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LARGE-SCALE SYNTHESIS AND PHOTOLUMINESCENCE OF ZnS HIERARCHICAL NANOSTRUCTURES ON SILICA GLASS SUBSTRATE

HONGMEI XU[a], YONG LIU[a*], HAI WANG[a], MING LI[a], WENXIA ZHAO[b], CHAOLUN LIANG[b] HONG HUANG[b], HUI SHEN[a]

[a] *School of Physics and Engineering, Institute for Solar Energy Systems , State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-sen University, Guangzhou, 510275, China*

[b]*Instrumental Analysis and Research center, Sun Yat-sen University, Guangzhou, 510275, China*

A novel hierarchical structured ZnS microsphere comprised of nanosheets on the silica glass substrate has been prepared on a large scale by a simple hydrothermal synthesis route. As an important II-VI semiconductor, large-scale hierarchical ZnS nanostructure has not been easily fabricated on silica glass substrate. Here, we confirm the formation of this hierarchical nanostructure by XRD, EDS and FESEM. Moreover, the photoluminescence (PL) properties of the ZnS films have been studied in terms of PL emission spectroscopy. Additionally, the effect of hydrothermal reaction temperature on the formation of ZnS film was investigated in this paper. The possible growth mechanism for the formation of this novel hierarchical ZnS microsphere was also proposed based on the FESEM observations.

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1. Introduction

Hierarchical structured nanomaterials have received particular interest owing to their potential applications in optoelectronics devices [1]. Complex nanostructures or films fabricated from zero-dimensional , one-dimensional, two-dimensional and three-dimensional morphologies have been variously investigated in previous literatures. Hierarchical structures are desirable for many applications, however, the fabrcication of these complex nanostructures on a large scale on silica glass substrate remains a significant challenge. Until now, there are few reports illustrating the formation process of this novel nanostructure on the silica glass substrate.

ZnS as a wide band (Eg=3.7 eV at room temperature) II-VI group semiconductor material has attracted much attention due to its applications in optoelectronic devices[2], catalysis[3, 4] and solid-state solar window layers[5], and so on. Currently, many reports have been focused on tailoring the size, crystal structure and the morphology such as nanorods[6, 7], nanobelts[8-10], nanotubes[11, 12] by various physical and chemical methods. However, the

* Corresponding Author: liuyong7@mail.sysu.edu.cn

synthesis of hierarchical nanostructured ZnS with well-defined morphologies has been diffcult to obtain and remains key challenges. Cheng[13] and co-workers reported the synthesis of ZnS with hexagonal pyramids of zinc blende structured single crystals through a chemical vapor deposition (CVD) method, which needed high-temperature reactions and consumed energy. Few papers report the synthesis and photoluminescence of the ZnS with hierarchical nanostructures on the silica glass substrates.

Here we report a new type of hierarchical structured ZnS microsphere directly synthesized on the silica glass substrate by a simple hydrothermal method without using any seeds or templates. As prepared hierarchical ZnS microspheres films were measured in detail by FESEM, XRD, EDS and PL spectra.

2. Experimental section

In a typical synthesis, 1.5 g of $ZnCl_2$ was dissolved in a mixed solvent of 30 mL of deionized water and 0.6 g of thiourea in a 100 mL Teflon-lined stainless autoclave. The mixture was stirred at ambient conditions for 3 min. A piece of silica glass was cleaned ultrasonically with deionized water, ethanol for 5 min and was placed against the wall of Teflon-liner with the conducting side facing up. Subsequently, the autoclave was sealed, put into an electronic oven and maintained at 160-230 ^{o}C for 12 h. After the hydrothermal reaction, the autoclave was cooled to room temperature. The silica glass substrate coated with homogeneous thin films was taken out, thoroughly washed with water and ethanol, and dried at 60 ^{o}C for 1 h in air for further characterization. A series of experiments were performed by ajusting hydrothermal reaction temperature. The crystal structure of the as-prepared films were measured by X-ray diffraction (XRD). The XRD pattern was recorded with a Bruker D8 advance X-ray diffractometer using Cu K_{α} radiation (λ=1.5418 Å), at an operating voltage of 40 KV and a current of 40 mA. Field emission scanning electron microscopy (FESEM, JSM-6330F) was used to study and morphologies of as-prepared thin film. The photoluminescence (PL) spectra of samples were investigated on a fluorescence spectrophotometer (RF-5301 PC) at room temperature.

