

# A solvothermal route to capped CdSe nanoparticles

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We present a convenient and safe one-pot route to capped 3 nm CdSe nanoparticles making use of common starting materials and inexpensive, low-boiling solvents under solvothermal conditions; H<sub>2</sub>Se required for the reaction is generated *in situ* through the aromatization of tetralin by Se.

In semiconductor nanocrystals of materials such as CdSe, the happy union of bulk and molecular properties results in a rich photophysics that is not only interesting in its own right, but also lends itself to a number of applications.<sup>1</sup> One such application is the use of CdSe nanocrystals as fluorescent probes in biological imaging.<sup>2</sup> The key to all semiconductor nanoparticle research is the ability to prepare stable (typically through surface passivation – also referred to as capping) monodisperse particles that have very few defects. A number of techniques have been used to achieve this and have recently been reviewed in this journal.<sup>3</sup> Perhaps most widely used is the method introduced by Bawendi and coworkers<sup>4</sup> which involves the reaction of an organocadmium precursor with an Se source in a high temperature solvent such as trioctyl phosphine oxide (TOPO), which also doubles as a capping agent.

We have been interested in the preparation of chalcogenide nanoparticles from inexpensive starting materials of low toxicity. Cadmium stearate is easy to prepare† and dissolves in organic solvents such as toluene, in which it is known to react with H<sub>2</sub>Se to yield chalcogenides. Since relatively high temperatures are required to prepare defect-free, monodisperse nanoparticles, we have carried out the synthesis in toluene using stainless steel bombs. H<sub>2</sub>Se is not easily handled under these conditions, so we have employed the aromatization of tetralin to naphthalene by elemental Se in order to prepare H<sub>2</sub>Se *in situ*. The addition of small amounts of dodecanethiol as a capping agent results in 3 nm nanoparticles with a narrow size distribution. The dark solution obtained from the reaction precipitates solid products when the solvent polarity is increased through the addition of propan-2-ol. The precipitated solid easily redissolves in toluene forming bright orange solutions.

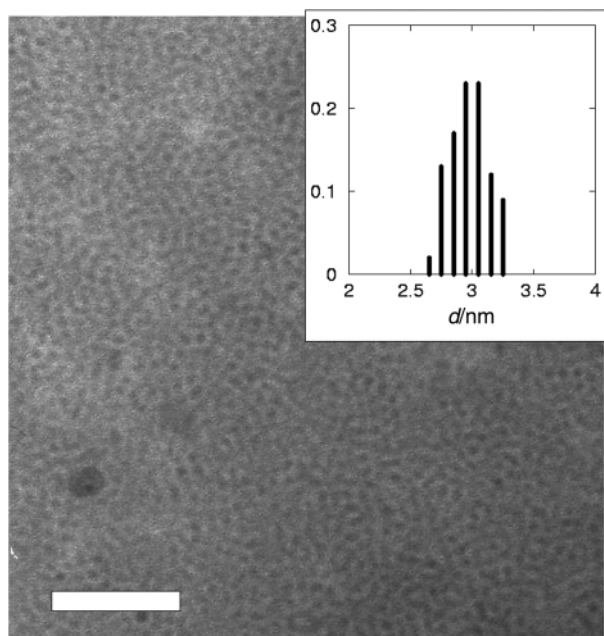
Our procedure is inspired by the simple method of Mitchell and Morgan<sup>5</sup> who prepared CuCr<sub>2</sub>Se<sub>4</sub> in mineral oil at 330 °C using stearate salts as the metal source and the aromatization of sitosterol as the H<sub>2</sub>Se source. Qian and coworkers<sup>6</sup> have recently reported the preparation of 7 nm CdSe nanoparticles under solvothermal conditions using ethylenediamine at 120 °C.

Fig. 1 displays a TEM image of the nanoparticles. While a few large particles (*ca.* 10 nm) are occasionally seen, the vast majority of the particles are smaller; with a mean diameter of 3.0 nm and a standard deviation of 0.16 nm (*ca.* 5% of the mean). The powder XRD profile of the nanoparticles acquired in transmission mode is displayed in Fig. 2(a). We find that the profile is well fitted by the Rietveld<sup>7</sup> method to the cubic (*a* = 6.01(1) Å) zinc blende structure rather than the usual hexagonal

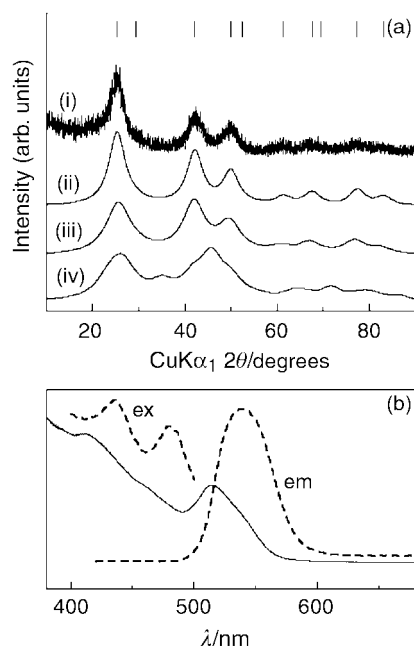
wurtzite structure. Stacking 3 nm × 3 nm slabs of CdSe along the *c* axis in hexagonal and cubic (in different proportions) arrangements permits simulations using the DIFFaX<sup>8</sup> program, which confirms a cubic zinc blende structure relatively free from hexagonal defects. The Rietveld fit and cubic and hexagonal DIFFaX simulations (using a correlation length of about 3 nm in the *c* direction) are also displayed in Fig. 2(a).

