

ZnS–Zn nanocables and ZnS nanotubes

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ZnS–Zn nanocables and ZnS nanotubes have been synthesized by a thermochemical process in a simple and safe way. The as-prepared nanocables consist of a single crystal Zn core with a diameter of 20 nm and a polycrystalline ZnS sheath with a thickness of 8 nm. The evaporation of the Zn core leads to the formation of ZnS nanotubes.

One-dimensional (1D) nanoscale materials are of special interest in the assembly of nanodevices.^{1–4} Various nanodevices including logic circuits,^{1,2} nanosensors, nanolasers,³ and nanothermometers⁴ have been assembled by using 1D nanoscale materials. The recent progress in the assembly of nanodevices has stimulated intensive studies on the synthesis of 1D nanoscale materials in various forms such as nanotubes, nanowires, nanobelts, and nanocables *etc.* Nanocables are an important category of 1D nanoscale materials due to their special structures. The core-shell-shaped nanocable is the assembly of a nanowire and a nanotube and thus may lead to novel properties and special applications in nanoelectronics and photonics.

Zinc sulfide is a II–IV semiconductor with a band gap energy of 3.6 eV. Zinc sulfide as a traditional phosphor has been widely used in the fields of displays, sensors and lasers.⁵ Since the initial report of Bhargava⁶ that high luminescence quantum efficiency were obtained from manganese-doped ZnS nanocrystals, many attempts have been made to dope ZnS nanoparticles with various rare earth and transition metal ions, from which strong and stable visible-light emissions with different colors have been achieved.^{6,7} Zinc sulfide is also used as catalysts for the photooxidation and photoreduction of organic groups.^{8,9} Almost all of these studies are focused on ZnS nanocrystals but only a few reports can be found on 1D nanoscale ZnS. ZnS nanowires have been obtained by a template method and a catalyst-assisted thermal process.^{10,11} Recently, ZnO–ZnS nanocables have been prepared by the reaction of ZnO belts with H₂S.¹² We report herein the synthesis of ZnS–Zn nanocables and ZnS nanotubes *via* a thermochemistry process from ZnS powders. The as-prepared ZnS–Zn nanocables have potential applications in the production of electroluminescent nanodevices by using the metal core as an electrode and the ZnS shell as a phosphor.^{13,14} The as-prepared ZnS nanotubes may be used as catalysts with high surface. Moreover, this report may give a general indication towards preparation of other sulfide nanocables and nanotubes.

The character of the present fabrication process is simple and safe without utilizing sulfur, H₂S, and H₂ gases. In a typical synthesis, commercial ZnS powders were used as precursors. The precursors were put into a graphite crucible, and the crucible was placed above the other one that contains graphite powders and fibers. The two crucibles were enclosed into a graphite susceptor, which was put in the center of a RF induction furnace with a flowing N₂ atmosphere (1.5 l min⁻¹). The positions of both crucibles were adjusted so that the graphite powders and ZnS powders were heated at 1500–1600 °C and 1250 °C, respectively. The N₂/H₂O stream (obtained from bubbling N₂ through distilled water) managed to pass through the graphite powders, where CO and H₂ gases were generated *in situ* *via* the reaction of graphite and water. Then the

N₂ stream together with the CO and H₂ gases passed through zinc sulfide powders. The products were collected on the quartz wall of the furnace in temperatures ranging from 400 to 600 °C. The as-prepared samples were characterized using a JEM-3000F (JEOL) high resolution transmission field emission electron microscopy (HRTEM) operated at 300 kV, which was attached with an X-ray energy dispersive spectrometer.

