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Low-temperature synthetic method for size-controlled CdSe nanocrystals: utilization of boron selenide

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By employing B_2Se_3 as a selenium source, we demonstrate that at reaction temperatures as low as 60 °C, relatively monodisperse, fluorescent CdSe nanocrystals can be conveniently prepared in various sizes selected from 2 to 13 nm.

Since the first preparation of nanocrystals of CdSe, many applications of the new material have been found in the areas of energy conversion, electronics, optics, and sensors.[1] Because of the high demand for the materials, various preparative methodologies have been developed which can operate under different reaction conditions.[2–9] Relatively monodisperse, highly crystalline, fluorescent nanocrystals are often prepared at high temperatures around 300 °C.[2–5] The growth of such nanocrystals requires instantaneous injection of a precursor and mixing of the reactants, following by uniform nucleation over the entire mass of the solvent and homogeneous mixing in the entire reactor during processing.[2–5] While less constricted low-temperature reaction methods have been developed, particularly through "arrested precipitation" of nanocrystals in structured matrices such as inverse micelles, porous glass, or zeolites,[7] the methods do not simultaneously provide flexible size selectivity, narrow size distribution and photoluminescent products, in addition to the possible problem of product extraction and purification.

In this communication, we report simple preparations of relatively monodisperse, fluorescent CdSe nanocrystals through a new synthetic method that can operate at temperatures as low as 60 °C. The method is convenient in such that the cadmium and selenium precursor solutions are mixed together at room temperature and that the growth of CdSe nanocrystals is controlled by heating the mixture in a closed reaction container in a conventional oven or by microwave irradiation. The utilization of microwave irradiation allows fast heating and short reaction time. A microwave irradiation method has been reported previously for preparation of CdSe nanoparticles in an aqueous solution, but size selection/control of the particles was not fully accomplished.[8,9]

The essential nature of the new method is the use of B_2Se_3 as a new selenium source. As an extension of our recent work on the solid/gas metathetical synthesis of metal-chalcogenide nanoparticles with boron chalcogenides,[10,11] it has been found that B_2Se_3 readily dissolves in various amines even at room temperature and can be used as a convenient source of selenide ions in solution synthesis of CdSe nanocrystals.

We prepared B_2Se_3 from a stoichiometric mixture of boron (99.99%, Alfa Aesar) and selenium (99.999%, Alfa Aesar), heated in a carbon-coated and evacuated fused silica tube at 850 °C for 24 hours.[12] All the loading of the reactions was carried out in a nitrogen-filled glovebox, and the chemicals were used without further purification. In a typical reaction, 0.15 g (0.58 mmol) of the prepared B_2Se_3 was dissolved in 10 ml oleylamine (70%, Aldrich) and heated in a lab oven to ensure complete dissolution. 0.31 g (1.7 mmol) of $CdCl_2$ (99%, Alfa Aesar) was also dissolved in 10 ml oleylamine in a separate container. The two solutions were removed from the oven and they remained clear without forming any precipitate. The two solutions were then transferred to the glovebox and mixed in appropriate volumes to produce a 1 : 1 Cd/Se ratio. No chemical reaction was observed to take place at room temperature. The resulting solution was taken out of the glovebox in a tightly-sealed container and heated to various temperatures ranging from 60 to 200 °C for different reaction periods between 10 seconds and 2 hours, and then quenched. There were no significant or systematic differences in the optical properties and crystallinity of the products from the oven reactions and from the microwave reactions, except that the photoluminescence of ~3-nm-size particles from the latter was slowly red-shifted over a week when in solution. An appropriate portion of ethanol was added to the product solution to flocculate and precipitate the CdSe nanocrystals. The precipitate was retrieved by centrifugation at 3000 rpm, and dried samples weighed more than the net theoretical weight of CdSe without consideration of capping molecules. In this report, we discuss six different samples labelled (a) through (f), whose synthetic conditions are summarized in the footnote.†

UV-Vis spectra were recorded on the nanocrystals redispersed in cyclohexane by using a Shimadzu UV-2100U spectrophotometer, and the photoluminescence (PL) experiments were carried out on a MD-5020 PTI spectrometer. The PL spectra were measured using a 365 nm excitation wavelength and were normalized to their intensity for comparison. The absorption spectra of the sample do not exhibit pronounced features in general. In our other set of experiments, we have found that the absorption characteristics can be improved upon using different Cd precursors such as Cd ethoxy acetate.

In Fig. 1, the emission peaks are bell-shaped and red shifted compared to the corresponding absorption peaks. The size distributions are relatively narrow for the samples (b)–(f) with the FWHM of their PL emission peaks ranging from 35 to 55 nm.

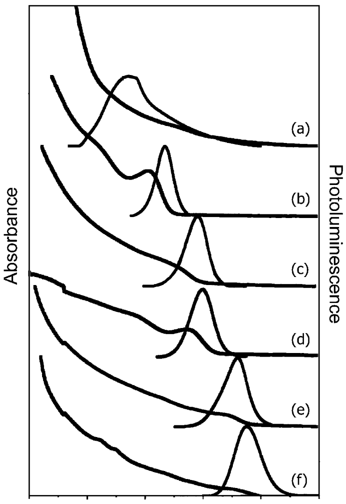

Fig. 1 Room-temperature absorption (thick curves) and PL (thin bell-shaped curves) spectra of CdSe nanocrystals in cyclohexane.

