JOURNAL OF Materials CHEMISTRY

In situ micelle–template–interface reaction route to CdS nanotubes and nanowires

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Received 2nd July 2002, Accepted 21st August 2002
First published as an Advance Article on the web 16th October 2002

CdS nanotubes and nanowires have been successfully synthesized *via* an *in situ* micelle–template–interface reaction (ISMTIR) route by adjusting the concentration of the surfactant. The whole reaction system is made up of SDS rod-like micelles as the template, CS_2 as the oil phase and sulfur source, NH_3 as the attacking agent and coordination-agent, and $CdCl_2$ in water. It was found that SDS rod-like micelles were excellent templates for the growth of nanotubes and nanowires of small size. Due to a micelle diameter of 10–20 nm, the CdS nanotubes formed have an outer diameter of 15 nm on average and a wall thickness of *ca.* 5 nm, within the exciton diameter of bulk CdS. In particular, the formation of CdS nanowires was thought to occur by a "rolling-broken-growth" (RBG) process, in which the micelles could not support the strain of the CdS produced rolling. Thus, the diameter of as-obtained CdS nanowires was *ca.* 5 nm, within the exciton diameter, too. The UV-vis absorption spectra show the as-obtained CdS nanotubes and nanowires are well quantum-confined. In the future, this method is expected to be used to prepare other metal sulfide nanotubes and nanowires.

Introduction

As we all know, the optical and electronic properties of materials are dependent on both the initial particle sizes and the manner in which they organized. Therefore, controlling the shape of nanostrucutures at the mesoscopic level is one of the most challenging issues presently faced by synthetic chemists. Many scientists have used some synthesis methods not only to prepare the starting particles but also to coax them into the desired nanostructures, including nanorods, nanowires, nanocables, and nanospheres.[1–4] Many studies focused on group II–VI semiconductor materials have been reported[5,6] because of their optical and electronic properties. As a result, many methods have been developed to obtain group II–VI semiconductor materials with all kinds of morphologies and nanostructures. For example, in our group, CdS hollow spheres were prepared *via* an *in situ* source–template–interface reaction route.[7] CdS nanowires with a diameter of 4 nm could be obtained by the molecular scissors method[8] and CdSe/polymer nanocables could be synthesized in a heterogeneous system by γ-irradiation.[3]

The discovery of fullerenes in the mid-1980s opened up a new field in materials research.[9,10] Nanotubes, a special type of fullerenes, are stimulating a great deal of activity owing to their unique characteristics: extraordinary mechanical properties, electrical properties determined by the helicity of the tube, unusual adsorption properties, *etc.*[9,10] Carbon nanotubes were discovered by Iijima in 1992 while examining carbon soot using electron microscopy.[11] Fullerenes and nanotubes have also been produced from BN,[12] WS_2,[13] MoS_2,[14] silica,[15] and vanadium oxide.[16] Recently, Rao and co-workers reported their work on II–VI semiconductor nanotubes and nanowires,[17] in which they obtained both nanotubes and nanowires of CdS and CdSe by using *tert*-octyl-$(OCH_2CH_2)_xOH$, $x = 9$ and 10 (Triton 100-X) or sodium bis(2-ethylhexyl)sulfosuccinate (AOT) as the surfactant. This is the first example of nanotubes of II–VI semiconductors. The wall thickness of the obtained CdS nanotubes and the diameter of the CdS nanowires are about 17 nm and above 40 nm, respectively. It is well known that the exciton diameter of bulk CdS is 6 nm. If the wall thicknesses of nanotubes and the diameters of nanowires can be controlled at this size, they are expected to show obvious quantum-confined effect. Thus, how to control the size of CdS nanotubes and nanowires becomes a challenge to us.

Surfactant-assisted methods have been widely used in the preparation and morphology control of materials. Water–oil system microemulsion solutions are transparent, isotropic liquid media with nanosized water (or oil) droplets that are dispersed in a continuous oil (or water) phase and stabilized by surfactant molecules at the water–oil interface. These surfactant-covered water (or oil) pools offer a unique microenvironment for the formation of nanoparticles. They not only act as microreactors for processing reactions but also inhibit the excess aggregation of particles because the surfactants could absorb on the particle surface when the particle size approaches that of the water (or oil) pool. Therefore, monodispersed particles could be obtained in such a medium.[18] Surfactant could also be used as the structure directing agent to prepare silica particles,[19] silica nanotubes,[15] carbon nanotube/polymer composites,[20] and CdS and CdSe nanorods.[21] On the basis of these previous reports, a new idea that micelles or vesicles can provide microenvironments of small size for the growth of CdS nanotubes and nanowires occurred to us. It is a pity that the sizes of as-prepared products in the literature are often much larger than those of micelles or vesicles (about 10–20 nm) and the length-to-width ratios are not as desired due to the local diffusion. Selecting an appropriate oil solvent as reagent can solve this problem, in which the reaction proceeds absolutely confined in these microenvironments. In the present paper, CdS nanotubes and nanowires with as-desired wall thicknesses or diameters (5 nm) and length-to-width ratios ($\sim$500) were prepared *via* an *in situ* micelle–template–interface reaction (ISMTIR) route.

