ChemComm
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One-step preparation of coaxial CdS–ZnS nanowires†

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A new approach was developed to prepare coaxial (core-shell) CdS–ZnS nanowires *via* a one-step metallo-organic chemical vapor deposition (MOCVD) process with co-fed single source precursors of CdS and ZnS. Single source precursors of CdS and ZnS with sufficiently different reactivity were prepared and paired up to form the coaxial heterostructure in a one-step process.

One-dimensional (1-D) nanosized semiconductor materials with well-defined heterostructures have attracted much research attention in recent years due to their unique optoelectronic properties and potential applications in nanodevice fabrication.[1] Nanowires and nanorods of semiconductors with heterostructures such as coaxial core-shell,[2] superlattice,[3] and composite[4] nanostructures have been successfully prepared. For coaxial nanowires, in general, *multi-step* depositions involving sequential charges of desired source materials[5] or surface modification by ambient species[6] were necessary to achieve the architecture. Unlike the *multi-step* method reported in the literature, a new approach is presented here for preparation of coaxial (core–shell) CdS–ZnS nanowires with a *one-step* metallo-organic chemical vapor deposition (MOCVD) process.

Previously, co-feeding practice of precursors was utilized to achieve co-deposition of TiO_2–SiO_2 composite particle films and *in situ* surface passivation of CdS nanoparticles with ZnS shells.[7] Here, the precursor co-feeding practice is incorporated with the vapor-liquid-solid (VLS)[8] growth mechanism for 1-D nanostructures to achieve *one-step* preparation of coaxial CdS–ZnS nanowires. The co-fed precursors of CdS and ZnS were designed to possess sufficient reactivity difference to enable sequential reaction for *in situ* formation of the core–shell structure. MOCVD was conducted in a simple hot-wall reactor.[7] Dialkyldithiocarbamate-based[9] single-source precursors of CdS ($Cd(S_2CN(C_3H_7)_2)_2$, denoted as Cd33) and ZnS ($[Zn(S_2CNBu_2)_2]_2$, denoted as Zn44), were synthesized[10] and co-fed into the reactor. Fused silica plates sputtered with Au were used as the substrates for growth of the nanowires, and the two precursors were heated to different temperatures (Cd33 at 160 °C and Zn44 at 120 °C) for generation of suitable amounts of precursor vapors. Depositions were run at carrier gas (N_2) flow of 200 sccm, system pressure of 30 Torr, reaction time of 6 h and deposition temperature of 280 °C.

The deposition was run at 280 °C separately for Cd33 and Zn44; it was found that only CdS nanowires were produced from the VLS growth mechanism and no ZnS at all. However, when Cd33 and Zn44 were co-fed into the system, the deposition run again at 280 °C gave nanowires consisting of both CdS and ZnS. This phenomenon implied that Zn44 would react to form ZnS in the presence of CdS nanowires. In other words, based on the reactivity difference existing between Cd33 and Zn44, Cd33 would be thermally decomposed first to form the core CdS nanowires *via* the VLS mechanism in the presence of Au catalyst, and these first-formed nanowires then served as the catalyst to promote the

thermal decomposition of Zn44. As a result, the later-formed ZnS was expected to grow on the surface of the first-formed CdS nanowires, and thus the *one-step* fabrication of coaxial nanowires was successfully achieved.

Typical transmission electron microscope (TEM, JEOL JSM-1200) images of the plain CdS and coaxial CdS–ZnS nanowires are shown in Fig. 1(a) and (b), respectively. These nanowires had a diameter of about 30–50 nm and grew up to be longer than 1 μm. The darkest regions at the wire tips represent the catalyst Au, confirming the VLS mechanism. More importantly, in Fig. 1(b), the evident contrast between the inner core and outer shell suggested the targeted coaxial structure. Such contrast can be more clearly observed in Fig. 1(d), a high resolution transmission electron microscope (HRTEM, JEOL JEM-2010) image of a section of the coaxial nanowire, as compared to that of the plain CdS nanowire in Fig. 1(c). The thickness of the shell layer was about 10 nm, while the diameter of the core was around 30 nm. From the EDS analyses† only Zn and S elements were found in the projected shell region, while in the projected core region Cd was richer than Zn, accompanied with a stoichiometric amount of S. This further confirmed the coaxial structure of the CdS–ZnS nanowires. Note that in the projected shell region, only the ZnS shell was sampled, while in the projected core region, both the CdS core and the ZnS shell were probed only that the thicker core contributed more than the thinner shell.

Fig. 2(a) and (b) show the enlarged HRTEM images in the marked regions of Fig. 1(c) and (d), respectively. The dot patterns of the inserted selected area electron diffraction (SAED) images showed that both the plain CdS and coaxial CdS–ZnS nanowires grew as single crystals. Different from the perfect crystallinity
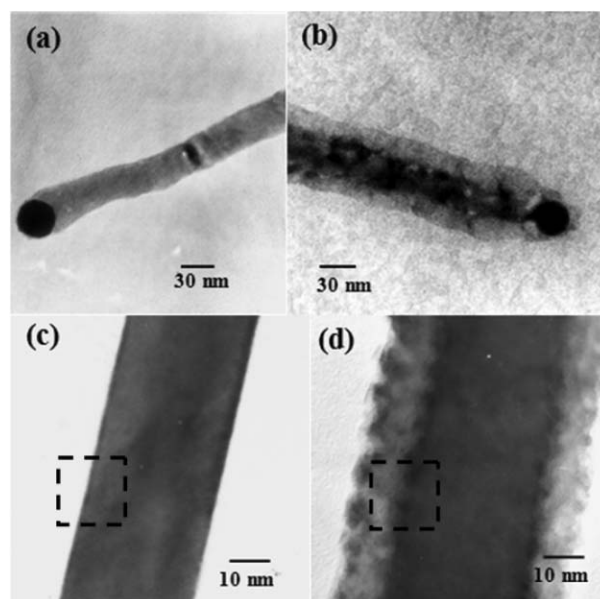

Fig. 1 TEM images of (a) a single plain CdS nanowire and (b) a single coaxial CdS–ZnS nanowire. HRTEM images of (c) a single plain CdS nanowire and (d) a single coaxial CdS–ZnS nanowire.