3. Results and discussion

The XRD patterns of the samples at different hydrothermal reaction temperature are given in Fig. 1, and all diffraction peaks can be conclusively indexed as cubic Zinc blend ZnS with the lattice constant of a=5.4 Å (Joint Committee on Powder Diffraction Standards (JCPDS) card: 65-0309), indicating that the as-prepared sample is of high quality. From the XRD peak intensity and shapes in Fig. 1, it can be inferred that the quality of crystal increased with the increase of the hydrothermal reaction temperature.

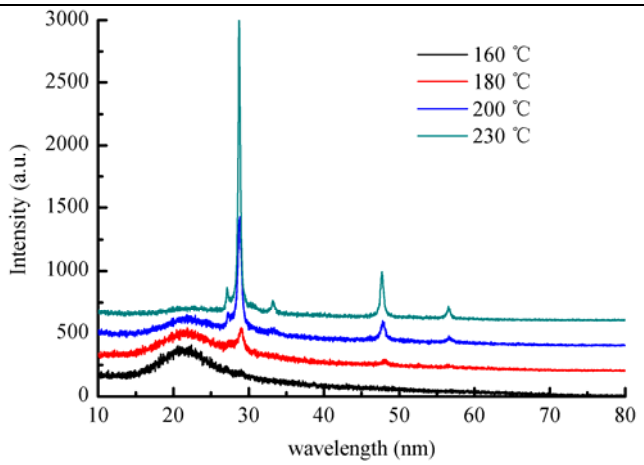

Fig. 1. The XRD patterns of as-prepared ZnS hierarchical nanostructure.

Additionally, FESEM and energy dispersion spectroscopy (EDS) were performed to characterize the samples. The FESEM in Fig. 2 shows the large-scale film deposited on the silica glass substrate. From the EDS data in Fig. 2, Zn/S molor ratio of the obtained sample is close to 1:1 (i.e. the stoichiometry of ZnS).

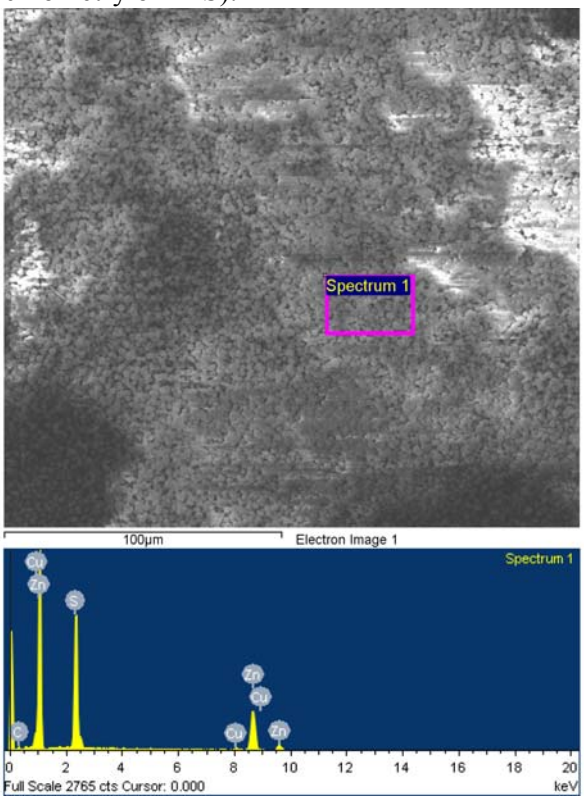

Fig. 2 A FESEM image and EDS spectrum of ZnS microspheres.