Experimental

In a typical procedure for the preparation of CdS nanotubes $CdCl_2$(0.57 g, 2.5 mmol) was dissolved in 47 mL distilled water

DOI: 10.1039/b206377h

contained in a beaker. The aqueous ammonia solution (the content of NH_3 was (28 wt%; 1.2 mL, 17.4 mmol) was introduced into the beaker to make Solution A. Octan-1-ol (1.5 mL, 9.5 mmol), CS_2 (0.5 mL, 8.2 mmol), and sodium laurylsulfonate (SDS) (1.25 g, 4.6 mmol) was added to a 100 mL jar. Then Solution A was all introduced into the jar. (The SDS–octan-1-ol–water is formed with a molar ratio of 2 : 1 for octan-1-ol–SDS and a total concentration of 5.0 wt% for amphiphiles. The concentration (98 mmol L^{-1}) of surfactant is nine times the critical micelle concentration (11 mmol L^{-1}).[22]) Then the jar was heated at about 4 °C s^{-1} from 25 to 60 °C, and kept at 60 °C for 3 h. The transparent mixture slowly turned bright yellow. All the steps above were carried out with magnetic stirring. The jar was then cooled to room temperature naturally. The precipitate was filtered off, washed with distilled water and absolute ethanol for several times, and then dried in vacuum at 60 °C for 4 h.

CdS nanowires were prepared by the same procedure except that the surfactant concentration was lower (with 0.6 g SDS as surfactant).

The samples were characterized by X-ray diffraction (XRD) pattern with a Japan Rigaku D/max rA X-ray diffractometer equipped with graphite monochromatized high-intensity Cu-Kα radiation (λ = 1.54178 Å). The field emission scanning electron microscopy (FE-SEM) images were taken on a JEOL JSM-6700F SEM. The transmission electron microscopy (TEM) images and electronic diffraction (ED) patterns were performed with a Hitachi Model H-800 instrument with a tungsten filament, using an accelerating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL-2010 TEM at an acceleration voltage of 200 kV. Thermal analyses (TGA) were performed with a Shimadzu TA-50 thermal analyzer. The samples were heated from room temperature to 300 °C at a rate of 10 °C min^{-1} in a steady flow of dry N_2 gas. Room temperature ultraviolet and visible light (UV-vis) spectra were recorded on a JGNA Specord 200 PC UV-vis spectrophotometer, and ethanol was used as a reference.

Results and discussion

CS_2–water is an interesting oil–water system, in which CS_2 is insoluble in water and can exist as oil droplets in water. It is interesting that when soluble NH_3 is added as the attacking agent and Cd^{2+} ions are introduced into the system, NH_3 can also dissolve in H_2O and coordinate with Cd^{2+} to form $[Cd(NH_3)_4]^{2+}$, so that Cd^{2+}, NH_3 and CS_2 can exist in an O/W heterogeneous system. NH_3 can react with CS_2 *in situ* at the oil-water interface and provide a type of sulfur source for producing CdS *in situ* around the oil droplet.[22,23]

$$2NH_3 + CS_2 \rightarrow NH_4NHCSSH \quad (1)$$

$$Cd^{2+} + NH_4NHCSSH + 2NH_3 \rightarrow CdS\downarrow + NH_4SCN + 2NH_4^{+} \quad (2)$$