† Electronic supplementary information (ESI) available: SEM, TEM and HRTEM images, EDS analyses, X-ray diffraction patterns and UV-visible absorbtion spectra of CdS–ZnS nanowires. See http://www.rsc.org/suppdata/cc/b4/b403932g/
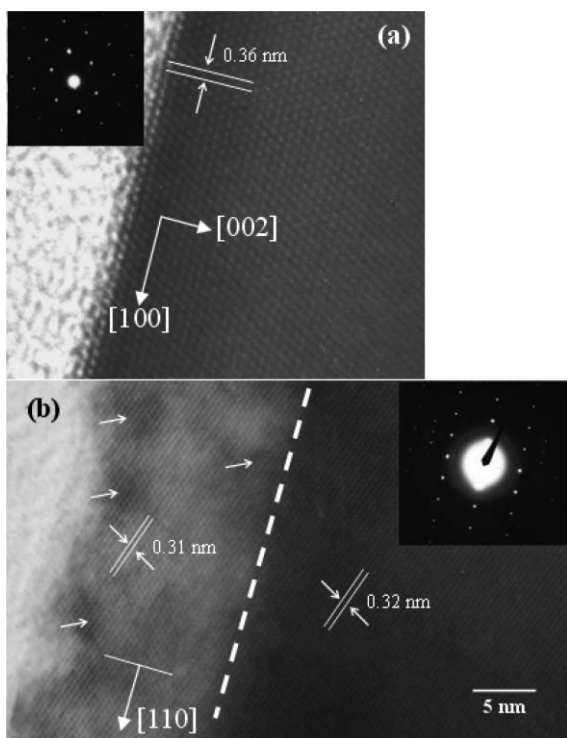
Fig. 2 Enlarged HRTEM images of plain CdS and coaxial CdS–ZnS nanowires shown in (a) and (b), respectively. The interface between the two semiconductor layers is highlighted with a dash line. The corresponding growth direction was also indicated.

observed in the plain CdS nanowires, with a 0.36 nm lattice in the [100] direction, the coaxial CdS–ZnS nanowires exhibited some microtwins and stacking faults at the core–shell interface and in the shell region (indicated by arrows in Fig. 2(b)). The ZnS shell showed an interlayer spacing of 0.31 nm, which agreed well with the lattice spacing of the (111) planes of cubic ZnS; while the CdS core gave a 0.32 nm interlayer spacing that agreed with the lattice spacing of the (101) planes of hexagonal CdS. The closeness of the two lattice spacings enabled the growth of coaxial ZnS shell on the CdS core wires *via* a minor atomic-level surface reconstruction.

The photoluminescence (PL) spectra of the coaxial CdS–ZnS and corresponding plain CdS nanowires are compared in Fig. 3. The two samples showed typical near edge emission of CdS with the peaks centering around 500–510 nm.[11] The coaxial CdS–ZnS nanowires exhibited basically PL behavior of the core material, CdS, with the shell material, ZnS, playing the modification role. The effective passivation of the surface electronic states of the CdS core by the ZnS shell led to dramatic enhancement in PL intensity and in the PL quantum yield (Qs) of the coaxial CdS–ZnS nanowires over the corresponding plain CdS nanowires.[7b,12]

A possible growth mechanism may be proposed to illustrate the formation of the coaxial nanowire structure. As the reaction was run at the deposition temperature of 280 °C, the precursor with higher reactivity (Cd33) decomposed to form CdS nanowires first on the Au-coated substrate surface through the VLS growth mechanism. And these first-formed nanowires served as the catalyst to promote the decomposition and deposition of the other precursor of lower reactivity (Zn44) on the surface of the first-formed
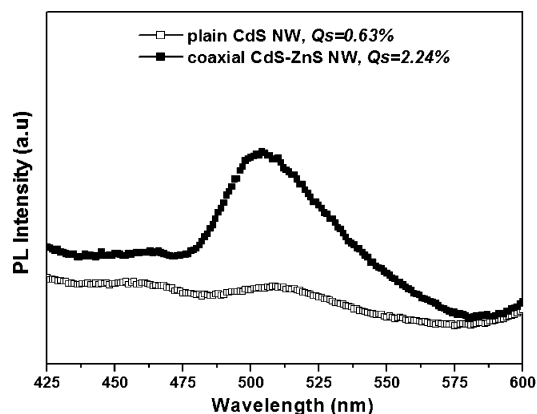

Fig. 3 Photoluminescence (PL) emission spectrum of coaxial CdS–ZnS nanowires in comparison to that of plain CdS nanowires, with the excitation wavelength set at 320 nm.

CdS nanowires. Consequently, by co-feeding precursors of CdS and ZnS of sufficient reactivity difference and running the deposition under appropriate conditions, the coaxial 1-D nanostructure can be obtained in one-step. If examined closely, the Au tip in Fig. 1(b) was also coated with the later formed ZnS shell.

Notes and references

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