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Synthesis and Characterization of Uniform ZnS Sphere Crystalline by Using a Zinc Coordination Complex as Precursor

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Without using any surfactant or chemical assistant, we just use $[Zn(phen)_2(H_2O)_2]_2L{\cdot}6H_2O$ complex as precursor to react with sulfourea as sulphur source under moderate conditions. Uniform ZnS sphere crystalline has been successfully synthesized *via* a convenient solvothermal method, in which ethanediol and ethanediamine were utilized as mixed solvent. The composition and morphology of as-prepared samples were, respectively characterized by X-ray diffraction and scanning electron microscope. Also the photoluminescence property of the as-synthesized ZnS materials was studied in this work.

Key Words: ZnS, Crystalline sphere, Photoluminescence.

INTRODUCTION

Along with technology advanced, semiconductor materials with micro or nano structure have induced more and more attention. Zinc sulphide is one of the very important semiconductors as a direct wide band gap compound and with a wide range of applications of optical materials[1-3], quantum dot light-emitting devices[4], LEDs materials[5], *etc*. Until now, zinc sulphide was usually prepared by high temperature gas chromatography method and wet chemical method. It is well known that the wet chemical method contains hydrothermal process and solvothermal method[6,7]. Solvothermal method often be used to controlled synthesis of uniform micro or nano materials with special structures. For example, Fang's group has obtained zinc sulphide nanoplates with wide length less than 10 μm on a silicon wafer which plated gold film with 40 nm thickness *via* firing made-up zinc sulphide[8] and Wu and his co-workers have successfully synthesized zinc sulphide nanospheres through the use of hydrothermal method[9].

In this study, our strategy for creating uniform ZnS sphere crystalline utilizes zinc coordination compound as precursor because such complex have already been proved to be promising materials for the synthesis of transition metal sulphides with special structure and shape[10,11], meanwhile, this kind complex also can easily be prepared under moderate conditions. Thus, a simple coordination complex $[Zn(phen)_2(H_2O)_2]_2L{\cdot}6H_2O$ was prepared, which was used as precursor for the purpose to control the concentration and release rate of Zn^{2+} ions. This study is believed to benefit for crystals growth. Uniform ZnS sphere crystalline was prepared under a convenient solvothermal method, in which ethanediol and ethanediamine were utilized as mixed solvent. Also the photoluminescence property of the as-synthesized ZnS materials was studied in this work.

EXPERIMENTAL

Sample preparation: All chemical reagents have been utilized in the present study were of analytical grade and used without further purification.

$$[Zn(phen)_2(H_2O)_2]2L{\bullet}6H_2O + CS(NH_2)_2 \xrightarrow[\triangle]{\text{ethanediol, ethanediamine}} ZnS$$

Coordination compound $[Zn(phen)_2(H_2O)_2]_2L{\cdot}6H_2O$ was employed as precursor according to the previous report[12]. As-prepared $Zn(phen)_2(H_2O)_2]_2L{\cdot}6H_2O$ (0.5 mmol) and sulfourea (0.5 mmol) were added into the mixed solution of 8 mL ethanediol and 8 mL ethanediamine, then stirred for more than one hour. After this pretreatment process, the mixed solution was transferred into a Teflon-lined autoclave with 20 mL capacity. Then we sealed the autoclave and heated it to 160 ºC, kept it at 160 ºC for 24 h. The autoclave was cooled to room temperature naturally. The resulting white products were collected and washed with distilled water and ethanol for several times and finally dried in vacuum at 50 ºC for 8 h.

Characterization: X-Ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance X-ray powder diffractometer *via* using CuK_α irradiation at a scan rate of 0.1°/s, measurements were carried out in the range of $20° \leq 2\theta \leq 80°$. The morphology of the product prepared was examined by Zeiss Evo LS-15 scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

The structure of the as-prepared ZnS sphere crystalline was determined by X-ray diffraction. As shown in Fig. 1, the peaks in the XRD spectrum of the as-grown sample can be ascribed to single crystalline zinc sulphide with wurtzite structure, JCPDS No. 36-1450. No peaks of other impurities were detected in the experimental error range, indicating the high purity of the obtained sample. The two theta degree of 26.91, 28.5, 30.53, 39.61, 47.56, 51.78, 56.39 correspond to the direction of 100, 002, 101, 102, 110, 103 and 112, respectively.

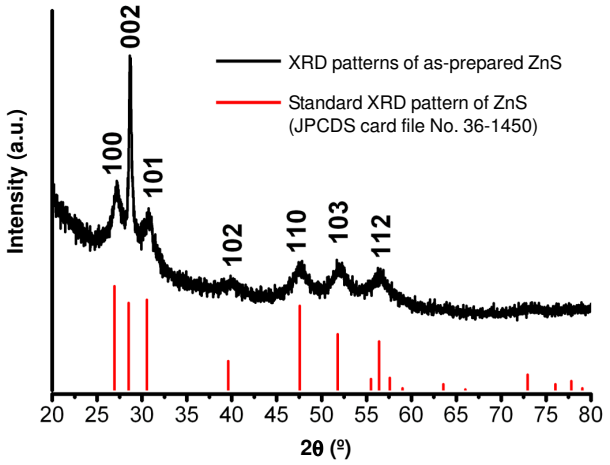
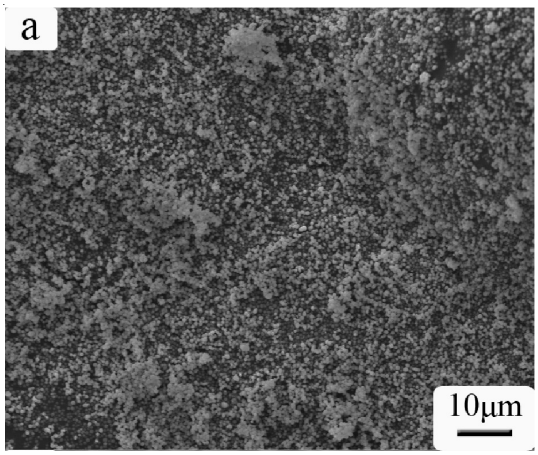