It is thought that if we can select a type of surfactant and cosurfactant to form rod-like micelles that can enwrap the CS_2 oil phase to give cylinders, NH_3 and Cd^{2+} will react with CS_2 to produce CdS *in situ* at the surface of the cylinders within the micelles (that is, the interface of micelle–CS_2). When the concentration of the surfactant is ten times the critical micelle concentration, the surfactant will form both hydrophobic and hydrophilic (O/W) rod-like micelles,[24] in which the CS_2 oil phase can be enwrapped to form CS_2 cylinders. Thus due to the concentration difference between the inside (CS_2 oil phase) and outside (water phase) of the rod-like micelles, the Cd^{2+} and NH_3 transfer from the water phase to the surface of the CS_2 cylinders (through the micelles), where they may react with CS_2 to produce CdS *in situ*. It is found that the product of reaction (1) has both hydrophobic and hydrophilic groups, enabling it to bridge the oil phase and the water through the micelles, and the coordination between Cd^{2+} and NH_3 helps transport the Cd^{2+} ions. These two factors also allow the transfer of Cd^{2+} and NH_3 from the water phase to the surface of CS_2 oil phase. As a consequence, the CdS produced will grow and roll around the CS_2 cylinders that are enwrapped in SDS micelles to form CdS tubular shells with CS_2 cylindric cores. When the unreacted CS_2 cylindric cores are evaporated at a temperature above the boiling point of CS_2 and the surfactant is removed by water and ethanol, the CdS tubular shells will be left as nanotubes. From the size of the micelles (10–20 nm), the outer diameters of the nanotubes formed are expected to range from 10 nm to 20 nm and the wall thicknesses should be below the exciton diameter of 6 nm.

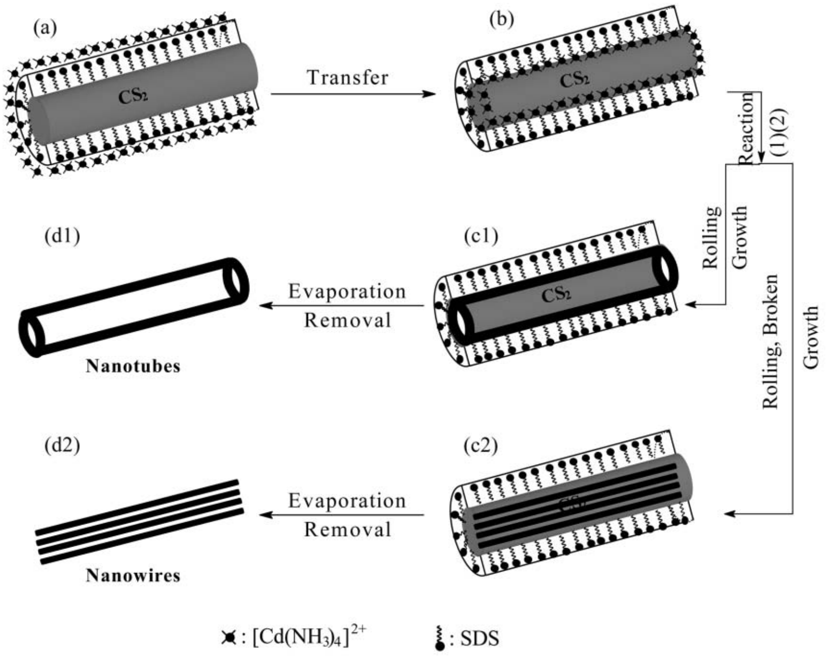
Based on this strategy, we designed an *in situ* micelle–template–interface reaction (ISMTIR) route: for the formation of micelles, we used sodium laurylsulfonate (SDS) as the surfactant and octan-1-ol as cosurfactant to form micelles that could enwrap the CS_2 oil phase as cylinders in the CS_2–water system. To evaporate the CS_2 cores, the reaction temperature was maintained at 60 °C which is above the boiling point of CS_2 (45 °C).[25] The whole process can be described by Scheme 1(a)–(d1).

In the of preparation of CdS nanowires, a new idea occurred to us: it has been reported that CdS lamellae can break into needle-like fragments when the folds in the lamellae agglomerate.[26] Now, it can be imagined that if the SDS cannot support the strain of CdS's rolling to form nanotubes, the growing nanotubes would probably break into nanowires. If the concentration of SDS was lower, the SDS micelles would probably be too loose to support the strain of the rolling. This process can be called "rolling-broken-growth" (RBG), which is described in Scheme 1(a)–(d2). Thus, to obtain CdS nanowires with diameters below 6 nm (similar to the wall thicknesses of the CdS nanotubes), the same process as the one described above was used to prepare nanotubes but with lower surfactant concentration.

