Preparation of CdSe Quantum Dots via Thermolysis of a Novel Single Source Cd/Se Precursor Derived from Cyclohexeno-1,2,3-selenadiazole

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(Received March 2, 2009; CL-090209)

Reduction of bis(2-bromocyclohexenyl)diselenide, prepared from cyclohexeno-1,2,3-selenadiazole by the procedure of Meier et al., followed by reaction with cadmium chloride, yielded the novel single source Cd/Se precursor [$Cd(SeC_6H_8Br)_2$], which upon thermolysis in a high boiling reaction medium formed CdSe quantum dots (Q.dots). Powder X-ray diffraction analysis showed them to contain cubic CdSe and TEM indicated the particle size to be <5 nm. The absorption spectrum of the as-prepared Q.dots had a blue shift of >200 nm with respect to bulk CdSe and photoluminescence measurements at an excitation energy of 350 nm showed shallow trap band-edge emission.

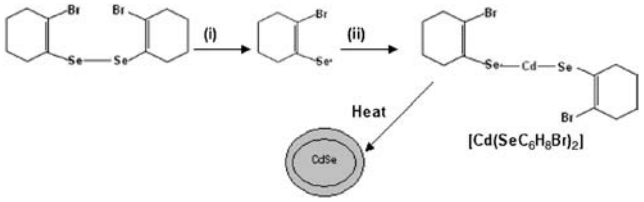
Cadmium chalcogenides have applications in solid-state solar cells, field effect transistors, sensors, biosensors, imaging, and transducers. Single source precursor methods are best suited for various types of quantum dots which ultimately decide their fate.[1–5] CdSe shows pronounced quantum confinement effect between particle diameter of 2–11 nm leading to tuned optical properties.

Organometallic Cd/Se compounds have often been employed for preparation of CdSe quantum dots, and the progress in the area has been slow but steady mainly due to high toxicity of precursors and its conversion to CdSe. The use of ever reliable TOP/TOPO and/or amines for preparation of surface-capped CdSe quantum dots has been trusted by majority of researchers. Multistage and painstaking synthesis of single source precursors thus warrants alteration in their synthetic strategy by involving simpler and relatively less hazardous or nontoxic reagents. Suppressing the use of phosphines and amines would generally be considered as one of the most desired options of "greening the quantum dot preparation." A number of single source precursors have been tested for such preparations, and most often the work of O'Brien et al.[2] has been considered handy for such materials, although there are others too who have exploited their expertise in this area. Recently cadmium alkoxides due to their thermal instability have been used for the preparation of CdE nanocrystal[4] Up until recently, for chemical synthesis of CdSe, most researchers followed the initial method developed by Murray et al.[6] but over the years this has been modified by several groups.[7,8] Thus, a large number of methods have been reported for preparation of CdSe quantum dots by use of cadmium precursors such as CdX_2 type salts (X = Cl, CH_3COO, etc.) or organometallic compounds such as dimethyl cadmium or cadmium/selenium molecular precursors.[6–11] Often famous TOPSe has been employed for such preparations, however, direct use of organoselenium compounds as source of selenium is not so common despite promising start in the early developments in CdSe synthesis where extensive use of two precursors in vapor-phase synthesis was made in famous MOCVD processes.[10]

We have recently shown that use of 1,2,3-selenadiazoles for the preparation of semiconductor quantum dots can offer more variety in the subject, and thus enhance the scope of organometallic compounds in nanotechnology.[12,13] 1,2,3-Selenenadiazoles serve as rich source of selenium due to their lower thermal decomposition temperatures than that is required for TOPSe. The present synthesis uses molecular precursor for preparation of CdSe quantum dots via thermal decomposition of a 2-bromocyclohexenyl selenolate Cd^{II} compound in conventional surfactant such as oleic acid. In addition, such chemistry does not involve toxic phosphines or amines thus making the synthesis virtually "green." We report herein, the preparation of CdSe Q.dots using bis(2-bromocyclohexenyl)diselenide,[14] $CdCl_2$, and oleic acid.

In a typical synthesis, cyclohexeno-1,2,3-selenadiazole (1 g, 5.35 mmol) was brominated by use of *N*-bromosuccinamide in carbon tetrachloride at room temperature under argon. The dark yellow-brown suspension was then dried and column chromatographed to obtain yellow oily bis(2-bromocyclohexenyl)diselenide.[14] The reduction of which in ethanol by using sodium borohydride lead to formation of 2-bromocyclohexenylselenolate. To this was added cadmium chloride and the reaction mixture was stirred overnight to obtain an insoluble yellow precipitate. Dry yellow powder was then suspended in oleic acid or oleic acid/diphenyl ether or oleic acid/dimethylformamide and was heated under argon at a temperature between 120–160 °C for 4–6 h. During this time the color changed from pale yellow to red. After cooling the reaction mixture, an excess of ethanol was added. The precipitate was centrifuged and was washed with toluene and methanol. The orange powder was dried at ca. 80 °C for a few hours. Yield of CdSe was ca. 40%.

