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A cluster growth route to quantum-confined CdS nanowires

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Quantum-confined CdS nanowires with diameters around 4 nm and lengths ranging from 150 to 250 nm were grown for the first time from cadmium bis(diethyldithiocarbamate) $[Cd(DDTC)_2]_2$ by removal of the four thione groups with ethylenediamine (en) at 117 °C for 2 min.

Semiconductor crystallites that are small in comparison to the bulk exciton diameter show quantum confinement effects, which have been intensely studied, and a number of good reviews have mirrored this development.[1,2] Various methods for the production of II–VI and III–V nanocrystals with narrow size distributions in the desired size range of between 1 and 15 nm in diameter have been developed.[3]

Special attention has been paid to one-dimensional structures, such as nanotubes and nanowires owing to their interesting properties.[4] However the challenge of fabricating such 1D structures is substantial because technologically useful quantum wires require lateral dimensions of $<$ *ca.* 10 nm. Such a precision level is a formidable technological challenge.[5]

Recently very long CdTe nanowires[6] were fabricated by the molecular-beam epitaxy (MBE) growth technique, however, their diameters are much larger than 10 nm. Considering the small exciton diameter of CdS (6 nm), the preparation of quantum confined CdS nanowires (of diameter $<$ 6 nm) is even more difficult. A promising route is deposition of semiconductors into anodic aluminium oxide membrane filters or nuclear track-etched polycarbonate membranes with small pores; the smallest semiconductor nanowire obtained by this method to date is 9 nm.[7]

Here, quantum confined CdS nanowires were successfully obtained for the first time from a cluster precursor $Cd_2(S_2CNEt_2)_4$, which can be regarded as an inorganic core $[Cd_2S_2]$ with four capping groups.[8] Nucleophilic attack by ethylenediamine at the thione carbon can lead to removal of the capping groups. This process is shown in Scheme 1 and the resulting organic product has been characterized.[9]

The inorganic Cd_2S_2 cores can then combine with each other and under appropriate chemical and physical environment, $[Cd_2S_2]$ may preferentially grow along a unique direction and result in a one-dimensional structure.

In a typical process, 1 g of $[Cd(S_2CNEt_2)]_2$, prepared by precipitation from a stoichiometric mixture of $NaS_2CN(C_2H_5)_2$ and $CdCl_2$ in water, was dissolved in 30 ml ethylenediamine in a flask, and then heated to reflux (117 °C), and maintained at this temperature for 2 min. The yellowish precipitate obtained was filtered off and washed with ethanol.

The X-ray diffraction (XRD)† pattern of the nanowires is shown in Fig. 1. All the reflections, to within experimental error, fit that of bulk hexagonal CdS.[10] The (002) diffraction peak, the second strongest peak in bulk hexagonal CdS, is unusually narrow and strong, indicating a preferential growth along the *c* axis in the product. Using the Scherrer formula[11] on the (*hk*0) peaks (100) (110) and (200), the average diameter of the nanowires is estimated as 4.0 nm. This is confirmed by transmission electron microscopy (TEM)‡ images (Fig. 2), which reveal straight-line shapes and uniform diameters of *ca.* 4 nm and lengths ranging from 150 to 250 nm. IR spectroscopy was carried out to examine the purity of the product, and indicated the absence of both DDTC and ethylenediamine, suggesting a high degree of purity.

Fig. 3(a) shows the absorption spectrum of a sample dispersed in distilled water. The clear maximum at 455 nm is assigned to the optical transition of the first excitonic state.[2] The average particle diameter, as calculated from the maximum of the absorption curve (λ_m = 455 nm) is 3.8 nm[2] in good agreement with the TEM and XRD results. Since the onset of the absorption spectrum generally represents the larger end of

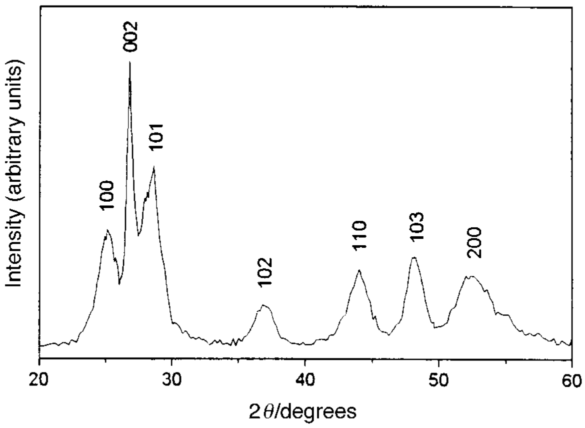


Fig. 1 XRD pattern for CdS nanowires.

