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A multiple injection method for exerting kinetic control in the synthesis of CdSe nanorods†

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The thermolysis reaction of a dual precursor system, comprising one that promotes a controlled nucleation event to produce a rod-shaped nanocrystal template, and the other introduced through a subsequent series of injections that maintain the reaction under kinetic drive, is shown to provide a means of controlling growth of CdSe nanorods with a predetermined aspect ratio.

Semiconductor nanocrystallites have been extensively investigated during the last decade because of their potential applications in many areas of technological importance.[1–3] Certain nanocrystals show size dependent optical and electronic properties, which make them intriguing candidates for applications such as light emitting diodes, solar cells, non-linear optical devices, and biological labelling.[4–10]

There are many synthetic routes by which high quality quantum dots with close to monodisperse size distributions can be prepared.[11] Popular methods include synthesis using inverse micelle templates and the organometallic route developed by Murray *et al.*[12] Single molecule precursor methods have been exploited more recently.[13–16] Nanoparticles with non-spherical shapes, including rods, cubes, nanowires, teardrops, and tetrapods have also been synthesized.[17–23]

Attempts have been made to determine the various factors that govern anisotropic crystal growth during nanocrystal synthesis.[17,18,20] It is believed that the intrinsic shape of the nucleated seed crystal plays an important role by templating the subsequent growth of the nanocrystals. During the kinetically controlled growth process, preferential growth of a particular crystallographic face can occur, for example by employing a structure-directing ligand. It has been shown that the chemical potential of elongated nanocrystals is higher than that of spherical ones, suggesting that growth in a preferred crystallographic direction requires a relatively high chemical potential environment in the reaction system.[17] Attaining such conditions necessitates use of a higher monomer concentration in the reaction medium.

Here we describe a new strategy for controlling the shape of colloidal CdSe nanocrystals using a dual precursor system and multiple injection method. We show that nanorods can be grown in this fashion while maintaining their aspect ratio—dictated by the nanorod template produced in the first step of the procedure. Thus quantum size effects as a function of size, at a fixed aspect ratio, can be systematically studied.

In the present study, CdSe nanorods of low aspect ratio were synthesised by suitable choice of precursor systems and kinetic control of growth exerted by multiple injections. To a solution of CdO, in tetradecylphosphonic acid (TDPA) and tri-*n*-octylphosphine oxide (TOPO), Se powder in tri-*n*-octylphosphine (TOP) was injected to initiate the nucleation. This procedure, identical to that reported previously by Peng and Peng,[17] provides a rod-shaped template for subsequent growth. The conditions employed for this first step dictate the aspect ratio of the final nanorods. For example, the amount of shape directing agent plays a decisive role in regulating the ultimate shape of the particles,[17,18] and variation of the Cd : Se ratio affects the aspect ratio of the nanorods, a higher Cd : Se ratio favouring a higher aspect ratio.[17]

The second stage of the synthesis involves growth, controlled by a series of injections of a solution containing $Cd(OAc)_2 \cdot 2H_2O$ and Se powder in TOP. This precursor system used for the multiple injections supplies a steady level of the monomers that maintain kinetic control of the growth process. In this manner, the anisotropic growth is ameliorated such that the crystal dimensions increase, but the initial aspect ratio is approximately maintained.

Transmission electron microscopy (TEM) images (Fig. 1) of the CdSe particles isolated from the reaction after each injection of the second precursor system, labeled A, B, C, and D, show the growth of nanorods with a mean aspect ratio of 1.5. This aspect ratio can be varied, according to the initial growth conditions.[20] The average length of the rod grows from 8.9 nm (A), to 13 nm (B), to ~14 nm (C and D). The XRD patterns of the sample (Fig. 2) can be indexed to hexagonal wurtzite CdSe with strong (110), (103), and (112)

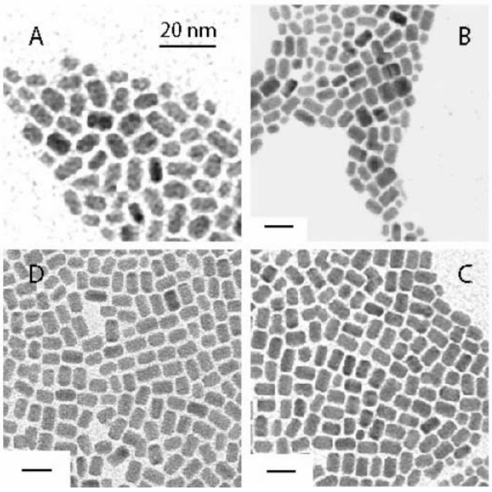

Fig. 1 TEM images of the CdSe nanorods during the second growth period. In each image the size bar corresponds to 20 nm.