Fig. 1 shows the XRD pattern of as-prepared CdS samples. All the peaks of the nanowires in Fig. 1b can be indexed to wurtzite CdS (JCPDS card NO. 41-1049) with cell parameters $a = (4.142 \pm 0.002)$ Å and $c = (6.724 \pm 0.004)$ Å. The breadth of the diffraction peaks is due to the small diameter size (5 nm) of the as-prepared nanowires, which was calculated by Scherrer's equation.[27] The XRD pattern of CdS nanotubes Fig. 1a is also similar to that of wurtzite CdS, except that the relative intensity of the peaks changes a lot. The unusual strong intensity of the (002) peak indicates that there only exists a one-dimensional period along the (002) plane in CdS nanotubes and it belongs to the wurtzite structure with some dislocations, here marked as "w-d phase". The breadth of the peaks may correspond to the small dimension (5 nm) of the tubular wall.

The micrographs of the CdS nanotubes are shown in FE-SEM and TEM images (Fig. 2a and b). From Fig. 2a, one can see that the nanotubes are generally long, with lengths up to 2.5 μm, and the yield of CdS nanotubes is above 95%. Based on the observations from TEM (Fig. 2b), the inner diameters of the nanotubes are *ca.* 5 nm and the outer diameters are 15 nm on average. These sizes are in agreement with those of micelles, indicating the success of our strategy. The strong contrast between the dark edges and the pale center provides evidence for the hollow nature of the nanotubes,[28] and that the walls of the nanotubes are relatively smooth.

Fig. 2b also shows a selected area electronic diffraction (ED) pattern within the wall of the CdS nanotubes. The three brighter dot-rings indicated by arrows correspond to the (100), (110), and (200) diffractions of w-d CdS. So the pattern can be indexed as the [002] diffraction of w-d structure.[29] The result shows that the CdS tubular walls are obviously orientated



Scheme 1 Strategy for the preparation of CdS nanotubes and nanowires. (a) CS_2 is the oil phase contained in rod-like SDS micelles and Cd^{2+} is carried from water to the interface of SDS–water by NH_3. (b) Cd^{2+} transfers to the surface of CS_2 due to the concentration difference. (c1) Releasing Cd^{2+}, NH_3 reacts with CS_2 and Cd^{2+} to produce CdS *in situ* at the surface of CS_2. Then the CdS rolls and grows to form a CdS tubular shell with CS_2 inside the shell. (d1) With unreacted CS_2 evaporating and SDS removed, CdS nanotubes form. (c2) Releasing Cd^{2+}, NH_3 reacts with CS_2 and Cd^{2+} to produce CdS *in situ* at the surface of CS_2. When the CdS rolls, the SDS micelles cannot support the strain, resulting in the breaking of CdS. Then the broken CdS grows into nanowires in the micelles. (d2) By evaporating unreacted CS_2 and removing SDS, CdS nanowires form.

along the (002) plane of w-d CdS. The difference in brightness of the dots on the same ring was due to the rotation of some of the cylinders.[30] The result of energy dispersive X-ray analysis (EDXA) of a nanotube shows that the nanotube consists of CdS, in the S to Cd ratio of 1 : 0.98. Though there is a little inconsistency in this value. it is very close to the stoichiometry of CdS.

The HRTEM image of a nanotube is shown in Fig. 2c. The singular fringe spacing of the CdS nanotube is 3.4 Å, which is nearly consistent with half of the cell parameters of wurtzite CdS (c = 6.7198 Å) and the (002) reflection plane spacing of the w-d CdS in the XRD pattern, indicating that the nanotubes roll along the (002) plane. Fig. 2d shows part of the layer-rolled wall in Fig. 2c at higher magnification (indicated by a box in Fig. 2c), where the different lattice features at the edge and in the center parts indicate a typical multi-walled tubular structure, as reported for multi-walled carbon nanotubes.[31]

The morphology of CdS nanowires is shown in Fig. 3a–d. One can see that the diameter of the nanowires is *ca.* 5 nm and the length is up to 2.5 μm, in agreement with the size of the nanotubes. Moreover, the HRTEM image (inset in Fig. 3d) of a nanowire shows they grow along the (002) plane, in agreement with the growth of the nanotubes. It reveals that the proposal that the rolling and growing CdS nanotubes break into nanowires is reasonable. The discovery of some nanotubes mixed in with the as-prepared CdS nanowires (indicated by an arrow in Fig. 3d) further confirms this conclusion.

