One-step fabrication of well-defined hollow CdS nanoboxes†

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Received (in Cambridge, UK) 10th June 2008, Accepted 12th August 2008
First published as an Advance Article on the web 12th September 2008
DOI: 10.1039/b809807g

Hollow CdS nanoboxes, having paper-thin walls of well-defined facets, were synthesized at 170 °C *via* a simple reaction using Na_2SeO_3 for interior quasitemplates and ethylenediamine for exterior molecular templates.

The spectroscopic, electronic, and chemical properties of nanostructured materials are of great interest in both basic and applied research.[1] In particular, nanostructures having hollow interiors have been extensively investigated because they can be applied to nanometre-sized chemical reactors, efficient catalysts, drug-delivery carriers, photonic building blocks, and energy-storage media.[2] Hollow nanostructures have been commonly synthesized by using two basic types of hard templates such as polymers and inorganic nanospheres and soft templates such as sacrificial templates and amphiphilic molecular assemblies. However, synthesis with hard templates requires the elimination of cores *via* optical excavation, chemical etching, or calcination in order to obtain the final products having hollow interiors.[3,4] Thus, soft templates have been utilized increasingly because it is unnecessary to remove cores separately after the synthesis.[5,6] Novel approaches based on the Kirkendall effect, galvanic replacement, Ostwald ripening, and salt quasitemplates have also been employed.[6] Attractive structures having void interiors have been developed to have diverse geometries of either single crystals or polycrystals. However, hollow nanoboxes of II–VI semiconductors have not been reported yet to our knowledge. Furthermore, the controlled construction of well-defined hollow structures *via* a simple process is still a task with a challenge in the engineering of nanomaterials.

In this Communication we report the fabrication of CdS hollow tetragonal nanoprisms having paper-thin walls of well-defined inner and outer wall facets *via* a one-step wet-chemical reaction with Na_2SeO_3 for interior quasitemplates and ethylenediamine for exterior molecular templates. CdS is an excellent material with possible applications in optoelectronics such as nonlinear optics and light-emitting diodes, solar cells, and displays.[7]

Fig. 1A shows a typical transmission electron microscopy (TEM) image of hollow CdS nanoboxes, which were synthesized in a Teflon-sealed autoclave at 170 °C *via* a simple one-step process using $Na_2SeO_3(s)$ for interior salt quasitemplates[8] and ethylenediamine(l) for exterior solvent-coordinating molecular templates.[9,10] Although nanoboxes were aggregated during evaporation for the TEM measurement, their morphology in TEM images can be discerned easily. The nanostructures have well-defined parallelepiped hexahedral morphology although they look like rectangles due to their orientation in the TEM measurement. In general, parallelepipedons of a kind can have only three different side-to-side length ratios regardless of their sizes. If they were oriented randomly in TEM measurements, their probability to show a face with two particular sides is proportional to the area of the face in 2-D TEM images. Thus, considering these, measuring angles between sides in TEM images, and averaging the side lengths of numerous faces with similar side-to-side length ratios separately, we have found that the shapes of the CdS hexahedra are tetragonal nanoprisms with the average side lengths of 240, 160, and 160 nm. It is noteworthy that the stable structures of Na_2SeO_3 used for interior salt quasitemplates are also tetragonal prisms. The closely viewed TEM image shows strong contrast in brightness between the dark edges and the bright central regions, indicating that the tetragonal prisms are empty in the interiors. Thus, CdS nanoparticles are hollow tetragonal nanoboxes in morphology. The high-resolution transmission electron microscopy (HRTEM) image of Fig. 1B designates that the wall thickness of a hollow CdS nanobox is 20 ± 2 nm. The pattern of selected-area electron diffraction (SAED) measured near the edge suggests that the hollow nanoboxes have polycrystalline structures of wurtzite CdS (JPCDS Card

