Growth and properties of ZnO/ZnS core/shell nanostructures

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Abstract. ZnO nanorods were prepared in aqueous solution of zinc acetate dihydrate and hexamethylenetetramine with two-step methods. ZnO/ZnS core/shell structures were prepared by immersing ZnO nanorods in Na₂S and nitrate hexahydrate aqueous solution alternately for different cycles. The structures were characterized by x-ray diffraction, scanning electron microscopy, high resolution transmission electron microscopy and spectrofluorometer. The results show that ZnO/ZnS nanocables formed by one cycle and then hollows appear in the core region. With increasing shell growth cycle, ZnO core dissolved completely in some region, and quasiperiodic distribution of ZnO and hollows in ZnS tubes were observed. Photoluminescence of ZnO/ZnS core/shell structures was found intense than that of pure ZnO nanorods.

1. Introduction
Surface modification has been recognized as one of the most advanced and intriguing methods to build tailored nanostructure materials effectively and reliably [1]. Core–shell composite materials have attracted a great deal of interest due to their versatile structures and properties for many significant applications in optics, biology and catalysts. ZnO is a wide gap semiconductor with bandgap of 3.3 eV at room temperature and its nanostructure arrays have been studied extensively in the last decades due to their unique nanoscale electronic and optoelectronic properties used in electronic and optoelectronic devices and gas sensors [2]. Surface modification of a semiconductor with semiconductors of wider band-gap has been recognized as one of the most advanced and intriguing methods to improve the luminescence properties. ZnS is a wide band gap semiconductor with bandgap of 3.7 eV and it is a well-known luminescence material having prominent applications in sensors and lasers [3]. Many researchers have studied ZnO/ZnS core/shell nanostructures. Square nanocables, rod nanocables of ZnO/ZnS core/shell structures synthesized by converting ZnO to ZnS have been reported [4-9]. ZnS nanotubes and ZnO/ZnS nanotubes were observed during sulfuration of ZnO nanorods. However, there are few reports on quasiperiodic structure formation during sulfuration of ZnO nanorods.

In this work, ZnO nanorods were growth in aqueous solution of zinc acetate dihydrate and hexamethylenetetramine with two-step method. ZnO/ZnS core/shell structures were prepared by immersing ZnO nanorods in Na₂S and nitrate hexahydrate aqueous solution alternately. Quasiperiodic distribution of ZnO and hollows in ZnS tube was reported for the first time. Nanostructure properties were measure and the formation of the order structure was discussed.
2. Experiments
Zinc acetate dihydrate, zinc nitrate hexahydrate, hexamethylenetetramine (HMT) and sodium sulfide were selected to synthesize ZnO/ZnS core/shell nanostructures. Glass plates were used as substrates. The substrates were cleaned ultrasonically in acetone, ethanol, and deionized water in order. Growth of ZnO nanorods were performed by two-steps method. First ZnO seeds were introduced by annealing methods [10]. Then ZnO nanorods were grown at 90°C in aqueous solution of 0.005mol/L zinc acetate dihydrate and hexamethylenetetramine (HMT) for 2h. ZnO/ZnS core/shell structures were prepared by a self-assembling route [5]. Typically ZnO nanorods were immersed at 60°C in 0.16 mol/L Na$_2$S aqueous solution for 2h and then in 0.16 mol/L nitrate hexahydrate aqueous solution for 1h for ZnS growth. To modulate the shell thickness, growth of ZnS was prepared by repeating ZnS shell growth for 1, 2 and 3 cycles and the samples were denoted as ZnO/ZnS1, ZnO/ZnS2, ZnO/ZnS3 relatively.

The as-prepared nanostructures were analyzed using x-ray diffraction (SHIMADZU XRD-6000) with a Cu Ka radiation. The morphology and dimension of the nanocrystal were observed by scanning electron microscopy (SEM, HITACHI S-4800) and high resolution transmission electron microscopy (HRTEM, JEOL Jem-2010). Room temperature photoluminescence spectra (PL) were recorded by a spectrofluorometer (Fluorolog-Tar-3) excited with 320nm light.

