



Synthesis and Characterization of Taper-Like ZnS Nanostructure and its Photoluminescence

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We report the synthesis and characterization of ZnS nanostructures, which were grown by thermal evaporation of the ZnS powders at high temperature using iron network as the collection substrate. Scanning electron microscopy investigations show that the products present taper-like morphologies. Transmission electron microscopy studies indicate that the ZnS nanostructures are well crystallized. The formation mechanism of the novel nanostructure is discussed on the basis of the experimental results. The nanostructure is formed due to a fast growth of ZnS nanowire along [0001] and the subsequent "epitaxial" radial growth of the ZnS nanocone along the six (01-10) surfaces around the nanowire. A strong room-temperature photoluminescence in ZnS nanostructures has also been demonstrated.

Key Words: ZnS, Microstructure, Growth mechanism, Photoluminescence.

INTRODUCTION

Since the discovery of carbon nanotube in the 1990, nanostructures and nanomaterials have attracted much interest, especially semiconductor nanowires, nanobelts and nanotubes, due to their potential applications as building blocks for the fabrication of nanodevices. Recently, great efforts have been made to synthesize semiconductor nanostructures and many novel nanostructures have been synthesized, such as nanorings^{1,2}, nanonails³, zigzag nanostructures⁴ and tetrapod nanostructures⁵⁻⁷, etc.

ZnS, an important II-VI semiconductor, has attracted considerable attention due to its applications in flat-panel displays, electroluminescent devices, infrared windows, sensors^{8,9} and lasers^{10,11}. Various techniques have been used to prepare ZnS nanostructures, such as laser vaporization, pyrolysis, physical vapour deposition, chemical vapour deposition (CVD) and soft chemical method¹²⁻¹⁶. It had been demonstrated that the morphologies of the products can be well controlled by the collection substrate. Various substrates such as silicon and sapphire wafers were used to synthesize ZnS nanostructures. Several ZnS nanostructures, including nanowires¹⁷ nanobelts/nanoribbons^{18,19}, nanosaws²⁰ nanocables²¹ and tetrapod structure²² have been reported. However using other materials as substrate remains a significant challenge. In present study, we report the growth of aligned ZnS nanocones by the evaporation of ZnS powder using iron network as collection substrate. The structures of ZnS nanocones have been characterized with

TEM and HRTEM. The probable nucleation and growth mechanisms of ZnO nanostructure were discussed. It is anticipated that these novel structures will have some unique application in nanophotonics.

EXPERIMENTAL

ZnS nanostructures were synthesized *via* a simple thermal evaporation method in a conventional furnace with a horizontal quartz tube (the inner diameter of quartz tube is 2 cm), commercial ZnS powder was put into the center of the quartz tube without any wrap. Iron network with the diameter about 50 microns was placed downstream in the quartz tube acting as the deposition substrate for the material growth. The quartz tube was purged with high-purity nitrogen (200 sccm) for 15 min to eliminate oxygen before heating, then the quartz tube was put into the furnace and heated to 1000 °C with the speed 10 °C/min. During the whole process, synthesis was carried out under a constant nitrogen flow of 50 sccm. After 0.5 h reaction, large amount of white powder was observed on the iron net surface at the downstream of the quartz tube. We collected the white powder and studied its properties. Morphology and crystal structure of the as-prepared samples were characterized by X-ray powder diffraction (XRD, ARL, X'TRA), scanning electron microscope (SEM FEI, XL-30), high resolution transmission electron microscope (HRTEM, FEI, Tecnai F20 equipped with super-twin holder). Chemical composition of the as-prepared samples was obtained using an energy-dispersive spectrometer (EDS, EDAX, USA). The

photoluminescence spectrum was obtained at room temperature with excitation wavelength of 325 nm.

RESULTS AND DISCUSSION

XRD technique was used to detect the phase and impurity of the ZnS nanostructure. Fig. 1 shows the XRD pattern of the products removed from the iron network substrate. All the diffraction peaks are clearly distinguishable and can be perfectly indexed to the wurtzite ZnS (JPCDS Card: 79-2204) with lattice constant $a = 0.3822$ nm and $c = 0.6260$ nm. Because no diffraction peaks due to other crystals are present in the XRD pattern, we conclude that ZnS nanocrystals formed on the iron network substrate.