As to the growth mechanism of nanotubes, Chopra *et al.*[12] and Falvo *et al.*[32] have speculated in detail about the formation of carbon and BN nanotubes, respectively. In general, the nanoscale rolling behavior has been accompanied by a preferential, three-fold, in-plane orientation, and rolling may occur only when both the nanotubes and the underlying layers have long-range order. Along with the recent discovery of

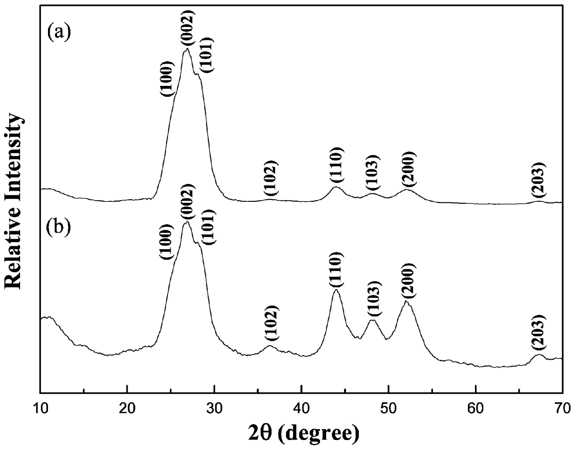


Fig. 1 XRD pattern of (a) the as-prepared CdS nanotubes and (b) the as-prepared nanowires.

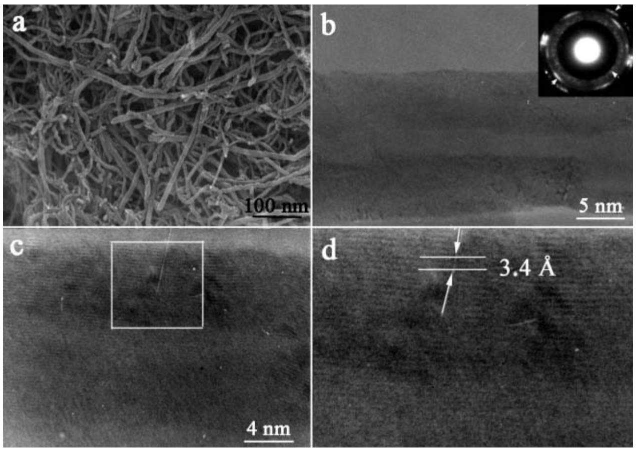


Fig. 2 (a) FE-SEM image of CdS nanotubes; (b) TEM image of a CdS nanotube; (c) HRTEM image of a CdS nanotube; (d) a magnified HRTEM image of the part of Fig. 2c indicated by the box.

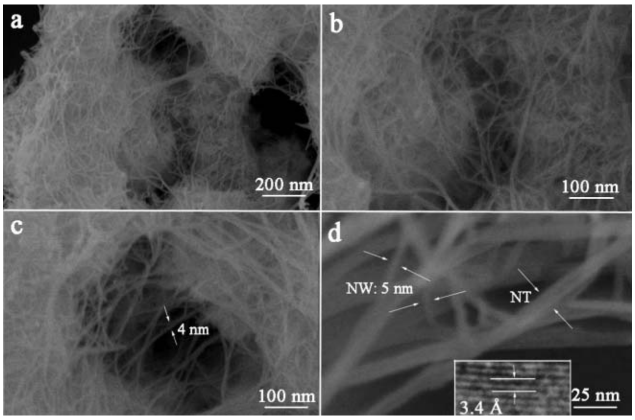


Fig. 3 (a)–(c) FE-SEM images of CdS nanowires; (d) FE-SEM images of CdS nanotubes (NT) with some nanowires (NW) (inset is HRTEM image of a nanowire).

MoS_2 and WS_2 nanotubes,[13,14] this suggests that the tubular structure may be stable for other layered materials. From the structural analysis, we thought that the CdS nanotubes were of the wurtzite structure, in which CdS_4 tetrahedrons stack closely in layers in the (002) direction. However, these layers are tightly bound to each other by chemical bonds, while layered materials are loosely bound by van der Waals forces. Here, the CdS nanotubes are thought to form by rolling the basal planes along the (002) direction into a cylindrical structure, thus destroying the periods of other directions except for the (002) plane and forming the above w-d phase.

