CdS/CdSe core/sheath nanostructures obtained from CdS nanowires

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CdS/CdSe core/sheath nanowires with diameters of 7.7/0.75 nm were prepared by treating CdS nanowires with selenium in tributylphosphine (TBP) at 100 °C for 24 h and were characterized by X-ray powder diffraction, transmission electron microscopy, high resolution TEM, UV–VIS absorption spectra, photoluminescence spectra and X-ray photoelectron spectroscopy.

Nanowires are of both fundamental and technological interest especially in the field of conductance quantization[1] and nanodevices.[2] Hybrid one-dimensional structures in axial or radial directions are essential to realize nanodevices. To date, both axial heterojunctions[3] and radial core/sheath structures[4] have been reported. Recently, routes to zero-dimensional core/shell II–VI semiconductors have been rapidly developed: core/shell semiconductors of CdS/Cd(OH)$_2$,[5] CdSe/ZnS,[6,7] CdSe/ZnSe,[8,9] CdS/HgS/CdS[10] and CdSe/CdS[11–13] are examples. These systems normally show decreased fluorescence lifetimes, higher stability and electronic accessibility in comparison with organic capped derivatives and are, in some cases, superior to existing fluorophores when applied as biological labels.[14] However, to our knowledge, core/sheath nanowires of II–VI semiconductors have not, as yet, been reported.

We have succeeded in preparing quantum confined CdS nanowires (4 × 200 nm)[15] using cadmium dithiocarbamate as a precursor,[16] and it is possible to prepare CdS/CdSe core/sheath nanowires by treatment of CdS nanowires. Since phosphine chalcogenides such as TBPSe,[12] Et$_3$PTe[17a] and TOPSe[18] have been widely used as chalcogen sources in the synthesis of II–VI nanocrystals we attempted to grow a CdSe sheath with Se in TBP. Here the reaction is described as a substitution-type process [eqn. (1)] considering the substantial difference between the solubility products of CdS ($K_{sp} = 1.4 \times 10^{-19}$) and CdSe ($K_{sp} = 1.4 \times 10^{-35}$). The detailed mechanism may involve chemical transportation of selenium by TBP [eqn. (2)] similarly to that of Te by R$_3$P.[17]

$$CdS + Se \xrightarrow{\text{TBP, 100 °C, 12 h}} CdSe + S \qquad (1)$$

$$TBP + Se \rightleftharpoons TBPSe \qquad (2)$$
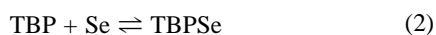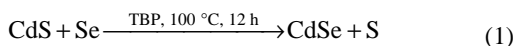
The CdS nanowires were synthesized by using a modification of our previous method:[15] cadmium diethyldithiocarbamate [Cd(Et$_2$NCS$_2$)$_2$]$_2$ (1 g) was dissolved in ethylenediamine (en) (30 ml) and heated in a Teflon-lined autoclave at 80 °C for 12 h, then the yellow CdS nanowires were filtered off and washed with ethanol. After being dried in vacuum at room temperature for 2 h, CdS nanowires (0.576 g, 4 mmol) and selenium (0.016 g, 0.2 mmol) were ultrasonically dispersed in 20 ml TBP, transferred to a Teflon-lined autoclave, kept at 100 °C for 24 h, and then cooled to room temperature naturally. The product was filtered off, washed with ethanol, and dried in vacuum at room temperature for 2 h.

The black selenium powder disappeared and the yellow CdS nanowires turned red, the characteristic color of CdSe. X-Ray photoelectron spectroscopy (XPS)† was used to measure the composition of the core/sheath nanowires, the signal was fitted

by Gaussians according to the literature[12] and gave a S/Se ratio of 93:7, consistent with the molar ratio of reactants added.

Fig. 1 shows the X-ray powder diffraction (XRD)‡ patterns for CdS and CdS/CdSe core/sheath nanowires, respectively. The (002) peak is much stronger and narrower than the other peaks for both nanowires, indicating that both were elongated along the c-axis and the shape was well preserved in the conversion reaction. According to the Scherrer formula, the average diameter is 6.5 nm for the CdS nanowires and 8.0 nm for the CdS/CdSe core/sheath nanowires. The reflection peaks of the core/sheath nanowires shifted only little from those characteristic of pure CdS to CdSe. The X-ray data may be consistent with both a core/shell structure[12] and a solid solution, so transmission electron microscopy (TEM) and high resolution TEM was carried out to confirm the former structure.
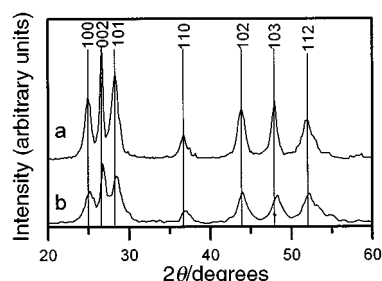

Fig. 1 XRD patterns of (a) CdS/CdSe core/sheath nanowires and (b) CdS nanowires.

TEM§ images of CdS and CdS/CdSe samples both show monodispersed wire-like shapes [Fig. 2(a) and (b)]. The average diameter is 6.7 nm for CdS nanowires and 8.5 nm for the core/sheath nanowires, which are consistent with the diameters estimated by the Scherrer formula. The retention of morphology unambiguously indicates a successful CdSe sheath growth since the likelihood for separately formed CdSe nanocrystals to be wire-like is very low. Further evidence for the core/sheath structure is from image contrast observations: CdS/CdSe core/sheath nanowires show much more contrast than the CdS nanowires owing to the stronger electron scattering power of selenium.