The UV–VIS absorption spectrum in toluene [Fig. 2(b)] shows absorption peaks at 514 and 412 nm, consistent with quantum confinement. Bawendi, Steigerwald and Brus<sup>9</sup> have discussed the correlation of absorption spectra and particle diameter for various nanoparticles. According to their correlation, the particle size corresponding to the spectrum in Fig. 2(b) is close to about 2.5 nm and not 3.0 nm as obtained here from TEM. The discrepancy could arise from (i) the different crystal structure obtained in the present case and (ii) the difficulty in estimating sizes from the very small, low-contrast particles seen in the TEM image. Toluene solutions of the nanoparticles also show strong photoluminescence as seen from the emission spectrum displayed in Fig. 2(b) as a dashed line.

The presence of the thiol capping was verified from C–H stretches in the FTIR spectrum, as well as by thermogravimetry in air. We observe a weight loss of 35% before 400 °C which, if ascribed to the thiol cap, suggests that for 3 nm particles there is one thiol molecule for every 22 Å<sup>2</sup> of nanoparticle surface.



**Fig. 1** TEM image of a relatively dense arrangement of CdSe nanoparticles showing a tendency to close packing in the plane (bar = 50 nm). The inset shows a histogram of particle sizes.



**Fig. 2** (a) (i) Powder XRD pattern of CdSe compared with (ii) the background-subtracted Rietveld fit ( $R_{\text{Bragg}} = 6.4\%$ ), (iii) DIFFaX simulation of 3 nm cubic zinc blende stacking of CdSe, and (iv) DIFFaX simulation of a 3 nm hexagonal wurtzite stacking of CdSe. The vertical lines at the top are expected peak positions for the cubic zinc blende structure. (b) UV–VIS absorption spectrum of the nanoparticles in toluene. Dashed lines display luminescence spectra: emission (em) following excitation at 400 nm, and excitation (ex) following emission at 540 nm.

Energy dispersive X-ray analysis (EDAX) suggested that the Cd:Se ratio is nearly 1:1 (within 4%). When S is included in the analysis, the atomic ratios of S: Cd:Se are close to 20:40:40 (within a 5% error). Using a model of 3 nm particles with a thiol every 22 Å<sup>2</sup> of surface, we obtain a calculated S: Cd:Se of 120:260:260 (atoms) in reasonable agreement with the EDAX.

In conclusion, we present a new and convenient route to prepare large quantities of capped CdSe nanoparticles. The route can easily be extended to other nanoparticle chalcogenides of interest. The major advantages of the present route are that (i) there is no need to handle materials under inert conditions, (ii)

inexpensive solvents can be used, and (iii) volatile, toxic organometallics can be avoided. Our method yields cubic (rather than hexagonal) CdSe nanoparticles, perhaps as a result of the autogenous pressure that develops during the preparative procedure.

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## Notes and references

† Cadmium stearate [Cd(St)<sub>2</sub>], prepared from the reaction of Cd(OH)<sub>2</sub> with molten stearic acid, could be reprecipitated from toluene and analyzed by FTIR and gravimetry. In a typical reaction 1.36 g (2 mmol) of [Cd(St)<sub>2</sub>], 0.158 g (2 mmol) of Se, 0.2 g (1.5 mmol) of tetralin and 0.1 g (0.5 mmol) of dodecanethiol were taken in 50 ml of toluene in a stainless steel bomb (ca. 70% filling, Teflon gasket) and placed in an oven that had been preheated to 250 °C. After 5 h the bomb was removed and cooled to room temperature. The solid product obtained by precipitation as mentioned in the text was dried at 50 °C in air overnight. XRD patterns were acquired on a STOE STADI-P diffractometer in transmission geometry using a 0.02° step scan. Samples were prepared for TEM by placing a drop of the toluene solution of CdSe nanoparticles on a carbon-coated, Formvar-covered Cu TEM grid and subsequently drawing off excess solution. The grids were examined using a JEOL 2000EX TEM operating at 120 kV. The EDAX analysis used a Link ISIS system attached to a JEOL JSM 5600LV scanning electron microscope. UV–VIS spectra were recorded on a Hitachi U3000 spectrophotometer and photoluminescence on a Perkin Elmer L50 B spectrometer.

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