence of a strong phosphorus peak in the EDAX pattern with a shift of 62 cm^{-1} in the IR peak for TOPO indicated that the particles are capped with TOPO and the SAED pattern showed the phase to be hexagonal‡.

We would like to dedicate this work to the memory of our friend and collaborator 'Mac' Zulu.

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‡A repeat of isolated ZnSe quantum dots appeared whilst this work was on the press.[25]

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