

Preparation of ZnS nanofibers by electrospinning and their photocatalytic properties

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ZnS nanofibers have been successfully prepared by electrospinning technique. The formation of ZnS nanofibers was carried out by reacting CS₂ with ZnO nanofibers. ZnO nanofibers were synthesized by calcining PVP/Zn(NO₃)₂ precursor composite nanofibers which were fabricated by electrospinning technique. The obtained products were characterized by X-ray diffraction(XRD), field-emission scanning electron microscopy(FESEM) and energy dispersive spectroscopy(EDS), respectively. XRD analyses revealed that the pure ZnS nanofibers with hexagonal crystal system were obtained. SEM images indicated that the surface of the ZnO nanofibers became coarser than that of PVP/Zn(NO₃)₂ composite nanofibers, and the average diameter of ZnS nanofibers was 200±79nm, and showed good fibrous morphology. The synthesis of PVP/Zn(NO₃)₂ composite nanofibers, ZnO nanofibers and ZnS nanofibers were further confirmed by EDS. In addition, the photocatalytic property of ZnS nanofibers was investigated by ultraviolet and visible(UV-vis) absorption spectra. The results showed that the photocatalytic degradation effect of ZnS nanofibers on rhodamine B(RhB) was better than that of ZnO nanofibers, and the photocatalytic degradation rate reached up to 98.8% after UV irradiation for 60min. Therefore, the prepared ZnS nanofibers had outstanding photocatalytic property.

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1. Introduction

As typical semiconductor materials of the II-IV group, ZnS nanomaterials have excellent optical, electrical and photocatalytic property. So enormous efforts have been devoted to the research of ZnS nanomaterials, which has led to many promising applications in ultraviolet light emitting diode, flat panel display, cathode ray tube[1], laser, sensor[2-3], photoluminescence[4-5], electroluminescence[6] and photocatalysis[7-8]. In recent years, various forms of ZnS nanostructures have been synthesized, including nanoparticles, nanotubes, nanowires, nanospheres, nanosheets and nanofibers, et al. The preparation technique of ZnS nanomaterials are numerous, such as emulsions synthesis [9-10], sol-gel method[11-13], hydrothermal synthesis[14-15], solid-state synthesis[16-17], spray pyrolysis synthesis[4-5] and electrospinning method[18], et al. For instance, Haiying Wang[19] et al. prepared ZnS:Cu(PVA) composite nanofibers successfully by electrospinning technique. The formation of ZnS:Cu/PVA nanofibers were carried out by reacting H₂S with Zn(AC)₂:Cu/PVA nanofibers, which were electrospun from the mixture aqueous solution of Zn(Ac)₂,Cu(Ac)₂ and PVA. Zhengfa Zhou[20] et al. presented a new synthetic route to hybridize ZnS semiconductor nanoparticles and PVA based electrospinning nanofibers. Yanbin Tong[21] et al.

prepared ZnS:Mn nanoparticles/PVP composite nanofibers by the electrospinning technique. Jun-ping Li[22] et al. prepared honeycomb-like superstructures consisting of ZnS nanosheets via hydrothermal synthesis using ethylene diamine tetraacetic acid(EDTA) as stabilizer and butylamine(BA) as the structure directing agents. Moreover, Jun-ping Li[23] et al. synthesized a novel sandwich-like structured ZnS/octylamine (OA) hybrid nanosheets with exclusively sheet-like morphology via a mild hydrothermal route using OA as structure-directing agent. Hollow ZnS nanospheres have also been synthesized in aqueous solution of a triblock copolymer[24]. Chenguang Wang[25] et al. prepared ZnS hollow nanostructures using ZnO nanostructures as precursors. However, electrospinning is a simple and convenient method for the preparation of one-dimensional nanomaterials.

In this paper, Zn(NO₃)₂ was used as raw material, PVP was used as template and DMF as solvent. PVP/[Zn(NO₃)₂] composite nanofibers were fabricated by electrospinning and ZnO nanofibers were prepared by calcination of PVP/[Zn(NO₃)₂] composite nanofibers. The formation of ZnS nanofibers were carried out by reacting CS₂ with ZnO nanofibers. The structure and morphology of PVP/[Zn(NO₃)₂] composite nanofibers, ZnO nanofibers, ZnS nanofibers were systematically investigated.