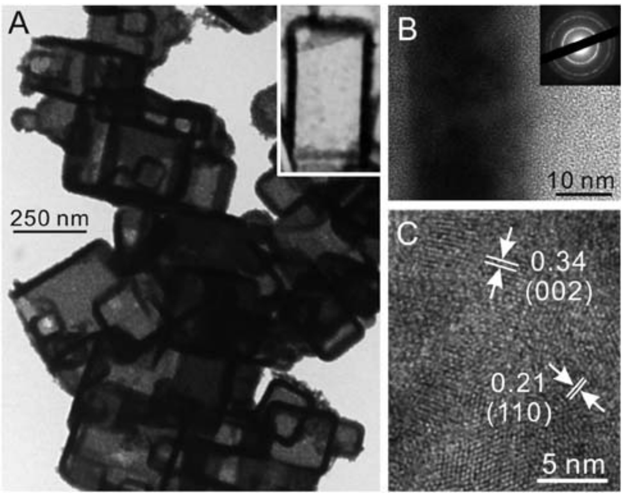

Fig. 1 (A) TEM image showing hollow CdS nanoboxes and (B,C) HRTEM images showing wall thickness and lattice plane distances. The inset of A shows an enlarged view while that of B shows a SAED pattern of the wall.

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† Electronic supplementary information (ESI) available: Experimental details, HRXRD patterns, and TEM images of samples prepared under other conditions. See DOI: 10.1039/b809807g

No. 06-0314). The HRTEM image of Fig. 1C monitored on a central area of a facet shows indeed that the wall of a hollow nanobox consists of small CdS nanocrystals ranging from 5 to 7 nm in size. The observed lattice-fringe distances of CdS nanocrystals are 0.34 and 0.21 nm, which correspond to the spacing lengths of the (002) and the (110) planes of the wurtzite CdS, respectively. The high-resolution X-ray diffraction (HRXRD) pattern of Fig. S1 (ESI†) also indicates that the nanoboxes are composed of wurtzite-crystalline CdS and numerous small nanocrystals. The mean crystallite diameter of small nanoparticles in hollow CdS nanoboxes has been estimated to be 6.6 nm, which is in good agreement with the value estimated with the HRTEM of Fig. 1C.

The scanning transmission electron microscopy (STEM) image of Fig. 2 shows that a hollow CdS nanobox has paper-thin walls of ~20 nm in thickness with well-defined inner and outer facets. The STEM image arises from the projection of a CdS hollow tetragonal nanoprism having the outer side lengths of 410, 260, and 260 nm. Although diverse types of hollow nanostructures were fabricated, to our knowledge, none of them were excavated as thoroughly as our reported hollow CdS nanoboxes. Furthermore, our hollow CdS nanoboxes show well-defined tetragonally parallelepiped vacant structures having entirely closed clean facets. Elemental distribution maps also designate that the nanobox consists of Cd and S, and that Na_2SeO_3 employed for the interior salt quasitemplates has been removed almost completely during washing processes. The fact that the distribution maps of Cd and S are similar to each other supports in addition that a single compound of CdS composes the nanobox. CdS projected in 2-D energy-dispersive X-ray (EDX) maps is located primarily at the edges of the nanobox because of the paper-thin wall character. The line-scanned elemental intensity profiles of Cd and S also display the characteristically sharp peaks of a hollow CdS nanobox very well. Fig. 2 indicates that the interior of the CdS nanobox is completely empty and that both the inner and the outer facets of the hollow nanobox are very neat and well defined.