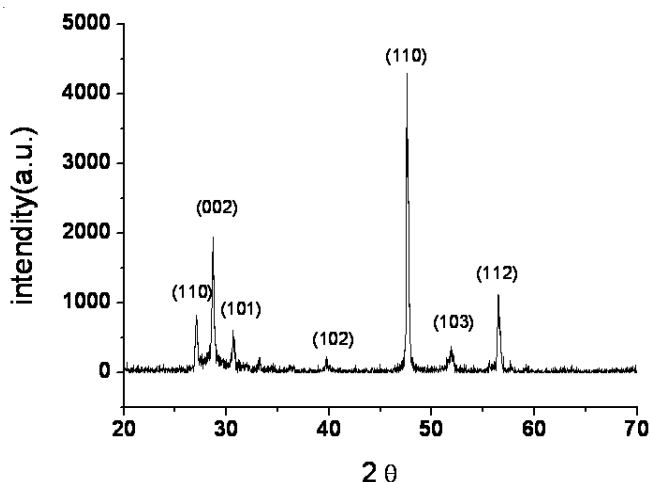


Fig. 1. XRD of the ZnS taper-like nanostructure

Fig. 2 (a) is a typical SEM image of the as-synthesized taper-like ZnS nanostructure, which reveals that the products in a high yield. Fig. 2(b) is a low magnification image of a single taper-like ZnS nanostructure, which shows that the taper-shaped ZnS nanostructure with the max diameter about 2μ and the length is about 4μ aligned along a ZnS wire, the distance between the two nanotaper is 4μ . Fig. 2(c) is a high magnification image of the area as marked in Fig. 2(b), three facets can be seen from the side view of the taper, indicating that the taper is a six-edge pyramid. The diameter of the wire is 350 ± 10 nanometers.

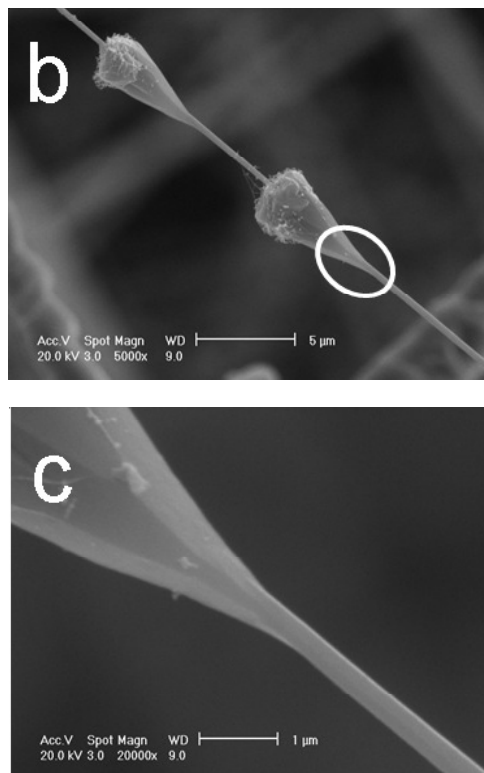
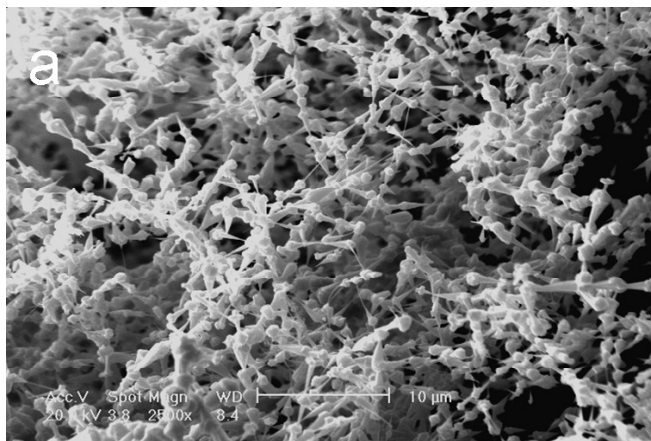


