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A one-step synthesis of cadmium selenide quantum dots from a novel single source precursor

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A new approach to the one-step synthesis of cadmium selenide (CdSe) quantum dots is reported using the air stable complex cadmium imino-bis(diisopropylphosphine selenide); the ligand is readily prepared from elemental selenium and the precursor, quantum dots of comparable quality to those prepared by conventional methods are obtained.

Quantum dots (QDs) of semi-conducting materials such as cadmium selenide (CdSe) have received considerable attention because of their tuneable band gaps, which can vary their optical response from the infra-red region to the ultra-violet depending upon the size of the nanoparticle.[1–5] The tunability of the band gap makes QDs valuable for many applications ranging from single-electron transistors[6] to biomarkers.[7] Group 12 chalcogenide QDs are of current interest as the bulk materials are one of the best known groups of semiconductors. Such materials that absorb or emit in the blue or near-UV regions of the electromagnetic spectrum are being extensively studied owing to their potential uses in optical sensors and lasers.[8] However many methods of preparing dots involve the use of highly toxic sources of chalcogenides, such as H_2Se or $^tBu_2Se$, in vapour phase or solution reactions.[9–11] The hazardous nature of the materials involved, limits the extent to which such reactions can be exploited.

Recent research has involved $CdCl_2$ and CdO as cadmium sources in the synthesis of high quality cadmium chalcogenide nanoparticles.[11,12] Air stable inorganic molecular clusters (*e.g.* $[M_{10}Se_4(SPh)_{16}]^{4+}$ where M = Cd or Zn) have also been reported as single-source precursors towards highly monodispersed nanoparticles.[13] The present work was undertaken in a search for less hazardous chalcogenide sources for selenide containing materials. We have demonstrated that selenocarbamates such as $M^n(Se_2CNR^1R^2)_n$[14] are excellent for the synthesis of group 12 chalcogenides. However, the diselenocarbamato ligand is prepared from toxic and noxious carbon diselenide. Imino-diisopropylphosphine selenides, are prepared by the oxidative insertion of elemental selenium.[15]

The cadmium imino-bis(diisopropylphosphine selenide) compound, $Cd[N(SeP^iPr_2)_2]_2$, was first synthesised by Woollins *et al.*[15] from diisopropylchlorophosphine *via* a two step strategy. Improved yields for $Cd[N(SeP^iPr_2)_2]_2$ above those reported[15] can be afforded by utilising $CdCl_2$–NaOMe conditions rather than metal carbonates.[16] Imino-bis(dialkylphosphine selenide) complexes have recently been used as CVD precursors.[17] The $NH(SeP^iPr_2)_2$ ligand is more thermally stable than bulky selenolate ligands, such as $[SeSi(SiMe_3)_3]^-$, and thermolysis of its complexes produces cleaner products with reduced contamination caused by undesired ligand degradation reactions.[18] One-step size controlled synthesis of QDs was carried by the thermolysis of $Cd[N(SeP^iPr_2)_2]_2$ [eqn. (1)].†

In the one step synthesis of CdSe, the sizes of QDs derived from $Cd[N(SeP^iPr_2)_2]_2$ can be varied accurately by the length of the reaction time. The dots luminesce in the visible region of the electromagnetic spectrum and the emission wavelength varies over a wide range (up to 650 nm) depending upon the particle size (Fig. 1a).

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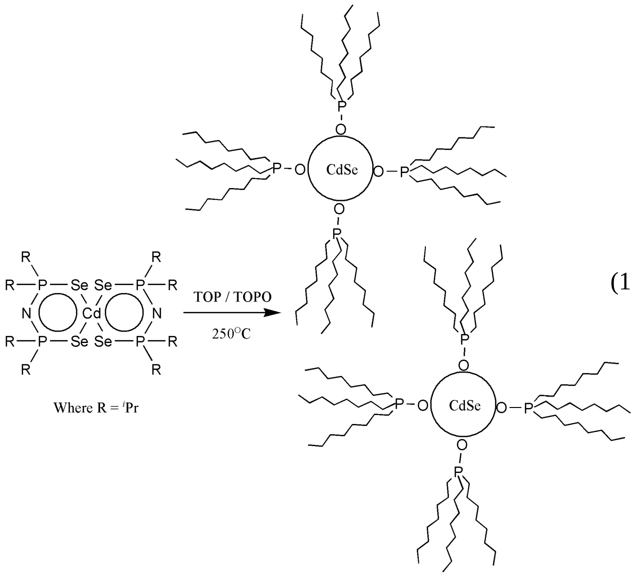

(1)

No further size selection was carried out. The CdSe QDs obtained are highly monodispersed with sizes that depend upon