The morphology of the ZnS–Zn nanocables is shown in Fig. 1a. The core of the cable has a diameter of *ca.* 25 nm and the sheath has a thickness of *ca.* 8 nm. The ED pattern taken from the area “m” in Fig. 1a shows that both diffraction dots and rings can be seen from the inset in Fig. 1b. The diffraction dots can be indexed as a single hexagonal phase with lattice constants of *a* = 0.26 nm and *c* = 0.49 nm recorded from the [001] zone axis, which is consistent with the ideal values of hexagonal Zn phase (JCPDS Card: 04–0831). The diffraction rings from the center to the outside can be indexed as the reflections of the (100), (110), and (103) planes of wurtzite ZnS polycrystallines (JCPDS card 36–1450). The correspondent HRTEM image of the nanocable as shown in Fig. 1b reveals that the core has single crystal fringes of Zn metal while the sheath has polycrystalline fringes of the zinc sulfide. That is to say, the nanocable is made up of the Zn core and the ZnS sheath. The

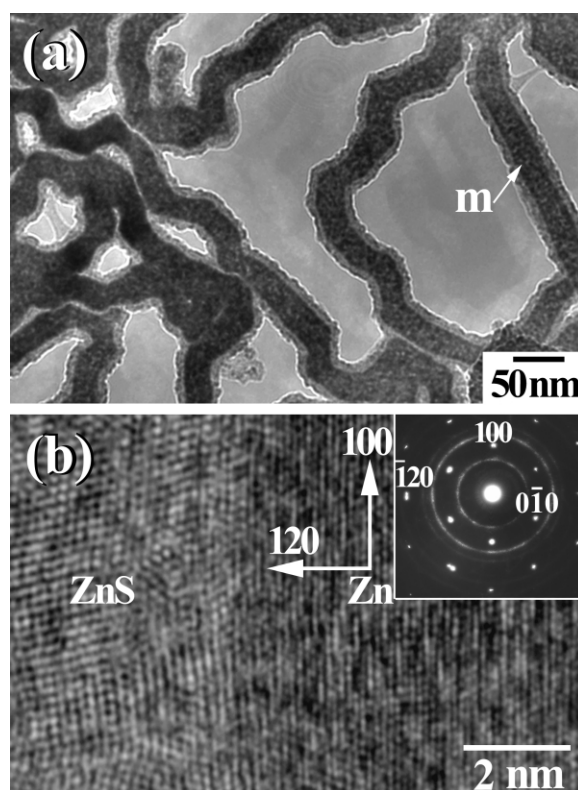


Fig. 1 Morphologies of ZnS–Zn nanocables. (a) TEM image of ZnS–Zn nanocables, the dark core is Zn and the gray shell is ZnS sheath. (b) HRTEM image of ZnS–Zn nanocables taken from part “m” in (a), the inset is the corresponding ED pattern taken from the [001] zone of the Zn core.

EDS analysis confirms that the nanocables are composed of the Zn and S.

The morphology of ZnS nanotubes is presented in Fig. 2a. The tubes have a diameter of *ca.* 35 nm and have a wall thickness of *ca.* 7 nm. The ED pattern of the nanotubes is shown in the inset of Fig. 2b. The diffraction rings are consistent with the diffraction lines of the hexagonal ZnS phase (JCPDS card 36–1450). The diffraction rings indicate that the ZnS nanotubes have a polycrystalline structure as further confirmed by the HRTEM image in Fig. 2b. The EDS analysis (inset in Fig. 2a) confirms that the nanobelts are composed of Zn and S. The carbon and copper signals should be contributions of the copper grid and the carbon film on the grid.

The formation mechanism of ZnS–Zn nanocables is proposed in three basic steps: (1) ZnS powders were evaporated and reduced into Zn vapors at high temperature regions; (2) the Zn vapors were transferred to the low temperature region and were nucleated to form Zn nanowires; (3) ZnS sheaths were deposited on the surface of Zn nanowires. The overall process of the formation of ZnS–Zn nanocables involves the following set of reactions. The Gibbs free energy values of these reactions were estimated based on thermodynamic properties,¹⁵ which are listed in brackets following the reaction equations.