Fig. 2. (a) Large amount of taper-like ZnS nanostructure grown on iron net; (b-c) ZnS taper-like nanostructure with larger magnification

TEM was explored to study its microstructure. Fig. 3(a) shows a typical TEM image of a taper-like ZnS nanostructure and Fig. 3(b) is the corresponding selected area electron diffraction (SAED) pattern. No split of the diffraction spots has been found here indicating that the nanowire is a single crystal. No matter the size of the taper-like ZnS nanostructures are, the recorded SAED pattern confirmed that they are all of wurtzite structure and grow along the c -axis direction. Fig. 3(c) is a high resolution TEM image taken from the central part of the taper-like nanostructure, which shows perfect lattice structure. The lattice spacings are 0.620 and 0.331 nm, corresponding to the separation between two (0001) lattice planes and two (2-1-10) lattice planes of hexagonal ZnS, respectively. The fastest growth direction of taper-like ZnS is [0001] direction. The energy dispersive X-ray spectrum (EDX) shows that the product is composed of S and Zn with atomic ratio is 48.60%:51.40%.

Photoluminescence results taken from the products are shown in Fig. 4. It can be seen that the taper-like ZnS showed a stable and strong green emission band centered at about 530 nm. For fully understanding the photoluminescence mechanism, the peak is deconvoluted into peak 1 at about 486 nm and peak 2 at about 544 nm by best fitting with Gaussian function. Recent reports indicated that transitional metal ion doped ZnS nanocrystals could show visible-region emission from blue to green²³. For example, Yang *et al.*²⁴ have reported that the emission band of Cu^{2+} and Cd^{2+} doped ZnS nanocrystal is 544 nm. Yang *et al.*²⁵ observed that the emission band of Pb doped ZnS nanocrystal is at 480 nm. In general, these transitional metal ion in ZnS nanocrystal act as the luminescence centers. In present experiment, iron network was used as collecting

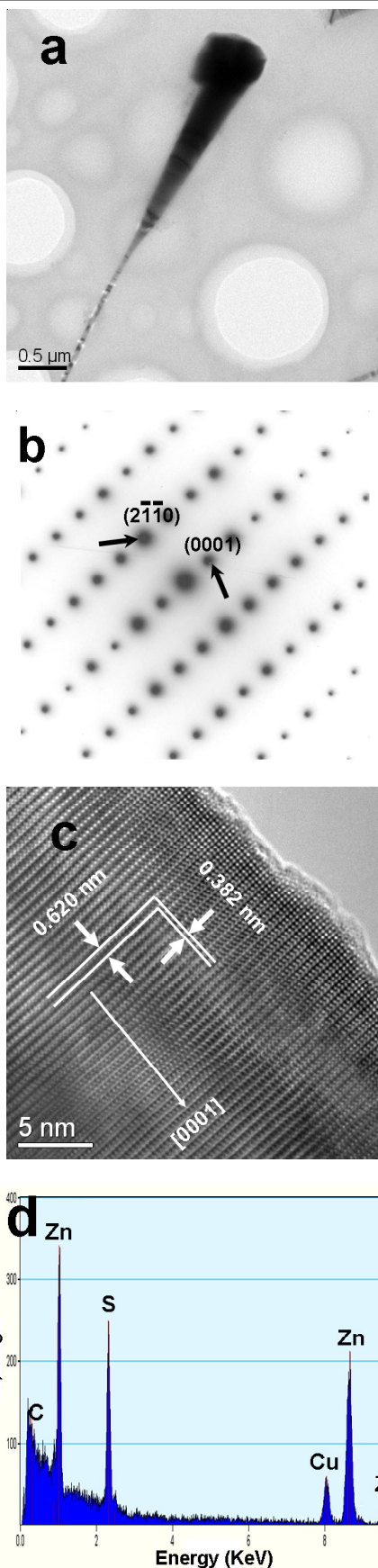


Fig. 3. (a) TEM image of a single taper-like ZnS nanostructure; (b) corresponding ED patterns; (c) corresponding high resolution TEM image; (d) EDX spectrum of the taper-like ZnS nanostructure, the Cu and C signal comes from the TEM grid used for supporting the sample

