One-step synthesis of size tuned zinc selenide quantum dots *via* a temperature controlled molecular precursor approach

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One-step size-controlled synthesis of ZnSe quantum dots is studied and the obtained QDs are luminescent with the emission wavelength varying over a wide range (up to 100 nm) depending on the particle size; the single-molecular precursor is an air-stable bis(phenylselenolato)zinc *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) complex, which effectively affords different sizes of ZnSe QDs depending on growth temperatures.

Nanomaterials are of great interest owing to the novel optical, electronic and catalytic properties that arise from the quantum size effects and large surface areas that are characteristic of these species. In particular, quantum dots (QDs) of semiconducting materials have received special attention because their electronic band gaps can be tuned, thus varying their optical response from the IR to the UV depending on the size of the dots.[1–5] The tunability of the band gap makes QDs useful for many applications such as light emitting diodes[5] and as ultrasmall luminescent tags for biological studies.[6]

Bulk materials that absorb or emit in the blue to near-UV regions of the electromagnetic spectrum are being extensively studied owing to their potential uses in optical sensors and lasers.[7,8] The best known bulk semiconductors with band gaps in this region are GaN (E_{gap} = 3.4 eV) and ZnSe (E_{gap} = *ca.* 2.7 eV). Synthetic studies on QDs of these two materials with decent electronic band tunings, however, have been very limited.[9,10] For isolated colloidal ZnSe QDs, the use of a diselenocarbamate single-source precursor and a dual source precursor system are two successful demonstrations.[10]

One of the important current issues of nanomaterials research is the controlled synthesis of QDs. In many cases, however, successful nanostructured materials syntheses[1,11] with desired size and shape criteria, require multi-step processes and thus developing a simple and controlled method of synthesizing QDs is of particular interest.

Here we present a one-step synthesis of ZnSe QDs the sizes of which can be precisely tuned by simple temperature control. We demonstrate that these are luminescent in the blue region and that the emission wavelength varies over a very wide range (up to 100 nm) depending on the particle size. The key to this synthesis is the proper choice of a molecular precursor which has good solubility, adequate thermal stability, and simple ligand elimination processes that produce desired materials. Notably, our obtained QDs have a high monodispersity without size selective precipitation.

The compound bis(phenylselenolato)zinc, $Zn(SePh)_2$,[12] is polymeric and poorly soluble in organic solvents, and is thus not particularly convenient as a precursor for the synthesis of QDs. We observe, however, that the polymer reacts with *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) to form a soluble, air-stable, monomeric adduct of stoichiometry $Zn(SePh)_2$(TMEDA) (Fig. 1).[13–15] As similarly observed by Yamamoto and Steigerwald in related work on alkyl- or phenyl-chalcogenolate ligand systems, this ligand is more thermally stable than other bulky selenolate ligands such as $SeSi(SiMe_3)_3$, and thermolysis of its complexes produces clean QDs with reduced contamination caused by undesired ligand fragmentation processes.[16]

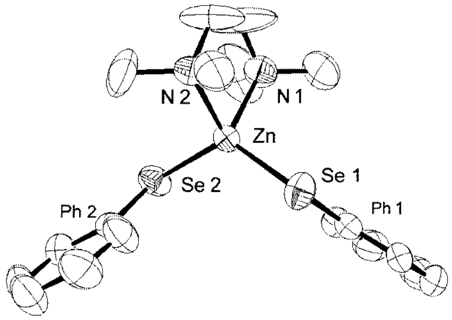

Fig. 1 ORTEP drawing of $Zn(SePh)_2$(TMEDA). Selected bond distances (Å) and angles (°): Se(1)–Zn(1) 2.398(2), Se(2)–Zn(1) 2.399(2), Zn(1)–N(1) 2.120(9), Zn(1)–N(2) 2.147(9); Se(1)–Zn–Se(2) 125.54(6), N(1)–Zn(1)–N(2) 86.3(3).