Fig. 1. XRD pattern of as-prepared ZnS sphere crystalline, the stick pattern is the standard pattern for ZnS with hexagonal wurtzite structure (JCPDS card file No. 36-1450)

The morphology and size of the as-synthesized products were characterized by scanning electron microscopy. As shown in Fig. 2a-d, the low magnification SEM images of the as-prepared ZnS microcrystals obtained at 160 ºC for 24 h, indicated that from which a large amount of ball-like ZnS microcrystals with diameters in the range of 0.4-0.5 μm.



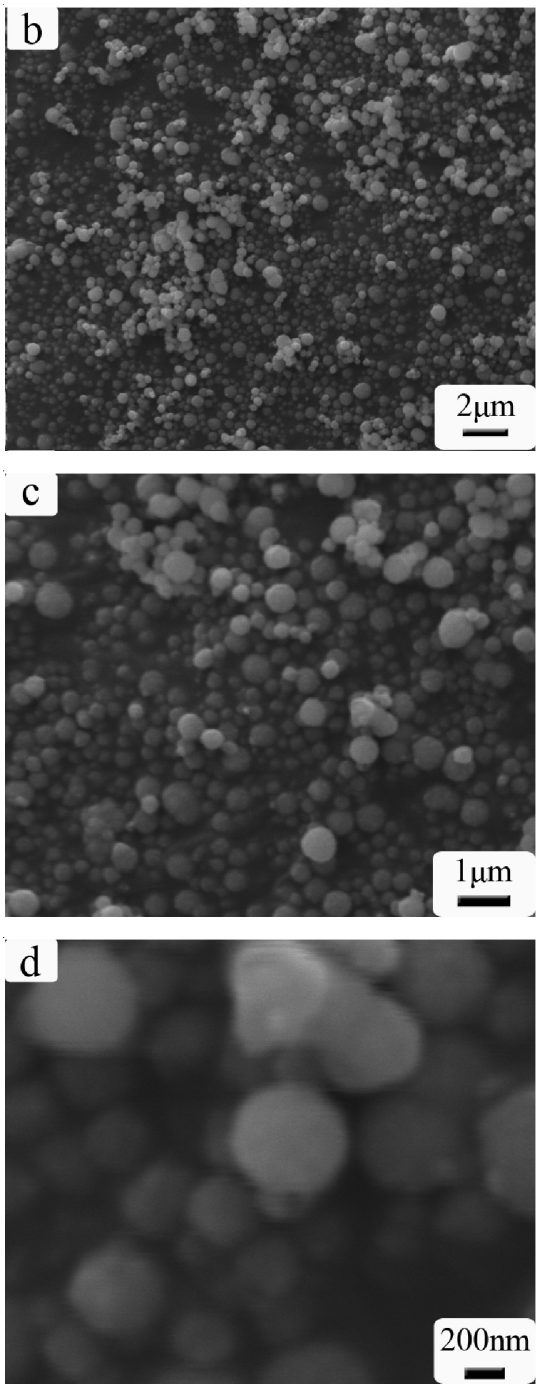


Fig. 2. Different magnification SEM images of as-prepared ZnS: a for 1000 times; b for 3000 times; c for 10000 times and d for 40000 times

The photoluminescence property of as-prepared ball-like ZnS was also studied. Fig. 3 gives the room temperature fluorescence spectrum of the sample under an excitation λ_{ex} = 250 nm. There is an emission band with a two-peak structure. This band could be Gaussian divided into two luminescent peaks at *ca.* 294 and 307 nm.

Conclusion

We have succeeded in synthesizing uniform ZnS microcrystals just by applying $[Zn(phen)_2(H_2O)_2]_2L \cdot 6H_2O$ and sulfourea as the precursor of Zn^{2+} and sulphide source *via* a solvothermal method. This preparation method is an environmentally friendly and low cost.

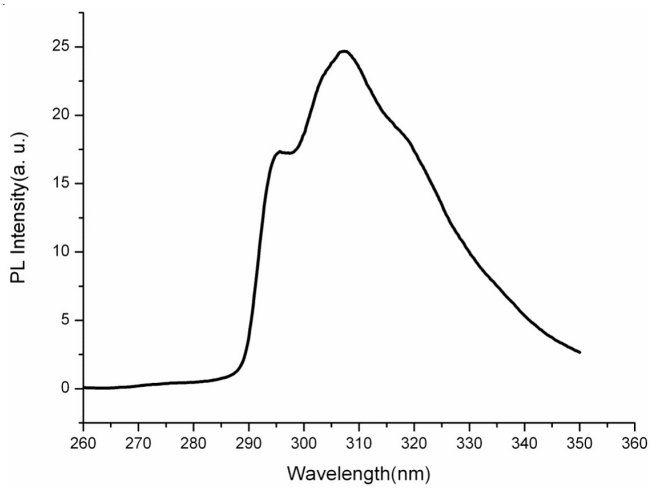


Fig. 3. Photoluminescence property of as-prepared ZnS

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