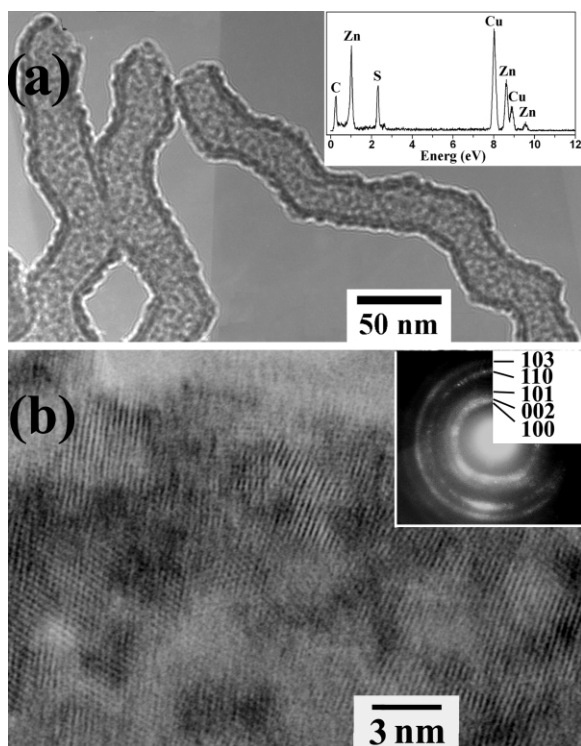
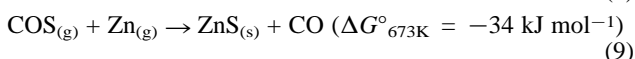
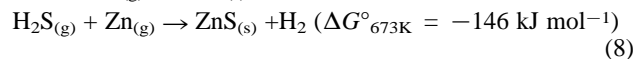
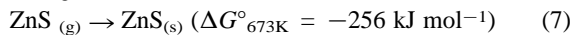
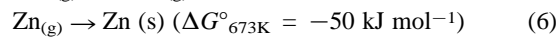
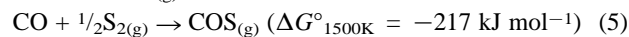
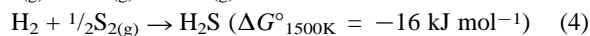
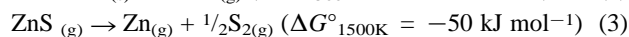
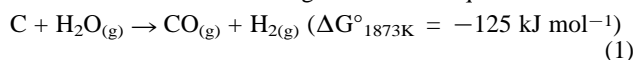


Fig. 2 Morphologies of ZnS nanotubes. (a) TEM image of ZnS nanotubes, the inset is the EDS spectrum of ZnS nanotubes. (b) HRTEM image of ZnS nanotubes, the inset is the ED pattern of ZnS nanotubes.

The reaction of C and H₂O produces CO and H₂, which provides a reductive atmosphere. At high temperature regions, ZnS powders may evaporate spontaneously into ZnS vapors due to the negative Gibbs free energy. The reaction for ZnS to decompose into Zn and S₂ vapors is also a thermodynamically spontaneous process since the Gibbs free energy is negative. S₂ vapors may be eliminated *via* the reactions with H₂ and CO that were carried by the N₂-flow. At low temperature regions, Zn vapors were solidified to form Zn nanowires, H₂S and COS gases were carried away by the N₂-flow. Zn vapors may partially react with H₂S and COS gases forming ZnS clusters *via* reactions (8) and (9). The ZnS clusters may coat on the surface of Zn nanowires forming a sheath. ZnS–Zn nanocables were obtained at a temperature region around 400 °C. ZnS nanotubes were found in the temperature range from 500 to 600 °C, which were formed when the Zn cores of ZnS–Zn nanocables were evaporated while the ZnS sheaths remained. The proposal is supported by the evidence that the morphologies of ZnS sheaths are very similar to those of ZnS nanotubes as can be seen in Fig. 1a and Fig. 2a.

ZnS was easily oxidized into ZnO at high temperatures even in an inert atmosphere with traces of oxygen, while it could be reduced into Zn with reductive agents.^{16,17} In this work, the atmosphere was controlled by mixing N₂ with the reductive agents of the CO and H₂ which were produced *in situ* from the reaction of C powders and H₂O steams.

In summary, ZnS–Zn nanocables and ZnS nanotubes have been synthesized *via* the thermochemical method in a simple and safe way. This approach has effectively avoided the oxidation of ZnS and controlled the reduction of ZnS leading to the formation of ZnS–Zn nanocables and ZnS nanotubes. The as-prepared 1D nanoscale ZnS materials may have potential applications in nanoelectronics and photonics. This method may be used to prepare other sulfides materials.

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