The size of the CdS/CdSe core/sheath nanowires is so small that only high resolution TEM (HRTEM) images give direct evidence of their formation. Fig. 2(c) and 2(d) show typical HRTEM¶ images for CdS and CdS/CdSe core/sheath nanowires respectively. The core/sheath nanowires consist of a 0.75 nm sheath and a 7.7 nm core, which is only a little larger than CdS only nanowires (6.9 nm) and in good agreement with the size estimated by the Scherrer formula. The sheath is thicker than expected from the Se to S ratio (7:93), one explanation is that the sheath is a compositionally graded interface between pure CdS and pure CdSe.

The UV–VIS absorption spectra of the CdS nanowires and CdS/CdSe core/sheath nanowires dispersed in water are shown in Fig. 3(a) and (b), respectively. There is little difference in the profile of the two spectra and an absorption peak at 472 nm is
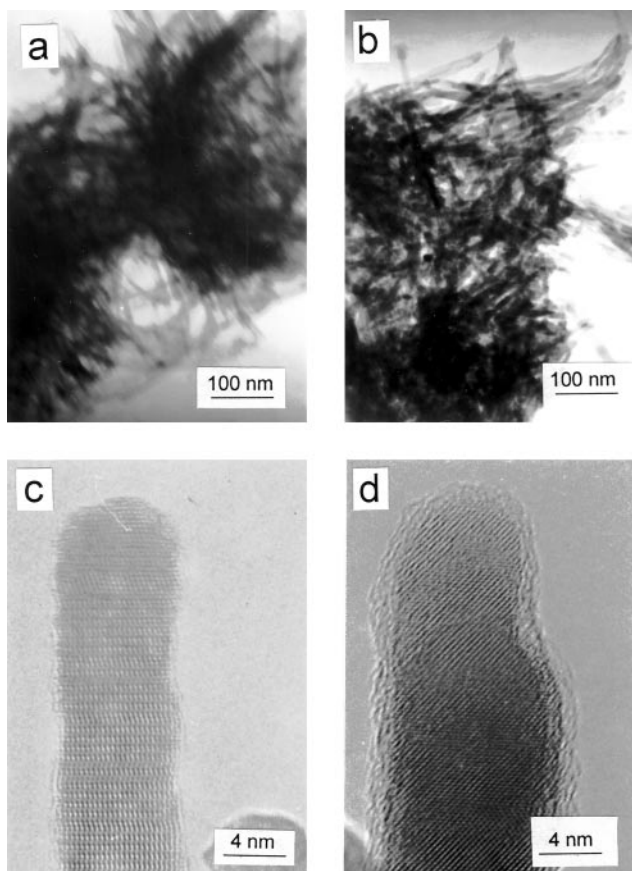
level [Fig. 3(e)]. Accumulation of Cd^{2+} at the surface may destroy sites where radiationless recombination of charge carriers can occur.[5]

In summary, CdS/CdSe core/sheath nanowires with diameters of 7.7/0.75 nm were prepared from CdS nanowires and this method may be modified to prepare other core/sheath nanowires.

Notes and references

† XPS were recorded on an ESCALab MKII instrument with Mg-Kα radiation as the exciting source.
‡ XRD patterns were obtained on a Japan Rigaku D/Max γA rotation anode X-ray diffractometer with Ni-filtered Cu-Kα radiation ($\lambda = 1.54178$ Å).
§ TEM measurements were made on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 kV.
¶ High-resolution electron microscopy (HREM) images of the as-prepared nanowires were taken on a JEOL-2010 transmission electron microscope.

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Fig. 2 TEM images of (a) CdS nanowires and (b) CdS/CdSe core/sheath nanowires along with HRTEM images of (c) CdS nanowires and (d) CdS/CdSe core/sheath nanowires.
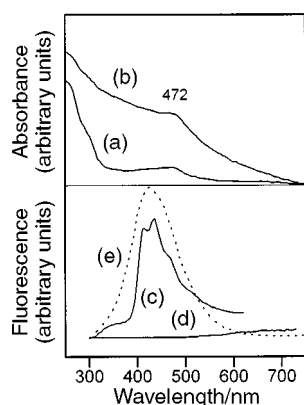

Fig. 3 Absorption spectra of (a) CdS nanowires and (b) CdS/CdSe core/sheath nanowires along with fluorescence emission spectra (excited at 250 nm) of (c) CdS nanowires, (d) CdS/CdSe core/sheath nanowires and (e) CdS/CdSe core/sheath nanowires dispersed in 1 M $CdSO_4$ solution.

common to both. This is consistent with a report that the major component of a core/shell particle dominates the absorption spectra.[9] By contrast, the photoluminescence (PL) spectra for the CdS-only and CdS/CdSe core/sheath nanowires are totally different [Fig. 3(c) and (d)] with the sheath completely quenching the fluorescence of CdS nanowires as found in the CdS/CdSe core/shell system.[11] When excess cadmium cations ($CdSO_4$) were added to a dispersion of the CdS/CdSe nanowires in water, the fluorescence was restored to virtually the previous