3. Results and discussions
Figure 1 shows the XRD pattern of the ZnO and ZnO/ZnS core/shell nanostructures. There are dominant peaks at 34.5° which belongs to the (002) diffraction of wurtzite structured ZnO. The strong (002) diffraction indicates that nanostructures grow preferential along c-axis orientation. For ZnO/ZnS core/shell samples, additional diffraction peaks at about 28.8° can be observed, which corresponds to diffraction from (111) planes of zinc-blend structured ZnS. This indicates that ZnS layer formed. The morphology of ZnO and ZnO/ZnS core/shell nanostructures observed by SEM is shown in Figure 2. ZnO nanorods are inclined to be vertical on the substrates. Obvious core/shell junction can be seen in the samples of ZnO/ZnS2 and ZnO/ZnS3. Core/shell junctions can not be seen clearly in ZnO/ZnS1 sample, but some fingers on the top surface of the rods can be observed. TEM images of ZnO and ZnO/ZnS nanostructures are shown Figure 3. No cavities are observed in ZnO nanorods (Figure 3(a)). Nanocables with solid cores form in the sample with the shell grown for one cycle and fingers stand on the top of the side wall can also be seen(Figure 3(b)). With an increase in growth cycle of ZnS shell, hollows form in the core region (Figure3(c)). With the further increase in growth cycle of ZnS shell, ZnO core dissolved completely in some region. ZnO and hollows distribute alternatively in ZnS tube (fig3(d)) and show a quasiperiodical distribution (fig.3(d)).

![Figure 1. XRD of ZnO and ZnO/ZnS nanostructure](image1)

![Figure 2. SEM images of (a) ZnO and (b)ZnO/ZnS1 (c) ZnO/ZnS2 (d) ZnO/ZnS3 grown on glass](image2)
To study the structures of the fingers and the core/shell structure with periodically distributed hollows, the high-resolution TEM image and a selected area electron diffraction pattern taken from the fingers and from a cable region (denoted as S) are shown in fig.4 and fig.5 separately. The finger is tube-like and composed of nanoparticles. The nanoparticles are inclined to arrange orientationally. The spacing between adjacent lattice planes in fig.4 is about 0.31 nm, which equals to the distance between two (111) planes in zinc-blend structured ZnS. The electron select area diffraction pattern of the finger is a set of rings, which is consistent very well with that of zinc-blend structured ZnS. All this indicate that the particles have zinc-blend structure.

Figure 3 TEM images of (a)ZnO and (b)ZnO/ZnS1 (c) ZnO/ZnS2 (d) ZnO/ZnS3 grown on glass.

Figure 4 (a) HRTEM images and (b) SAD pattern of the finger observed in figure 3b
It can be seen from Fig. 5(a) that the conjunction of the core and shell is compact. The nanocable has a single crystal ZnO core. The spacing between adjacent lattice planes (denoted as A) is about 0.52 nm, which corresponds to the distance between two (001) planes in wurtzite structured ZnO. At the interface of core and shell (B region), TRTEM image is different from that of ZnO core. The space is about 2.2 nm which corresponds to the distance between two (102) planes in wurtzite structured ZnS. Nanoparticles are observed at the region farther from the interface. The spacing between adjacent lattice planes (denoted as C) is about 0.31 nm which corresponds to the distance between two (111) planes in zinc-blend structured ZnS. The select area diffraction of the cable shown in Fig. 5(b) displays a spotted pattern and a set of ring diffraction pattern. The spots correspond to diffraction of ZnO with [0 1 1 2] zone axis. The rings are diffraction of zinc-blend structured ZnS which is similar to that observed in Fig. 4(b). From figure 4 and 5 we can deduce that a transitional thin layer of wurtzite ZnS forms between ZnO core and zinc-blend structured ZnS nanoparticle shell. Wang et al. [4] and Yan et al. [12] also observed zinc-blend structured ZnS formation in ZnO/ZnS nanocables. The formation of zinc-blend structured ZnS is due to the low growth temperature.

