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A single-source route to CdS nanorods

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We report the preparation of CdS nanorods using a thiosemicarbazide complex of cadmium [$Cd(NH_2CSNHNH_2)_2Cl_2$]. The precursor was decomposed in tri-*n*-octylphosphine oxide (TOPO) at 280 °C to give TOPO capped CdS nanoparticles; nano-dimensional rods of the material are clearly visible in transmission electron microscopy (TEM); the particles have been further characterised by X-ray diffraction (XRD) and selected area electron diffraction (SAED) and optical measurements.

Efficient synthetic methods for the preparation of high quality, monodispersed, surface passivated semiconductor nanocrystals have been of considerable recent interest and several reviews on the subject have been published.[1–3] There has also been work on carbon nanotubes (CNTs), which have been used as templates for the synthesis of nanowires and nanotubes[4] and reports of the synthesis of nanotubes of WS_2,[5] MoS_2,[6] and GaN[7] and also nanowires of metal,[4] metal oxides,[4,8] metal chalcogenides[9–13] and GaN.[4]

Other methods employed to achieve shape control in nanostructured materials include the use of templates such as: liquid-crystal, self assembled monolayers, polymers or porous aluminium oxide which enhance the growth rate of one crystallographic face over another. Alivisatos *et al.*[10,11] have controlled the shape of the nanoparticles of semiconductors by varying the concentration of growth modifiers *e.g.* the ratio of surfactants [hexylphosphonic acid] : [tri-*n*-octylphosphine oxide] and /or the volume of the initial injection, time of reaction or the precursor concentration all of which can be optimized to enhance the formation of CdSe nanorods over oblate CdSe nanoparticles. The synthesis of nanorods has also been achieved using a solvothermal route,[12,13] for CdE (E = S, Se, Te). Chen *et al.*[14] have recently reported the synthesis in microemulsion of star shaped CdS materials composed of rod-like nanoparticles with diameters of 4–7 nm and length in the range 150–200 nm. The synthesis of water-soluble CdS nanorods with various aspect ratios has been achieved by arrested precipitation from a micellar solution.[15]

Here we report the synthesis of CdS nanorods by the thermolysis of $Cd(NH_2CSNHNH_2)_2Cl_2$ in TOPO. The precursor was prepared by reacting $CdCl_2{\cdot}H_2O$ and thiosemicarbazide in 1 : 2 mol ratio in ethanol. The nanorods were synthesized by a method as previously described for CdS nanoparticles.[16] $Cd(NH_2CSNHNH_2)Cl_2$ (1.0 g) was dissolved in tri-*n*-octylphophine (TOP) (10 mL). The solution was injected to TOPO (25 g) and heated to 270 °C. The resulting yellow solution was heated to 280 °C for 3 h, cooled to 70 °C and methanol was added to give a fine deposit of CdS, which was separated by centrifugation.

The morphology of the as prepared CdS sample was investigated by transmission electron microscopy (TEM). The TEM image (Fig. 1) shows the rod-like appearance of the CdS particles with lengths in the range 10–24 nm and diameters in the range 3–5 nm. The particles are close to monodispersed with an aspect ratio of 4 (±11%) (Fig. 1), The X-ray diffraction (XRD) pattern of the particles can be indexed to hexagonal CdS with strong (110), (103) and (112) reflections (Fig. 2(a)).‡ The peaks are sharper than those observed for spherical CdS nanoparticles.[17] The mean crystallite 'diameter', *d*, calculated from the Scherrer[18] formula, $d = 0.94\lambda/B \cos \theta$ on the 2θ = 28.219° (101) peak gives a value of 32 nm. The selected area electron diffraction (SAED) pattern (Fig. 2(b)) shows the presence of distinct diffraction rings, confirming the crystalline nature of the particles.‡

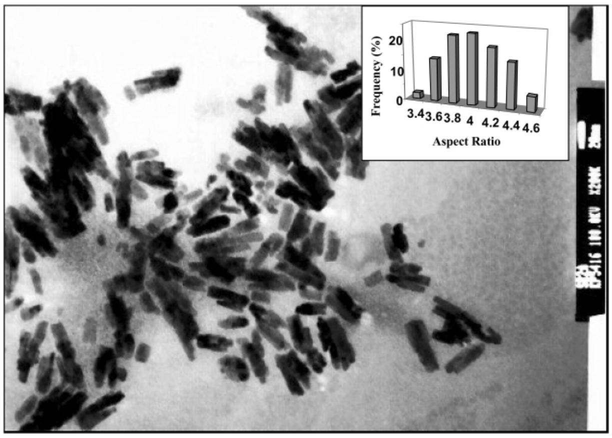

Fig. 1 TEM image showing rod-like CdS and the histogram showing the aspect ratio of the particles (insert).