We have in the past described conversion of cycloocteno-1,2,3-selenadiazoles to its bis(2-bromocyclooctenyl)diselenide by adopting the approach reported by Meier et al.[14] and their reduction followed by alkylation to prepare thermally unstable but useful selenium ligands which subsequently were used for synthesis of platinum(II) complexes.[15] Taking advantage of this approach, we herein reacted 2-bromocyclohexenylselenolate with cadmium salt to obtain interactable yellow solid of probable molecular formula as shown in Scheme 1. Although we do not have any spectroscopic or analytical data to support such structural formula but based on the behavior of other cadmium selenolates, it is reasonable on the basis of its insolubility, to suggest a polymeric structure based on bridging Se atoms.



Scheme 1. Formation of single source Cd^{II} precursor and CdSe QDs (i) $NaBH_4$/EtOH, argon, ice-salt temperature; (ii) $CdCl_2$/EtOH.

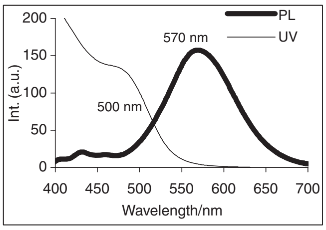


Figure 1. UV–vis and PL ($\lambda_{ex} = 350$ nm) spectra of CdSe Q.dots.

Thermal decomposition of $[Cd(SeC_6H_8Br)_2]$ in dimethylformamide (DMF) or oleic acid alone resulted in wide distribution of the product (λ_{abs} 575 nm), but when oleic acid was used in combination with diphenyl ether at 120 °C, good quality quantum dots were isolated via centrifugation (λ_{abs} 500 nm) due to excellent quantum confinement. The absorption bands from different reactions showed the absorption at 500 (2.48 eV) and at ca. 575 nm (2.15 eV; bulk CdSe band-gap value is 1.74 eV). The absorption and the photoluminescence (PL) spectra of redispersed CdSe are shown in Figure 1. The PL spectrum of the product prepared in diphenyl ether at 120 °C having an absorption band at 500 nm showed a band-edge emission at 570 nm when excited at 350 nm, indicating a few electronic defects sites. The broadened emission profile indicates that the emission is from the shallow trap state formation. Using the effective mass approximation equation,[9] the particle size from absorption band at 500 nm was calculated to be <4 nm as per eq 1.

$$\Delta E_g = h^2/8a^2(1/m_e + 1/m_h) \qquad (1)$$

where E_g is band-gap shift, a is the particle size, and m_e and m_h are the effective electron and hole mass, respectively; $m_e = 0.13m_0$, $m_h = 0.44m_0$ (data from bulk CdSe), where $m_0 = 9.1095 \times 10^{-31}$ kg is the electron rest mass.

X-ray diffraction (Figure 2) indicated cubic crystal structure of CdSe with reflections at (111), (220), and (311) crystal planes. The appearance of minor diffraction peak (331) confirmed good crystallinity of the product. By applying Scherrer's equation, particle size was estimated to be ca. 4 nm. The TEM micrographs (Figure 3) showed high-quality nonagglomerated spherical particles with an average diameter of 4–5 nm. Selected area electronic diffraction pattern (SAED) showed relevant concentric rings to further authenticate the cubic structure. Particle size calculated from absorption spectra, XRD and those obtained from TEM match well.

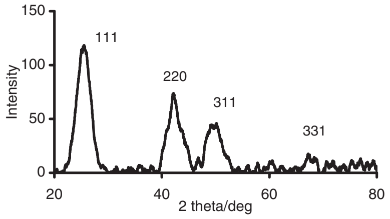


Figure 2. X-ray diffraction pattern of CdSe.

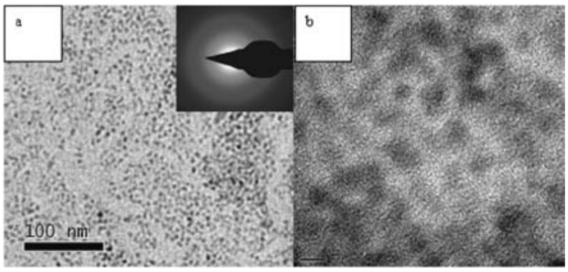


Figure 3. (a) TEM and (b) HRTEM with SAED (inset) of CdSe Q.dots.

The results show the usefulness of cyclohexeno-1,2,3-selenadiazole and its derivative i.e. bis(2-bromocyclohexenyl)diselenide for single source molecular precursor of cadmium and selenium for preparation of good quality zinc-blende CdSe quantum dots without the use of TOP or other toxic reagents.

PKK thanks DST, Govt. of India for financial support (grant no. SR/S1/PC-17/2006). TEM facility of Unit on Nanoscience and Nanotechnology Initiative of the DST at IIT Delhi (Project No. SR/S5/NM-22/2004) is gratefully acknowledged. PKK is grateful to one of the referees for improving the content of the manuscript.

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