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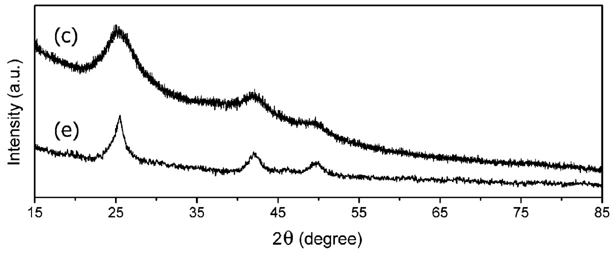

Fig. 2 XRD patterns of the CdSe samples (c) and (e) with CuK$_\alpha$-radiation. The three Bragg peaks at $2\theta = 26$, 42 and 49° correspond to the zinc-blend structure of CdSe.

However, the sample (a) exhibits a very broad emission peak. The PL quantum yield was obtained using a conventional method by integrating the PL band of CdSe in cyclohexane and comparing the intensity to that of Rhodamine B in ethanol.[5] The quantum yield was found to be over 3% for (f) and 5% for (a), comparable to the values in previous studies.[5] The PL spectra were used to estimate the sizes of the nanocrystals in our samples, assuming that the PL energy is proportional to the absorption energy at the band edge. From the observed PL energies of our samples, the estimated average diameters are (a) 2.3 nm; (b) 3.4 nm; (c) 5.0 nm; (d) 5.4 nm; (e) 11 nm; (f) 13 nm by fitting the literature data[13] with a simple model proposed by Brus.[14]

The XRD patterns of the samples (c) and (e) are shown as representatives in Fig. 2. The Bragg reflection peaks of the sample (c) are much broader than those of (e), reflecting the small particle size. The samples (a) and (b) did not provide significant peaks in their XRD pattern with a 12-hour scanning time. In Fig. 2, the Bragg reflections at $2\theta = 26$, 42 and 49° indicate that the product exhibits a good crystallinity, consistent with their good PL, purely in a zinc-blend structure, and that there is little presence of the wurtzite structure. The preference of the zinc-blend structure has been noted in previous amine solution synthesis.[3] We also have observed occasional coexistence of zinc-blend and wurtzite structures in our experiments, but the wurtzite structure nanoparticles were never found in a significant amount in the XRD powder pattern. The wurtzite structure impurities did not produce remarkable differences in the optical spectra among the samples, possibly due to the small amounts.

Samples for high-resolution transmission electron microscopy (HRTEM) studies were prepared by dispersing a few drops of the suspensions of the nanocrystals in ethanol on holey carbon grids. A JEOL 4000 EX transmission electron microscope (TEM), operated at 400 kV, was used to obtain HRTEM images. HREM images recorded on photographic films show that the monodispersed nanocrystals are oriented along various zone axes. Fig. 3 shows the HRTEM images of the sample (c) as a representative, while TEM studies on the samples (a) and (b) were not satisfactory. The images show relatively monodisperse nanocrystals with distinctive lattice fringes.

In conclusion, we have prepared relatively monodisperse fluorescent CdSe nanocrystals in various sizes under mild low-temperature reaction conditions by employing a new preparative method. The relatively narrow fluorescence spectral range (FWHM = 35–55 nm) is well within the practical limit for stringent applications such as lasing (FWHM < 75 nm).[15] The method is inherently less hazardous, because the container remains closed during the reactions and the reaction temperatures are relatively low. The premixing and subsequent heating of the stock solutions in the new method can be advantageous, particularly when the synthesis of the nanocrystals should be carried out in a small confined space such as a continuous-flow microfluidic reactor or nanoscopic pores and channels.[6] The utilization of microwave heating may allow a high-throughput combinatorial approach for the CdSe nanocrystal preparations.

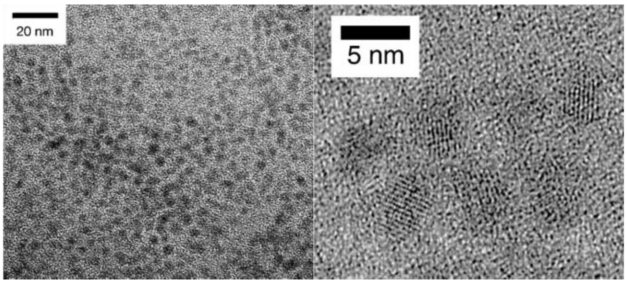

Fig. 3 Representative HRTEM images of the sample (c).

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Notes and references

† Reaction conditions: (a) 60 °C for 30 minutes, conventional oven; (b) 60 °C for 2 hours, conventional oven; (c) 135 °C for 5 seconds, microwave; (d) 150 °C for 30 seconds, microwave; (e) 200 °C, overnight, conventional oven; (f) 180 °C for 60 seconds, microwave. Microwave reactor: a CEM Discover System™.

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