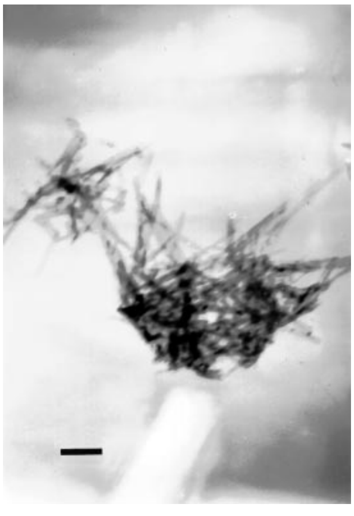
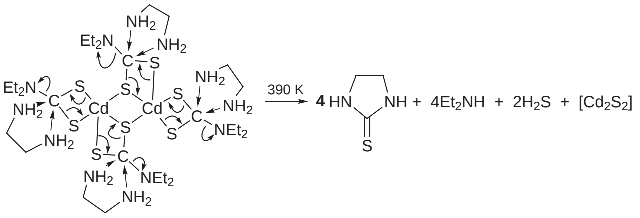


Fig. 2 TEM images of the nanowires (scale bar, 50 nm).



Scheme 1

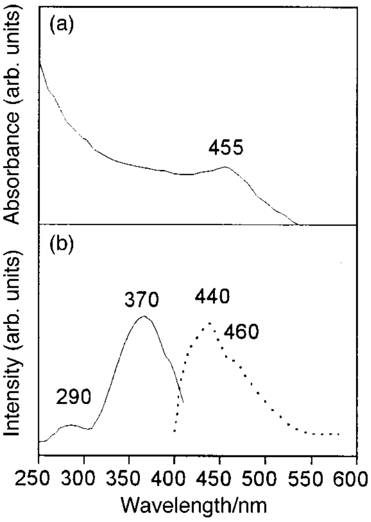


Fig. 3 (a) Absorption spectrum of a CdS sample dispersed in H_2O. (b) Excitation (solid line) and photoluminescence (dashed line) spectra of CdS nanowires. The spectra were taken in reflection geometry. The excitation wavelength for the emission spectrum was 370 nm, and the monitoring wavelength for the excitation spectrum was 440 nm.

the size distribution,[12] the position of the absorption edge (λ_e = 515 nm) shows that the lengths of the nanowires (150–250 nm) are much larger than the exciton diameter of CdS (6 nm). The large difference between sizes calculated from λ_e and λ_m, which can be related to the width of the particle size distribution, is characteristic for nanowires. The clear appearance of a blue-shift of the absorption peak relative to bulk CdS indicates that the CdS nanowires are quantum-confined. The excitation spectrum (monitoring wavelength at 440 nm) shows absorption bands at 290 and 370 nm [Fig. 3(b)]. Under photoluminescent excitation at 370 nm, the nanowires emit blue light at 440 and 460 nm [Fig. 3(b)] with a 55 nm blue shift relative to bulk CdS. These features are close to the optical absorption edge of CdS, suggesting a near band-edge emission.

When $[Cd(DDTC)_2]_2$ is thermolyzed at 250 °C for 30 min in trioctylphosphine oxide (TOPO), the morphology for most of the CdS nanocrystallites was reported to be thin plates.[13] In our experiments, other nucleophiles such as pyridine and diethylamine were also tested to remove the capping groups, however, no wire-like products were obtained. These results show that ethylenediamine plays a critical role in the formation of wire structures and probably serves as a director for the growth of the intermediate inorganic $[Cd_2S_2]$ core. Ethylenediamine has been extensively used as a template in solvothermal processes. For example, Li *et al.*[14] reported that elemental reaction of Cd and S in ethylenediamine resulted in CdS nanorods with diameters of 25–40 nm[14] although no detailed mechanism was proposed.

In summary, quantum-confined CdS nanowires with diameters of *ca.* 4 nm and lengths ranging from 150 to 250 nm have been grown for the first time from $[Cd(DDTC)_2]_2$, by removal of the four thione groups with ethylenediamine (en) at 117 °C for 2 min. Further studies may extend the method for the preparation of other quantum-confined nanowires.

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Notes and references

† XRD patterns were obtained on a Japan Rigaku D/Max γA rotation anode X-ray diffractometer with Ni-filtered Cu-Kα radiation (λ = 1.54178 Å).

‡ TEM measurements were made on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 kV.

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