Hollows are observed in ZnO/ZnS2 and ZnO/ZnS3 samples shown in Fig. 3 (c) and (d). Ge et al. [13] observed the formation of tube-like ZnS crystals during conversion from ZnO crystals to ZnS. They attributed tube-like structure to the ion exchange reaction and the diffusion between zinc and sulfide ions. Wang et al. [9] studied the conversion from ZnO crystals to ZnS. They proposed that the conversion from ZnO to ZnS took place on the outer surface of ZnO columns and continued across the side wall. Then the top surface was broken and ZnO dissolved in solution and reacted with S precursor inside and outside the arrayed structures. The newly formed zinc sulfide inside the surface of arrayed columns prevented the diffusion of zinc ions and the remained zinc oxide crystals were sulfurred in situ into zinc sulfide. Tube-like fingers stand on the surface wall are observed in Fig. 3(b) and Fig. 3(c). This suggests that formation mode of ZnS in this work is different from that proposed by Wang et al. Formation of the fingers indicates that ZnS grows preferentially along the side wall direction. Zn ions come from ZnO core during sulfuration. ZnS forms at the surface and wall initially. With an increase in growth time or growth cycle, the formed ZnS layer on the side wall would prevent Zn ions from diffusing out the wall. Then Zn ions diffuse to the top surface along the interface of the core and shell and supply Zn ions for finger growth. Then fingers joint together and supply as additional wall. Hollows would form due to the out diffusion of Zn ions from the rods. Self-organization of the quasiperiodic distribution hollows may be due to the compensation of Zn ions diffusion from different regions along the interface.

The PL spectra of ZnO nanorods and ZnO/ZnS nanostructures are shown Fig. 6. Both ZnO and ZnO/ZnS nanostructures have strong emission around 400 nm. ZnO bandgap is 3.3 eV and ZnS
badgap is 3.7 eV. The emission centered at 400 nm is corresponding to ZnO band edge emission. The stronger emission of ZnO/ZnS nanostructures indicates that growth of ZnS on ZnO nanorods will enhance ZnO nanostructure band edge emission.

![Figure 6 PL spectra of ZnO and ZnO/ZnS nanostructures](image)

4. Conclusions

ZnO/ZnS core/shell nanostructures have been synthesized from ZnO nanorods by a chemical route. ZnO core is wurtzite structured single crystal and ZnS shell consists of nanoparticles with zinc-blend structure. Thin layer of wurtzite structured ZnS forms at the interface. Nanocables form when ZnS shell is grown for one cycle. With an increase in shell growth cycle, hollows form in the core region. As the growth cycle of ZnS shell increases, ZnO core dissolved completely in some region, and ZnO and hollow alternately distribute in ZnS nanotubes. Photoluminescence of ZnO/ZnS core/shell is intense than that of pure ZnO nanorods.

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References

[1] Gao T, Li Q H and Wang T. H. 2005 *Chem. Mater.* **17**, 887
[2] Wang Z L, 2007 *Materials Today* **10**, 20
[3] Zhu Y, Bando Y, Xue D and Golberg D 2003 *J. Am. Chem. Soc.* **125**, 16196.
[4] Wang D Y, Gao P X, Li J, Summers C J and Wang Z L 2002 *Adv. Mater.* **14**, 1732.
[5] Li J H, Zhao D X, Meng X Q, Zhang Z Z, Zhang J Y, Shen D Z, Lu YM and Fan X W 2006 *J. Phys. Chem. B* **110**, 14685
[6] Shao H F, Qian X F and Huang B C 2007 *Mater. Lett.* **61**, 3639
[7] Zhang H, Yang D R, Ma X Y and Que D L 2005 *Nanotechnology* **16**, 2721.
[8] Sun C W, Jeong J S and Lee J Y 2006 *J. Crys. Growth* **294**, 162
[9] Wang Z, Qian X F, Li Y, Yin J and Zhu Z K 2005 *J. Solid State Chem.* **178**, 1589
[10] Greene L E, Law M, Tan D H, Montano M, Goldberger J, Somorjai G and Yang P D 2005 *Nano Lett.* **5**, 1231
[11] Li Q C, Kumar V, Li Y, Zhang H, Marks T J, and Chang R. P H 2005 *Chem. Mater.* **17**, 1001
[12] Yan C L and Xue D F 2006 *J. Phys. Chem. B* **110**, 25850
[13] Ge J P and Li Y D 2004 *Adv. Funct. Mater.* **14**, 157.
[14] Strite S and Morkoc H 1992 *J. Vac. Sci. Technol. B* **10**, 1237