One-step size controlled synthesis of QDs was carried out by the thermolysis of $Zn(SePh)_2$(TMEDA) (eqn. 1).[17,18]

$$[Zn(SePh)_2][TMEDA] \xrightarrow{heat} ZnSe + TMEDA + Ph_2Se \quad (1)$$

In a typical QD synthesis, $Zn(SePh)_2$(TMEDA) (0.5 g, 0.101 mmol) was dissolved in trioctylphosphine (10 ml) and the resulting solution injected into hot trioctylphosphine oxide (3.92 g, 10.1 mmol). The latter solution is kept at one of four different temperatures: 320, 340, 367 or 385 °C. After 1 h, the resulting yellow solution was cooled to 80 °C and treated with an excess of methanol to generate a yellow flocculate, which is separated by centrifugation and washed with methanol. The resulting pale yellow powder was readily redispersed in toluene. No further size selection is carried out.

The QDs obtained are highly monodispersed with sizes that depend on the growth temperature. Relative to the position of the 460 nm (2.7 eV) absorption band edge for bulk ZnSe, the absorption band edges of the ZnSe QDs are blue-shifted. Larger shifts are seen for higher growth temperatures. Thus, the absorption band shifts are 0.95, 0.37, 0.29 and 0.17 eV for QDs grown at 385, 367, 340 and 320 °C, respectively. Similar blue shifts are also observed in the photoluminescence spectra: the band maxima are 387 (3.20 eV), 429 (2.89 eV), 443 (2.80 eV) and 451 nm (2.75 eV) for samples grown at 385, 367, 340 and 320 °C, respectively (Fig. 2). These results show that smaller quantum dots are obtained at higher growth temperatures where more nucleation sites are present and relatively less ZnSe material is available for each nucleus during growth kinetics. High resolution transmission electron micrographs show that the ZnSe QDs are roughly spherical and that the particles within a single sample have relatively uniform sizes (Fig. 3). The average sizes of the ZnSe QDs are 2.7 ± 0.2, 4.0 ± 0.35 nm, 4.4 ± 0.35 and 4.9 ± 0.29 nm for samples grown at 385, 367, 340, 320 °C, respectively (Fig. 2C). The ZnSe particles are in the cubic phase, as determined by X-ray diffraction and selected area electron diffraction.[18] Energy dispersive X-ray emission analysis of the QDs confirms that the particles have a 1 : 1 Zn : Se stoichiometry.

The results above demonstrate that monodispersed ZnSe QDs can be prepared by means of a simple and convenient one-pot

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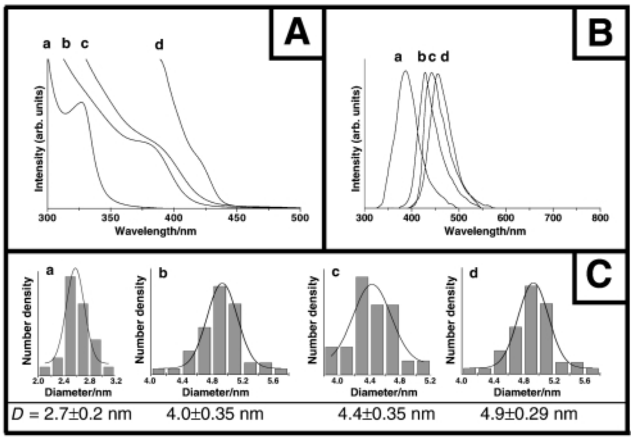

Fig. 2 Optical spectra and size distribution of ZnSe QDs grown at (a) 385 (b) 367 (c) 340 (d) 320 °C. (A) UV–VIS absorption spectra, (B) photoluminescence spectra and (C) size distribution.

