ZnS nanorods with tripod-like and tetrapod-like legs

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Abstract
Single-crystal ZnS nanorods with tripod-like and tetrapod-like legs were synthesized by a simple thermal evaporation process on the Si substrate. The microstructures and properties of the as-synthesized products were analyzed by x-ray diffraction (XRD), scanning electron microscope (SEM) and photoluminescence (PL) measurements. The results show that the as-grown tripod-like nanorods have average diameters of 600 nm and the tetrapod-like nanorods have average diameters of 800 nm. The as-grown ZnS nanorods were perfectly single crystalline. A photoluminescence study shows a 429 nm emission peak from ZnS nanorods due to the self-activated luminescence.

Keywords: nanorods, ZnS, semiconductor, synthesis

Classification numbers: 4.00, 4.06

1. Introduction
Nanotechnology is promising to provide revolutionary solutions to a variety of challenging issues we are facing today, including healthcare, energy crisis and environment conservation. The progress of this technology relies on the innovation of methodologies for the creation of functional nanomaterials. In spite of intensive research efforts, it is still a great challenge to synthesize nanomaterials in a controlled manner in terms of their functions, architectures and processabilities.

Stimulated by the discovery of carbon nanotubes in 1991 [1], many researchers have devoted themselves to all kinds of low-dimensional nanomaterials. In particular, the synthesis and characterization of one-dimensional semiconductor nanomaterials have been the focus of increasing research interest due to their size, morphology-related properties and potential applications in nanowire-based nanolasers [2], field-effect transistors [3, 4], nanocantilevers [5, 6] and photocatalysis [7].

Zinc sulfide, as an important II–VI group semiconductor compound, with a wide bandgap energy of 3.7 eV at 300 K, has attracted considerable attention. It is widely used in flat-panel displays [8], sensors and lasers [9]. To date, one-dimensional nanostructures of ZnS, such as nanobelts [10, 11], nanowires [12, 13], nanofishbones [14], nanosaws, nanocombs and nanowindmills [15–17], and some other heterostructures [18, 19], have been synthesized. Herein, we report unique tripod-like and tetrapod-like ZnS nanorods by simple thermal evaporation of ZnS powder on a Si substrate. The characterization, growth mechanism and photoluminescence property of the ZnS nanorods are all investigated.

2. Experimental
The synthesis process was performed in a traditional horizontal tube furnace, as shown in figure 1. The diameter and length of the quartz tube are 45 mm and 800 mm, respectively. The raw material ZnS powder was located on a ceramic boat at the center of the quartz tube. After the quartz tube was pumped to 0.1 Torr for 3 h to drive residual oxygen gas, a carrier gas of high-purity Argon premixed with 5% hydrogen was kept flowing through the tube from the gas inlet. The flow rate and pressure inside the tube were kept, respectively, 50 sccm
Figure 1. Schematic diagram of the horizontal quartz tube system.

Figure 2. SEM images of as-synthesized nanorods deposited on a single-crystalline Si substrate.

Figure 3. X-ray spectrum of as-synthesized ZnS nanorods.

Figure 4. EDS spectrum of as-synthesized ZnS nanorods.

3. Results and discussion

Figure 2 shows the field-emission scanning electron microscopy (FE-SEM) images of as-synthesized nanorods deposited on a gold-coated single crystalline Si substrate. Figure 2(a) is the total profile of as-synthesized ZnS products, where tripod-like and tetrapod-like nanorods were found. Figures 2(b)–(d) are high-magnification images of single nanorods. These clearly reveal that as-grown nanorods are uniform in diameter and length. Tripod-like nanorods have diameters ranging from 400 nm to 1 \( \mu \)m, while those for tetrapod-like nanorods range from 600 nm to 1 \( \mu \)m.

Figure 3 shows the XRD spectra of ZnS nanorods with all of the peaks representing the hexagonal wurtzite phase with the lattice constants \( a = 0.382 \) nm and \( c = 0.625 \) nm, which match well with the PDF card (No: 36–1450). The sharp peak located at 28.4° is a (0002) crystal face, which implies a good crystal. The chemical composition of as-grown products was investigated through EDAX. Figure 4 shows an EDS spectrum of the as-grown nanorods, which showed that only Zn and S were found, with an atomic ratio of Zn to S equal to 1 : 1 within the experimental errors.

Due to the large diameters of the nanorods, HRTEM analysis is not trivial. Even so, we can still speculate a temporary growth mechanism for as-grown nanorods through XRD data, SEM images and experimental parameters. The nanorods presented here were synthesized by a thermal evaporation method. Thus, high vapor pressure is necessary for the growth of the tripod-like and tetrapod-like ZnS nanostructures. We cannot obtain the desired nanostructures in the low substrate temperature zone by leaving other reaction parameters unchanged. So the temperature of the substrates and the concentration of the vapor are critical experimental parameters for the formation of ZnS nanorods.

The possible steps for nanorods are as follows. Zn vapor and sulfur vapor were transported to the downstream of the source reactants by the controlled carrying gas. A part of the Zn reacted with sulfur in the vapor to form small
ZnS particles, which were separately deposited onto the Si substrate. Those small particles acted as a nucleus, probably as the seed. The legs of the tri-/tetrapods can thus grow further out from the nucleus crystals simultaneously via a VS mechanism with continuous condensation and diffusion of Zn and sulfur under the medium supersaturation of Zn vapor and sulfur. This is similar to the growth of ZnO tetrapods [20]. The illustration of the ZnS nanorod growth with tripod-like and tetrapod-like legs are shown in figure 5.

The photoluminescence (PL) measurement of the as-grown ZnS nanorods was carried out at room temperature with 325 nm excitation. Figure 6 shows the strong and broad emission spectrum from the ZnS nanorods, which was located at 429 nm. Theoretically, near band edge emission of ZnS should be located at 337 nm due to the combination of free excitons. Thus, the PL peak at 429 nm probably results from the recombination of the photo-generated holes with the electrons occupying the singly ionized oxygen vacancy. Yang and Zhang [21] have reported emissions from the ZnS nanowires around 421 nm and attributed the peak to the well-known self-activated luminescence. Our results were consistent with the report from Yang and Zhang and the emission peak was induced by vacancies and other fault states.

4. Conclusion

In summary, we have synthesized a kind of novel ZnS nanorod with tripod-like and tetrapod-like legs by thermally evaporating ZnS powder on a Si substrate. The temperature of the substrates and the concentration of the vapor are the critical experimental parameters for the formation of ZnS nanorods. This work is far from complete in the aspects of synthesizing all of the possible symmetrical nanostructures of ZnS, the microstructures studies and the growth mechanism. However, ZnS nanorods with tripod-like and tetrapod-like legs reported here will have numerous potential applications in a variety of fields, such as field emission, photovoltaics and fuel cells. The method reported to synthesize such ZnS nanostructures is applicable to many other sulfides, carbides, nitrides, etc.

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