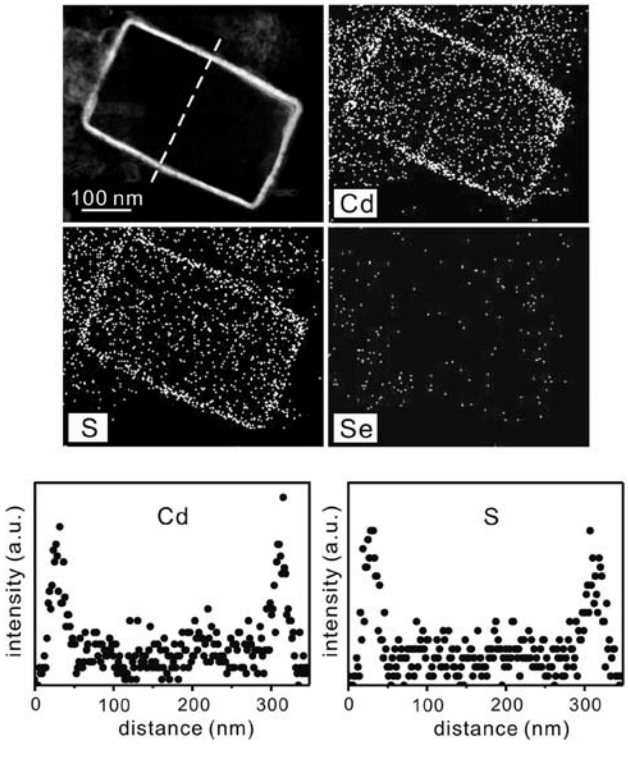

Fig. 2 STEM image and EDX elemental distribution maps of a hollow CdS nanobox and EDX line-scanned elemental intensity profiles along the indicated white dashed line of the hollow CdS nanobox.

The band-edge absorption of hollow CdS nanoboxes, estimated from the reflectance spectrum of Fig. 3A, is at 512 nm (2.42 eV). This is consistent with the direct band gap of CdS(s),[11] as the sizes of our hollow CdS nanoboxes are too big to show the quantum-confinement effect of electronic transition. The emission maximum of hollow CdS nanoboxes in Fig. 3B is at 520 nm. The small Stokes shift of photoluminescence from absorption also supports that Na_2SeO_3 has been eliminated very well. Considerable contamination of CdSe, having a smaller band gap of 1.74 eV, would shift photoluminescence to the red significantly.[12] The resonance Raman spectrum of hollow CdS nanoboxes at room temperature (Fig. 3C) is dominated by overtones of the longitudinal optical phonons.[13,14] Two strong peaks located at 302.4 and 599.4 cm^{-1} are ascribed to the first- (1LO) and the second-order longitudinal optical phonon (2LO) modes of CdS(s),

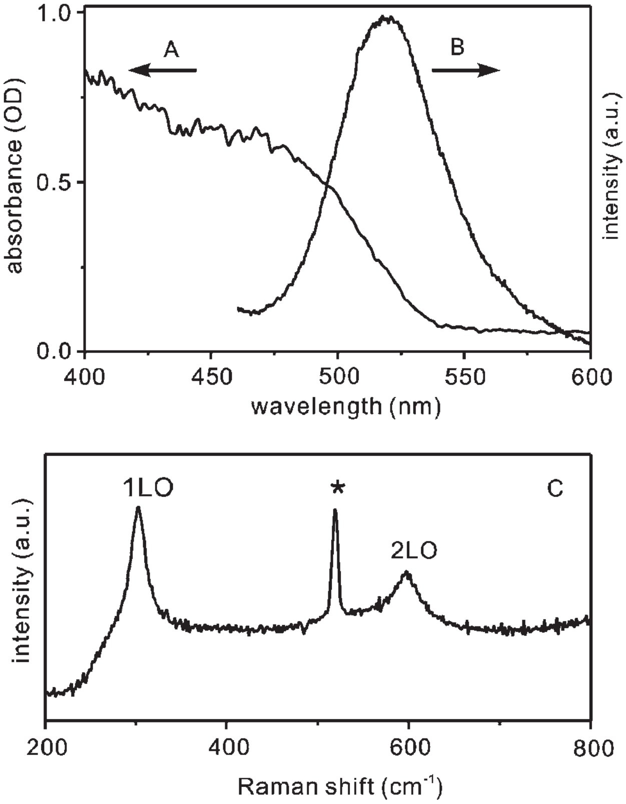

Fig. 3 (A) Reflectance spectrum of hollow CdS nanoboxes in powder, (B) luminescence spectrum of hollow CdS nanoboxes suspended in ethanol with excitation at 355 nm, and (C) resonance Raman spectrum of hollow CdS nanoboxes on a silicon wafer with excitation at 488 nm. The asterisked peak of C arises from silicon wafer scattering.

respectively. The 1LO mode is downshifted by 4.8 cm^{-1} from that of bulk CdS(s).[8] This feature likely arises from the confinement of optical phonons in a hollow CdS nanobox, as described with Fig. 1C and Fig. S1. The ratio of the 2LO mode intensity to the 1LO mode intensity, which reflects exciton–photon coupling, was calculated to be 0.48. This magnitude also supports the above suggestion that optical phonons are confined in the small nanocrystals of a hollow CdS nanobox. The ratio is known to decrease upon a decrease in the particle size of CdS(s).[15]