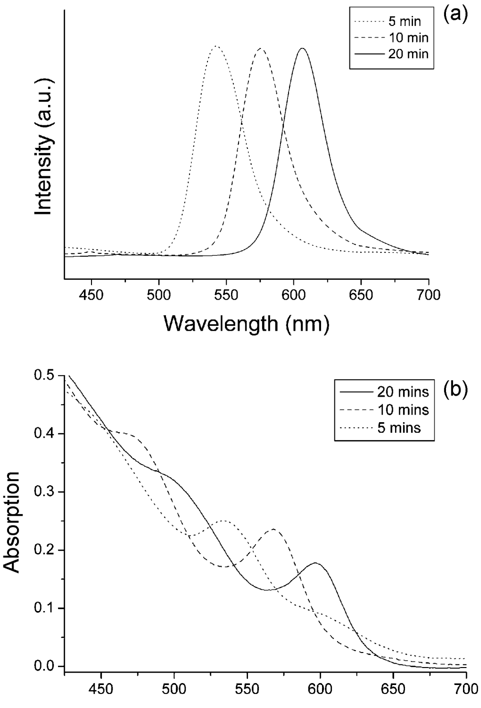

Fig. 1 (a): Photoluminescence spectra of CdSe QDs at various time intervals. (b) UV/Vis spectra of CdSe QDs at various time intervals.

the growth time. Relative to the position of the 716 nm (1.73 eV) absorption band edge of bulk CdSe, the absorption of the CdSe QDs are all blue-shifted. Smaller shifts are seen for longer growth times: the absorption edge band shifts are 0.35 (2.08 eV), 0.31 (2.04 eV) and 0.23 (1.96 eV) eV for QDs isolated after 5, 10 and 20 minutes respectively. (Fig. 1b). Transmission electron micrographs (TEM) show that the CdSe QDs are roughly spherical and particles within the same sample have relatively uniform sizes (Fig. 2). The estimated particle size[19] based on the absorption band edges are 5.4 nm, 5.75 nm and 6.42 nm for QDs isolated after 5, 10 and 20 minutes respectively.

X-Ray diffraction analysis of the CdSe QDs show broad peaks, characteristic of small particles of the hexagonal phase (Fig. 3). The average sizes of the CdSe QDs, determined by the Scherer equation, are 5.80 ± 0.6 nm for samples grown at 30 minutes (Fig. 2). EDAX analysis indicates the presence of the elements in a 1 to 1 ratio; phosphorus is also present due to the TOPO capping agent.

The above results demonstrate that monodispersed CdSe QDs can be prepared by means of a simple and convenient one-pot synthesis from the air stable $Cd[N(SeP^{i}Pr_2)_2]_2$ molecular precursor. These observations constitute a good illustration of size control in semiconductor QDs with visible region characteristics. We believe that this strategy can be extended to facile size controlled synthesis of other materials, that are at present difficult or complicated to prepare, since the imino-bis(diisopropylphosphine chalcogenide) ligand has been used to prepare a plethora of transition metal chalcogenide coordination complexes.[20]

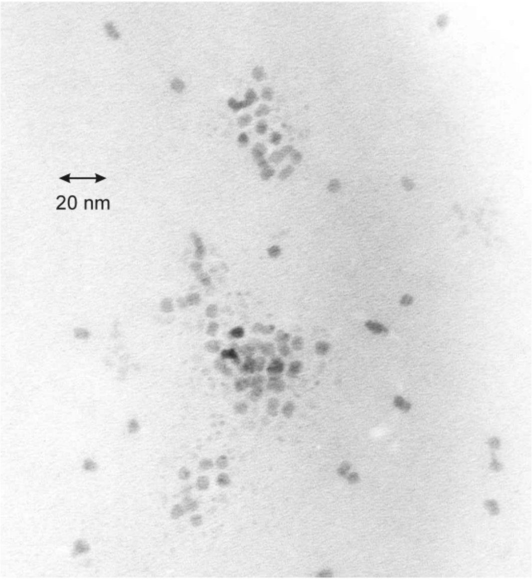

Fig. 2 TEM micrograph of CdSe QDs isolated after 30 minutes reaction time.

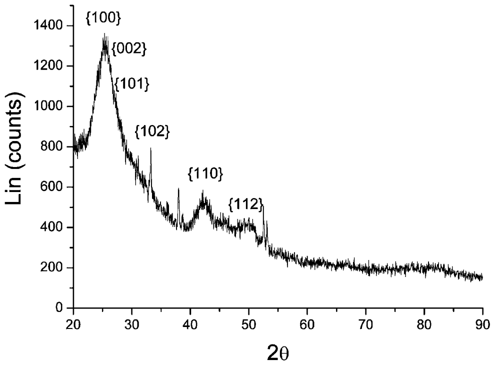

Fig. 3 X-Ray diffraction pattern (with Miller indices) of CdSe QDs isolated after 30 minutes.

Notes and references

† In a typical experiment $Cd[N(SeP^{i}Pr_2)_2]_2$ (0.5 g, 0.1 mmol) was dispersed in trioctylphosphine (TOP) (5 cm^3) and the resulting suspension injected into hot trioctylphosphine oxide (TOPO) (250 °C) (10 g, 26 mmol) and kept at this temperature for 30 minutes. The reaction progress was monitored at various intervals by ultra-violet/visible (UV/Vis) spectroscopy. After 30 minutes, the resulting (dark red) solution was cooled to (60 °C) and treated with an excess of methanol to generate a flocculate precipitate, which was separated by centrifugation and washed with further methanol. The isolated fractions were readily redispersed in toluene, showing a range of luminescent colours depending upon the size of particle ranging from green (isolation after T = 3 minutes) to red (isolation after T = 30 minutes).

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