Fig. 3 shows the FESEM images of the ZnS microspheres after hydrothermal treatment for 12 h with temperature varying from 160 to 230 □*C*. From the lower magnification FESEM images (Fig. 3a, 3d, 3g and 3j), it is clearly that the hierarchical ZnS microspheres were grown on the silica glass substrate. The corresponding structural details were further revealed in the higher magnification FE-SEM images (Fig. 3b,c, Fig. 3e,f, Fig. 3h,i and Fig. 3k,l) and clearly showed the ZnS nanosheets possessed smooth surfaces, which closely connected to each other to assemble into the well-defined ZnS microspheres with hierarchical nanostructures. Compared to Fig. 3a-3l, the diameters of the ZnS microspheres are about 300 nm, 2-3 μm, 4-5 μm and 2-3 μm, respectively. From the results of Fig. 3a-3i, it is found that the ZnS microspheres began to grow and the size became larger with the increase of the hydrothermal

reaction temperature. At 230 □C, the thickness of the nanosheets became thicker while the size of ZnS microsphere decreased.. The results show that the grow rate of ZnS microspheres increased by elevating the reaction temperature from 160 to 230 □*C*. When the solution reaches equilibrium at 230 ℃, the microspheres began to decrease in diameter, and as a result, the thickness of nanosheets began to increase.