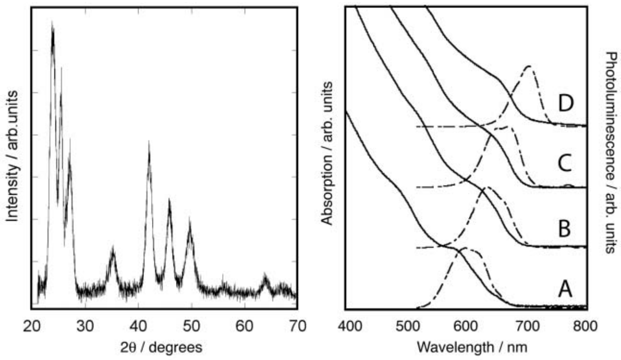

Fig. 2 (a) PXRD data for the CdSe nanorods. (b) Absorption and photoluminescence spectra for samples removed from the reaction after the

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† Electronic supplementary information (ESI) available: multiple injection synthesis procedure. See http://www.rsc.org/suppdata/cc/b4/b409972a/

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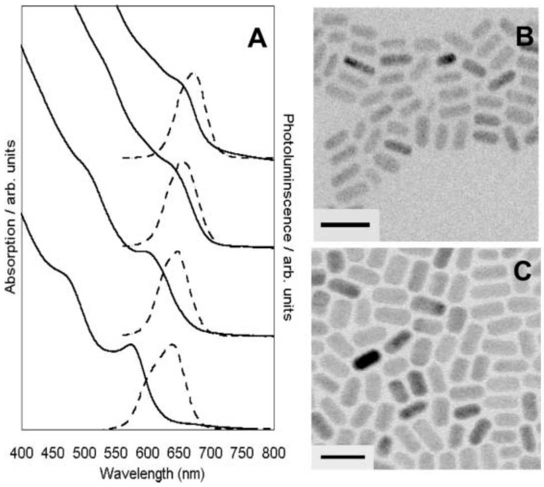

Fig. 3 (a) Absorption (solid lines) and photoluminescence (dashed lines) spectra for CdSe nanorods prepared from higher aspect ratio nanorod templates. (b) TEM image of these nanorods after the first injection of the second precursor system, and (c) after the final injection. The average aspect ratio was found to be 1.8. In each image the size bar corresponds to 20 nm.

reflections. HR-STEM studies and analysis of the PXRD data have revealed that these nanorods grow along the wurtzite *c*-axis and have a hexagonal cross-section.[24]

The evolution of quantum confinement during the reaction period was monitored by measuring the UV–vis absorption and fluorescence spectra of the samples A–D. A progressive red shift in the band gap was observed with growth time, concomitant with growth of the particles, from 580 nm (A), to 620 nm (B), to 630 nm (C) to 650 nm (D), Fig. 2. We found that the particle polydispersity decreased during this second growth period. The fluorescence spectra were found to be narrow, but display dual peaks, indicative of a bimodal size distribution formed in the initial steps of the synthesis.

To demonstrate how tuning of the template nanocrystal controls the aspect ratio of nanorods grown during addition of the second precursor system, we grew longer nanorod templates by waiting 10 minutes before initiating the second growth stage. In Fig. 3 we show absorption, photoluminescence, and TEM as a function of the multiple injections. The aspect ratio of these rods is constant at ~1.8 as they grow from 10 nm (A) to 15 nm (D) in length.

We chose different precursor systems for each of the two key steps, templated nucleation and kinetically-controlled growth, that occur during the formation of the nanocrystals. A slow nucleation is favourable for anisotropic growth, and hence we avoided the use of dimethylcadmium, or any simple salt of Cd, owing to their high reactivity. It is known that Cd-phosphonic acid salts are less reactive than both dimethylcadmium and simple salts of Cd, thus promoting a slow nucleation.[20,25] Upon heating, the CdO reacts with the phosphonic acid to form the salt, which is indicated by the disappearance of the red colour of the solution. Under these conditions Cd^{2+} ions are coordinated by both TDPA and TOPO.

Our strategy for the growth stage was to optimize conditions for kinetic growth, in order to bias the reaction towards uniform growth of the nanorods with aspect ratios that were templated during the first growth period. This is accomplished by maintaining a high monomer reagent concentration. Thus, after nucleation *via* the first precursor system, we injected a solution containing $Cd(OAc)_2{\cdot}2H_2O$ and TOPSe. Since $Cd(OAc)_2{\cdot}2H_2O$ decomposes rapidly, it supplies the Cd^{2+} ions required at the growth stage, while TOPSe supplies the Se at a similar rate. A continuous and controlled supply of monomers was maintained throughout the growth stage by the slow addition of this second precursor system. Evidently, at the high monomer concentrations maintained by the multiple injections, growth on other facets occurs in concert with the growth on the [001] face, so that preferential elongation along the crystal *c*-axis, that is, uniaxial rod growth, is attenuated. Thus the aspect ratio of the rods is preserved during this second growth period.

To summarize, we report a new synthetic procedure for the controlled preparation of CdSe nanorods with various sizes, but all with an aspect ratio of ~1.5 (and ~1.8). These nanorods are model wurtzite structures with hexagonal cross-sections. We have used dual-precursor systems and a multiple injection process to customize kinetic growth conditions such that the first step of the synthesis provides a nanorod template that grows approximately isotropically in the second growth regime. Thus quantum size effects at constant aspect ratio can be systematically explored for nanorods.

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