The band edge of the particles as observed in the UV/Vis spectrum is at 490 nm (2.52 eV), a slight blue shift in relation to bulk CdS (515 nm) (Fig. 3). Eqn. (1),[19]

$$E_{gn} = [E_{gb}^2 + 2\hbar^2 E_{gb}(\pi/R)^2/m^*]^{1/2} \qquad (1)$$

where E_{gb} is the band gap of the bulk semiconductor, R is the particle size and m^* is the effective electron mass was used for the calculation of the band edge. The size of the particles as calculated by this equation was found to be 17.5 nm. This value is different to that found by the TEM and XRD measurements. The discrepancy is probably due to the non-spherical nature of the particles. The photoluminescence spectrum (λ_{ex} = 480 nm) shows an emission maximum at 515 nm, a slight red-shift in relation to the band edge.

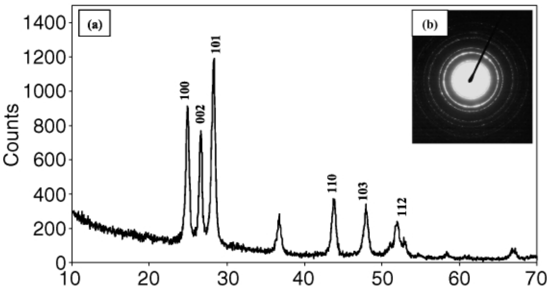

Fig. 2 CdS nanorods: (a) XRD pattern and (b) SAED pattern.

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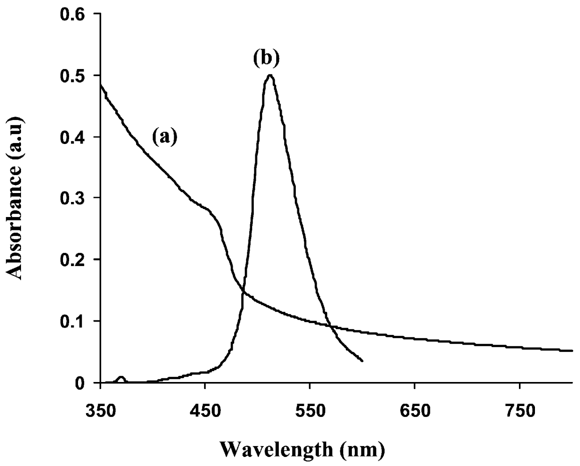

Fig. 3 (a) Optical absorption spectrum and (b) photoluminescence spectrum of CdS nanorods.

CdS nanorods have been prepared using Cd$(NH_2CSNHNH_2)_2Cl_2$ as a single-molecule precursor. The elongated morphology of the particles is clearly visible in the TEM images. The XRD pattern shows the particles to be hexagonal. The blue shifted band edge in relation to the bulk material and Stokes' shifted photoluminescence confirms the nanocrystalline nature of the material. We propose that the elongated 'rod-like' morphology of the CdS particles is due primarily to the nature of the precursor. We have previously reported the use of various metal dithio- and diseleno-carbamates thermolysed in TOPO to give close to spherical, oblate nanodispersed semiconductors. We can conclude from this work that the nature of the precursor can influence the shape of the particles and we are further investigating the mechanism of this process.

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Notes and references

‡ The X-ray powder diffraction (XRD) pattern of the nanorods was recorded using Philips X'Pert Materials Research Diffractometer. Measurements were taken using glancing angle incidence detector at an angle 3° for 2θ values over 5–60° steps of 0.04° with a count time of 2 s. UV–VIS absorption spectrum was recorded on a Perkin Elmer Lamda 20 UV–VIS Spectrophotometer. A Jobin Yvon-spex-Fluorog-3-Spectrofluorimeter with xenon lamp was used to measure the photoluminescence of the nanorods. TEM images were taken on a JEOL JEM-1200 EX II Transmission Electron Microscope using an accelerating voltage of 80–100 kV.

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