Fig. 1–3 have shown that hollow CdS nanoboxes having paper-thin walls were synthesized in a Teflon-lined stainless-steel autoclave at 170 °C *via* a facile one-step process. The walls, composed of small wurtzite CdS crystals, have well-defined inner and outer facets since Na_2SeO_3 and ethylenediamine was washed away effectively. Na_2SeO_3(s) has substantial advantages over conventional templates. Although it is so insoluble as to form interior templates in the reaction solvent of ethylenediamine, it can be easily and thoroughly washed away with water after the reaction. Because templates are generated *in situ*, presynthesized hard templates are unnecessary so that hollow nanostructures of extremely high purity can be synthesized readily. Moreover, because the stable structures of Na_2SeO_3(s) are crystalline tetragonal prisms, fabricated hollow CdS nanoboxes have well-defined structures, with well-defined facets in particular, showing specific crystalline morphologies. Two molecules of ethylenediamine (en), introduced for solvent-coordinating molecular templates, chelates Cd^{2+} to form a chemically stable complex of $[Cd(en)_2]^{2+}$. It is generally suggested[14,16] that S^{2-} approaches to the *z*-direction of $[Cd(en)_2]^{2+}$ to form wurtzite CdS(s). In the presence of salt quasitemplates in the organic solvent of ethylenediamine, $[Cd(en)_2]^{2+}$ ionic complexes adsorb preferentially to the ionic surfaces of the Na_2SeO_3 tetragonal nanoprisms and bind S^{2-} ions at a high temperature of 170 °C to form wurtzite CdS(s). Infinite wurtzite CdS nanocrystals grow simultaneously on the exteriors of the quasitemplates to produce Na_2SeO_3@CdS core-shell tetragonal nanoprisms. The subsequent dissolution and removal of the core Na_2SeO_3 with water results in the fabrication of CdS hollow tetragonal nanoboxes. EDX intensity profiles of Na, Se, and O have revealed that Na_2SeO_3 employed for interior salt templates remains somewhat inside incompletely washed CdS hollow nanoboxes. This indeed supports the theory that CdS crystals grow on the surfaces of Na_2SeO_3 nanocrystals.

We have tried the diverse reaction conditions of the S : Se molar ratios, CdO(s) and $CdCl_2$(s) for the cadmium source, reaction temperatures, and an autoclave and a reflux flask for the reaction vessel in order to find the best fabrication method of hollow CdS nanoboxes. The optimal molar ratio of S : Se was found to be about one. When the ratio is below one, hollow CdS nanoboxes form to some degree (shown in Fig. S2 in ESI†). However, CdS nanowires form instead when the ratio is above one. The solvothermal synthesis of CdS nanostructures often results in nanowires.[8,9] CdO(s) instead of $CdCl_2$(s) for the cadmium source also produces CdS nanowires rather than CdS hollow nanoboxes. The reaction was found to proceed facilely at a high temperature of 170 °C in a Teflon-sealed autoclave.

In summary, CdS hollow tetragonal nanoprisms having paper-thin walls of well-defined inner and outer facets were fabricated in a Teflon-sealed autoclave at 170 °C by reacting CdO(s) and $Na_2S{\cdot}9H_2O$(s) and using Na_2SeO_3 for interior salt quasitemplates and ethylenediamine for exterior solvent-coordinating molecular templates. 2-D wurtzite CdS nanocrystals grow on the surfaces of Na_2SeO_3 tetragonal nanoprisms. The dissolution of the core templates in water produces CdS hollow tetragonal nanoboxes having the exterior side lengths of 240, 160, and 160 nm with the wall thickness of 20 nm. The walls of the nanoboxes are composed of infinite wurtzite-crystalline CdS nanocrystals with a mean diameter of 6.6 nm.

This work was supported by the Nano R&D Program (M10703000871-07M0300-87110) and the SRC Program (R11-2007-012-01002-0) of KOSEF. M.R.K. also acknowledges the BK21 Program.

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