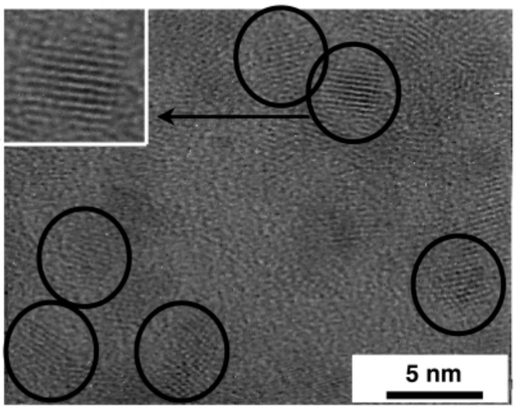

Fig. 3 HRTEM images of ZnSe QDs grown at 340 °C.

synthesis from an air-stable monomeric molecular precursor. The growth of QDs follows a simple ligand elimination reaction and by varying the growth temperature it is possible to control their size. The results constitute a good demonstration of controlling the size of semiconductor QDs with band gaps in the blue region of the electromagnetic spectrum. We believe that this strategy can be extended to facile size controlled synthesis of QDs of other materials that, at present, are difficult or complicated to prepare.

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12 $Zn(SePh)_2$ was prepared according to a modification of literature procedure (M. Bochmann, G. Bwembya and K. J. Webb, *Inorg. Synth.*, 1997, **31,** 19). Selenophenol (2.14 g, 13.54 mmol) was slowly added to $Zn[N(SiMe_3)_2]_2$ (2.61 g, 6.76 mmol) in toluene (50 ml) for 30 min. A white precipitate began to form and the mixture was stirred at room temp. for 12 h, after which heptane (10 ml) was added. The precipitate was collected by filtration, washed with heptane (5 ml), and dried *in vacuo*, to give a white powder (2.32 g, 90%).

13 TMEDA (1.07 g, 9.17 mmol) was added to a suspension of $Zn(SePh)_2$ (1.81 g, 6.11 mmol) in toluene (50 ml). The mixture was stirred for 24 h to give a pale yellow solution, which was filtered, treated with pyridine (5 ml) and heptane (30 ml), and cooled to −24 °C to give colorless crystals (1.765 g, 59%), mp 137–138 °C. Anal. Calc. for $C_{18}H_{26}N_2Se_2Zn$: C, 43.8; H, 5.27; N, 5.67. Found: C, 43.1; H, 5.34; N, 5.37%. δ_H($CDCl_3$, 25 °C): 7.90 (t, 2H, J_{HH} 7 Hz, *o*-CH), 6.86 (*m*, 3H, *m*-CH and *p*-CH), 2.67 (s, 2H, NCH_2), 2.48 (s, 6H, NMe_2).

14 An X-ray crystallographic study of $Zn(SePh)_2$(TMEDA) (Fig. 1) shows that the zinc center adopts a distorted tetrahedral geometry with a large Se–Zn–Se angle of 125.55° and a small N–Zn–N angle of 86.33°. The Zn–Se and Zn–N bond lengths are 2.398 and 2.134 Å, respectively. The bond lengths and angles are similar to those seen for other zinc complexes with organochalcogen and amine ligands.[15] *Crystal data*: $C_{22}H_{16}N_2Se_2Zn$, M_r = 531.69, monoclinic, space group $P2_1/c$, a = 11.202(2), b = 12.7326(14), c = 15.125(3) Å, β = 107.050(18)°, U = 2062.5(6) Å^3, Z = 4, D_c = 1.340 g cm^{-3}, $F(000)$ = 1040, μ(Mo-Kα) = 47.2 cm^{-1}, R_1 = 0.0623, wR_2 = 0.1634. CCDC 182/1665. See http://www.rsc.org/suppdata/cc/b0/b002983l/ for crystallographic files in .cif format.

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17 Upon themolysis of $Zn(SePh)_2$(TMEDA), the generation of Ph_2Se was identified by ^1H NMR spectroscopy.

18 X-Ray diffraction spectra show three broad peaks at 2θ = 27.41 (111), 48.04 (200) and 68.76° (311), similar to the cubic phase observed in CdSe.[4] Interestingly, the synthesis of hexagonal ZnSe QDs has previously been reported.[10a]