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Hydrothermal synthesis and characterization of ZnS hierarchical microspheres

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ABSTRACT

In the present work, wurtzite ZnS hierarchical microsphere nanostructures composed of nanowires were synthesized through hydrothermal method. The morphologies and microstructures of the as obtained wurtzite ZnS sample were investigated by scanning electron microscopy and transmission electron microscopy. The results show that the diameter of the nanowires is about 10 nm, the length is about 500 nm, growing along the [001] direction. UV–visible spectroscopy shows that the band gap of the as obtained ZnS hierarchical microspheres is 3.4 eV. Room temperature photoluminescence measurements reveals a strong green emission peak at around 516 nm. The N_2 adsorption–desorption isotherms experiment at 77 K exhibits that the surface area of the ZnS sample is 99.87 $m^2\,g^{-1}$.

1. Introduction

Controlling the size and the morphology of the materials at the nanoscale has received much attention because of their special physical and chemical properties during the past years [1]. Recently, there are many reports focused on the synthesis of one dimensional (1D) nanostructures such as nanowires, nanobelts, nanorods, nanotubes. Compared with these 1D nanostructures, complex 3D architecture structures needs more efforts to explore its properties owe to their low density, high surface area and has been widely used as microelectronics, photocatalysis, biosensors, and information storage.

Zinc sulfide, an important II–VI group direct bandgap semiconductor material, has been extensively studied for a very long time due to its various applications in many areas [2–6]. At present, considerable efforts have been made to synthesize various morphologies about ZnS, from 1D nanostructures,

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2D nanosheet structures to 3D hierarchical structures such as hollow micospheres structures, hierarchical nanohelices structures and so on [7–17]. At the same time, many synthetic methods were carried out to fabricate these morphologies, especially, the fascinating 3D hierarchical morphologies, such as hydrothermal or solvothermal method, chemical vapor deposition method, template-assisted route and thermal evaporation method [18–22]. Among these methods, hydrothermal or solvothermal method is probably the most cheap and effective method to synthesize 3D hierarchical morphologies.

Although many reports have been made to fabricate various ZnS hierarchical structures in the past [14,23–27], it still remains a great challenge to synthesize the special 3D hierarchical morphologies through different methods. In this manuscript, we synthesized wurtzite phase ZnS hierarchical microsphere nanostructures through hydrothermal route. The Nitrogen adsorption–desorption isotherms experimental and optical properties of the as obtained ZnS hierarchical microspheres were investigated.

2. Experimental details

Hydrothermal method was employed in the synthesis of ZnS hierarchical microsphere nanostructures. In a typical process, 1 mmol $Zn(NO_3)_2 \cdot 9H_2O$ and 3 mmol thiourea ($CS(NH_2)_2$) were dissolved in 30 ml mixed solvent composed of 15 ml distilled water and 15 ml ethylenediamine. The solution was stirred for about 10 min to ensure that all the reagents were dissolved completely. Then the above solution was transferred to a 35 ml teflon-lined stainless steel autoclave which was heated at 170 °C for 16 h in an electric oven. The autoclave was took out and cooled to room temperature in air. The obtained white precipitate was washed with a lot of distilled water and ethanol several times to remove the impurities. The obtained product was then dried at 60 °C for about 6 h.

The crystal phase of the product was characterized by X-ray diffraction (XRD). The morphology and microstructure of the sample was checked by scanning electron microscope (SEM) and transmission electron microscope (TEM). UV–Vis absorption spectrum was carried out on a Shimadzu UV–vis spectrophotometer. The Brunauer–Emmett–Teller (BET) surface areas were measured on the ASAP 2020 instrument at 77 K using N_2 as the adsorbate. Room temperature photoluminescence (PL) measurements were carried out on a visible–ultraviolet spectrophotometer with 325 nm He–Cd laser as the excitation source.

3. Results and discussion

Fig. 1 shows the typical XRD patterns of the as obtained sample. From the XRD results, all the peaks can be indexed as wurtzite ZnS (JCPDS 36-1450) without any impurities. The as obtained ZnS sample shows a hexagonal structure with lattice constants $a = 3.821$ Å, $c = 6.258$ Å. The composition of the sample was checked by energy dispersive spectra (EDS), which is shown in the inset of Fig. 1. It exhibits

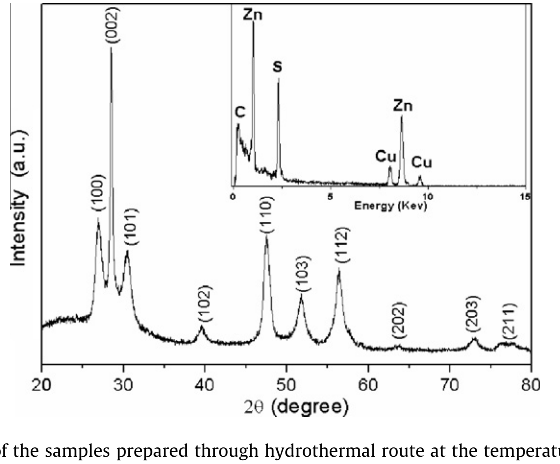

Fig. 1. XRD patterns of the samples prepared through hydrothermal route at the temperature of 170 °C for 16 h.