However, why should CdS overcome the strain, roll and grow into nanotubes? We speculate that its growth mechanism is similar to that of tubular V_2O_5[33] and SiO_2[34] structures obtained with amines as structure-directing agents or organogels as templates at a low temperature. In the present case, it is obvious that the SDS micelles played a role as template in the CdS's rolling and caused the dislocations in the CdS wurtzite phase and to have only a one-dimensional period. The interface between the SDS micelles and the CS_2 oil phase provided a unique microenvironment for CdS's to roll and grow to form nanotubes, due to its tubular shape and nanoscale size. However, was there still some SDS left in the as-obtained product to keep the tubular shape? The as-obtained nanotubes were studied by thermal analysis (DTA) and no weight loss was found, indicating that the as-obtained nanotube is composed of pure CdS without any remaining SDS. When the temperature was raised to 300 °C, as-obtained w-d CdS were transformed to the sphalerite structure at 300 °C. The phase-transformed product after DTA characterization was studied by TEM. It was found that the nanotubes were all changed into nanoparticles with sizes of *ca.* 5 nm, indicating that the wurtzite phase of CdS with only the (002) period was crucial to the rolling of CdS. The results of the ED pattern and HRTEM image show that the CdS tubular walls have an obvious orientation along the (002) plane. It is concluded from all these results that the period along (002) plane of wurtzite CdS determined the ability of CdS to roll and grow into nanotubes. from the principles of crystal chemistry, sphalerite CdS could not maintain the tubular shape, perhaps because sphalerite CdS does not have a one-dimensional period along the (111) plane (corresponding to the (002) plane of wurtzite phase).

To examine the quantum-confined effect of the products, UV-vis absorption spectra and PL excitation spectra were obtained. The UV-vis absorption spectra (Fig. 4) show that there is an obvious absorption peak due to CdS nanotubes at 459 nm, which is assigned to the first excitonic peak of CdS in the absorption spectrum. As expected, there is blue shift between the result and the reported data for bulk CdS,[35] due to the small dimension of the CdS tubular wall. Employing the Brus and Henglein formula,[36,37] the small average size of the wall is calculated to be *ca.* 5 nm, which is in close agreement with the sizes observed in the TEM analysis. The larger difference between the peak and the onset, which might be related to the width of particle size distribution, is characteristic of the difference between the length and diameter of the nanotubes. It is also found that there is an obvious absorption peak for the as-obtained CdS nanowires at 452 nm in the UV-vis absorption spectra, from which the diameter of the nanowires is determined to be *ca.* 5 nm. These features indicate the as-obtained CdS nanotubes and nanowires are well quantum-confined.

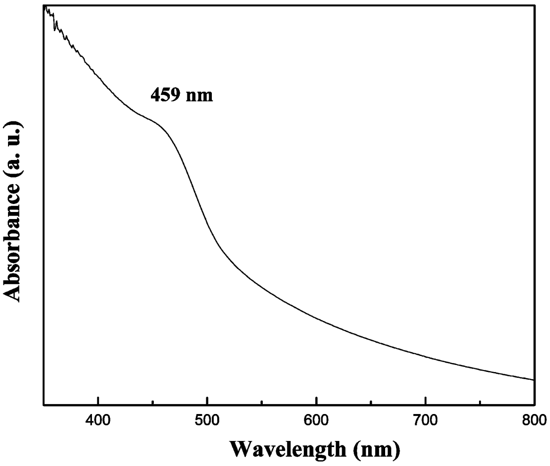


Fig. 4 UV-vis absorption spectrum of CdS nanotubes.

Conclusion

CdS nanotubes and nanowires have been successfully synthesized *via* an *in situ* micelle–template–interface reaction (ISMTIR) route by adjusting the concentration of surfactant. The whole reaction system is made up of SDS rod-like micelles as the template, CS_2 as the oil phase and sulfur source, NH_3 as the attacking and coordination agent, and $CdCl_2$ in water. It was found that SDS rod-like micelles were excellent templates for the growth of nanotubes and nanowires of small size. Due to a diameter of 10–20 nm of the micelles, the CdS nanotubes formed have outer diameters of 15 nm on average and wall thicknesses of *ca.* 5 nm, within the exciton diameter of bulk CdS. In particular, the formation of CdS nanowires was thought to occur through a "rolling–broken–growth" (RBG) process, in which the micelles could not support the strain when the CdS produced rolls. Thus, the diameter of as-obtained CdS nanowires was *ca.* 5 nm, within the exciton diameter, too. The UV-vis absorption spectra showed the as-obtained CdS nanotubes and nanowires were well quantum-confined. In the future, it is expected that this method could be used to prepare other metal sulfide nanotubes and nanowires.

Acknowledgements

Financial support from the National Natural Science Foundation of China and the Chinese Ministry of Education is gratefully acknowledged. The authors thank Professor Shuyuan Zhang for technical assistance in HRTEM experiments and Professor Guien Zhou for his helpful suggestions for our paper.

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