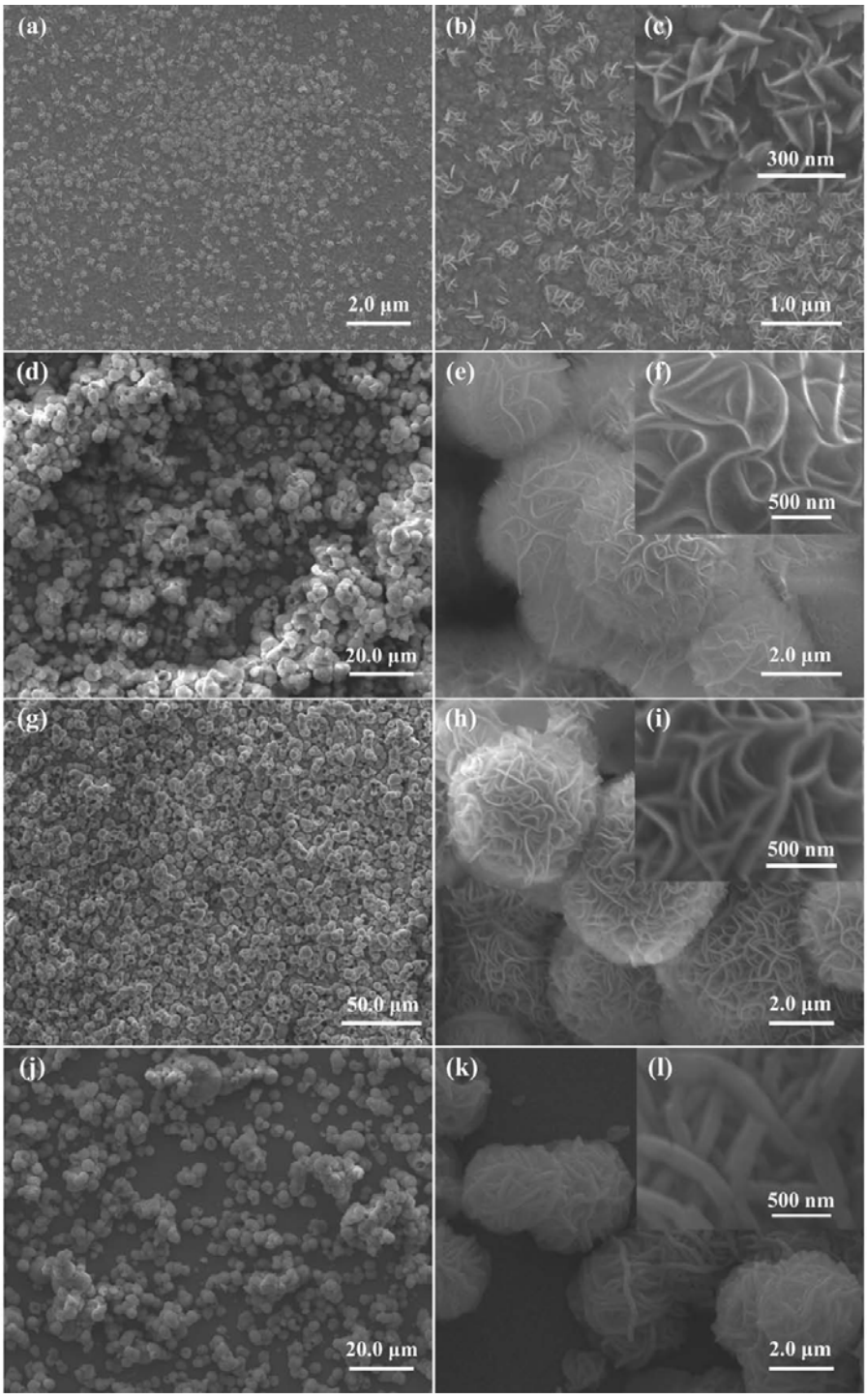

Fig. 3 FESEM images of hierarchical nanostructured ZnS microspheres at different hydrothermal reaction temperature. (a,b and c: 160 □C; d, e and f :180 □C; g, h and i: 200 □C; j, k and l: 230 □C)

Based on the above FESEM images observation, the growth process of ZnS microspheres with hierarchical nanostructures is proposed. In the first stage, the $ZnCl_2$ reacted with the thiourea aqueous solution and the ZnS seed layer were created and covered onto the

surface of silica glass substrate. Under the hydrothermal condition, the ZnS seed gradually transformed into a nucleus, from which the ZnS microsphere began to be self-assembled on the silica substrate. The small latter mismatch between the silica glass and the ZnS plays a critical role in driving the nucleation growth of the ZnS microspheres on the silica glass substrate.

The room-temperature PL of the samples synthesized at different reaction temperature were measured. As shown in the PL spectra (Fig. 4), the PL emission peak exhibited the green shift with the increase of the growth temperature. We attributed the green shift to the increase of the crystal quality of hierarchical nanostructured ZnS microspheres. The results showed that the PL emission can be tuned via different hydrothermal reaction temperature.

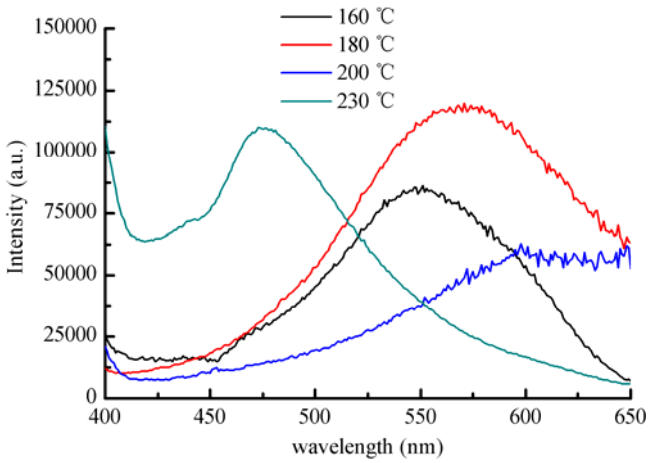

Fig. 4. Room-temperature photoluminescence spectra of the hierarchical nanostructured ZnS microspheres.

4. Conclusions

In summary, large-scale ZnS hierarchical nanostructured microspheres film were fabricated on silica glass substrate through a simple hydrothermal method. By simply changing the hydrothermal reaction temperature, one can tune the morphology and PL emission properties of the ZnS microspheres. The unique morphology of ZnS nanomaterials may have potential significance in future scientific research and application such as photocatalyst and ZnS-based photoelectrical devices.

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