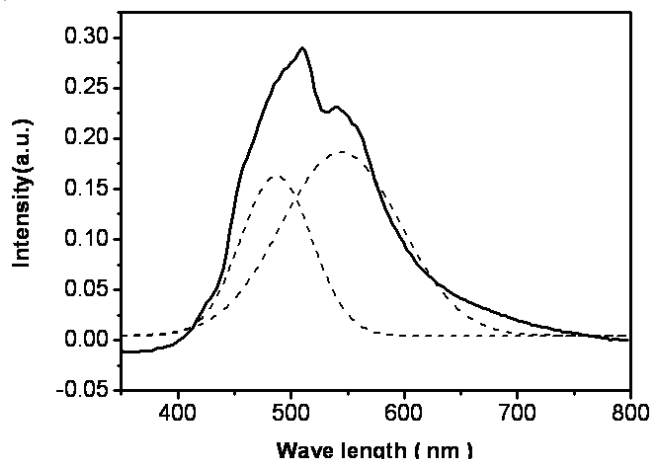


Fig. 4. Photoluminescence spectrum of the taper-like ZnS nanostructure. The photoluminescence was measured under an excitation wavelength of 325 nm

substrate at 70 °C, a small quantity of iron ion may be doped in taper-like ZnS nanocrystal. Therefore, the strong green emission at 530 nm could be attributed to the presence of iron ion.

The morphologies of the products are different with the previous reported results, this may be attributed to the unusual substrate. In present experiment, iron network were used as substrate, which consists of periodic mesh, the interspaced structures played a significant role in the formation of ZnS nanocones. The formation of the taper-like ZnS follow a vapour-solid mechanism, since no catalysts have been adopted in the experiment and no alloy particles have been observed at the tips of the nanocones. It is speculated that the most possible growth steps for typical nanocones are as follows: During the synthesis process, ZnS powder was separated into Zn and S vapour under high temperature, the vapour phase of S and Zn were carried by N₂ to the deposition site and reacted to form ZnS clusters in the iron network mesh. After the nucleation, small nanorods sprouted out from the substrate along the fast growth direction [0001] based on Zn self-catalyst mechanism. During the fast growth process, mass of Zn and S vapour was expended, which lead to lower molecular concentration in the iron network mesh, the reacting vapour preferentially deposited on the centre of top surface, formed some sidesteps on the surface. A slight fluctuation of the reaction conditions may occur due to the partial pressures of the reactants and temperature. The incoming ZnS vapour deposited epitaxially on both top surface and sidesteps rapidly, which cause the fast growth perpendicular to the axes direction, therefore from taper-like morphology. Concerning this, a schematic illustration was also presented in Fig. 5.

Conclusion

In summary, we have described a novel method for controlled synthesis of taper-like ZnS nanocrystals in a large scale using iron network as collection substrate. The microstructures of ZnS nanocrystals were carefully studied and the growth mechanism has also been discussed. The as-prepared ZnS display strong emission band at 530 nm. The ZnS nanostructures reported here are likely to be useful for optoelectronic devices.

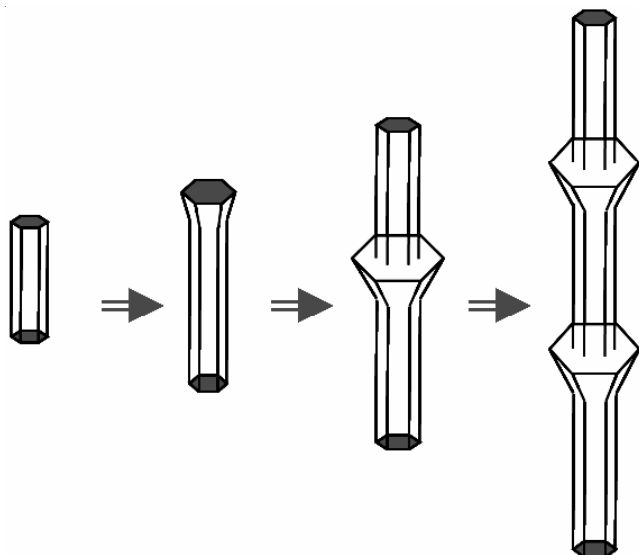


Fig. 5. Schematic diagram of the growth process of ZnS taper-like nanostructures

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