2. Experimental section

2.1 Raw materials

poly(vinyl pyrrolidone)(PVP, Mw=90,000), Tianjin city Tiantai Fine Chemicals Company Limited; DMF:AR, sinopharm chemical reagent Co., LTD; $\text{Zn}(\text{NO}_3)_2$:AR, Tianjin Kernel Chemical Reagent Development Center; CS_2 :AR, Tianjin Fuchen chemical reagent factory.

2.2 Preparation of ZnO nanofibers

Precursor solution was prepared by dissolving an amount of $\text{Zn}(\text{NO}_3)_2$ in DMF, and by adding an amount of PVP into the above solution, followed by stirring at room temperature and then remaining motionlessly for a period of time. (The mass fraction of $\text{Zn}(\text{NO}_3)_2$, PVP and DMF were 6%, 13%, 81%, respectively). PVP/ $\text{Zn}(\text{NO}_3)_2$ composite nanofibers were fabricated by electrospinning of the precursor solution. The above precursor solution was placed in a syringe and dosed at a constant flow rate using a plastic capillary. The anode was placed in the solution, and a grounded aluminum foil served as counter electrode and collector. When a high voltage (12 kV in this

work) was applied, and the distance between the capillary tip and the collector was fixed to 18 cm and relative humidity (RH) was 75%, a dense web of PVP/ $\text{Zn}(\text{NO}_3)_2$ composite nanofibers was collected on the aluminum foil.

These nanofibers were placed in program-controlled high temperature furnace and were calcinated at a rate of $1^\circ\text{C}/\text{min}$ and remained for 2h at 700°C , followed by cooling down to room temperature. Then the ZnO nanofibers were obtained.

2.3 Preparation of ZnS nanofibers

The crucible loaded with ZnO nanofibers was placed in vacuum tubular furnace and was sealed, installed water seal equipment and gas generator of CS_2 . Schematic diagram of reaction setup was shown in Fig. 1. Argon was ventilated into the tubular furnace for 30 min in order to remove the air from the system before heating. When the vacuum tubular furnace was heated to 800°C at a rate of $5^\circ\text{C}/\text{min}$, CS_2 was ventilated into the tubular furnace and remained reacting for 1h at 800°C , followed by cooling down to room temperature. Then the ZnS nanofibers were obtained.

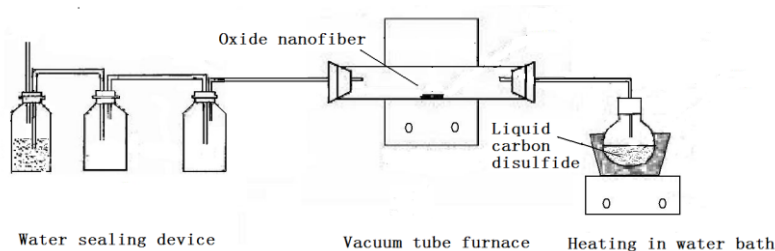


Fig. 1. Schematic diagram of vulcanization reactions setup.

2.4 Characterization methods

The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The crystalline structure of the products obtained was analyzed by XRD using a Y-2000 X-ray diffractometer with $\text{Cu K}\alpha_1$ radiation, with the working current and voltage at 20mA and 40kV, respectively (made by Dandong Aolong Radiative Instrument CO., LTD.). Scans were made from 20° to 80° at the speed of $4^\circ/\text{min}$, and the step was 0.02° . The morphology and size of the samples were characterized by SEM on an XL-30 scanning electron microscope made by FEI Company. The photocatalytic property of ZnS nanofibers was investigated by ultraviolet and visible (UV) absorption spectroscopy on Shimadzu UV-1240PC UV-vis spectrophotometer.

3. Results and discussion

3.1 XRD analysis

The crystal phases of the ZnO nanofibers and ZnS nanofibers were characterized by XRD, as indicated in Fig. 2. Fig. 2(a) exhibited prominent peaks which were accordant with standard card (PDF#75-0576) of ZnO, and diffraction peaks were indexed to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202) crystal facet, and the sample was hexagonal crystal system in structure and the space group was $\text{P63mc}(186)$. It showed that ZnO nanofibers were obtained. From Fig. 2(b), XRD patterns displayed some obvious diffraction peaks which were indexed to (100), (002), (101), (102), (110), (103), (112), (202) and (203) crystal facet, and the d values and relative intensity are consistent with those of standard card (PDF#36-1450) of ZnS. The sample was hexagonal crystal system in structure and the space group was $\text{P63mc}(186)$. Therefore, the pure ZnS nanofibers with

hexagonal crystal system and the space group was $P63mc(186)$ were obtained.

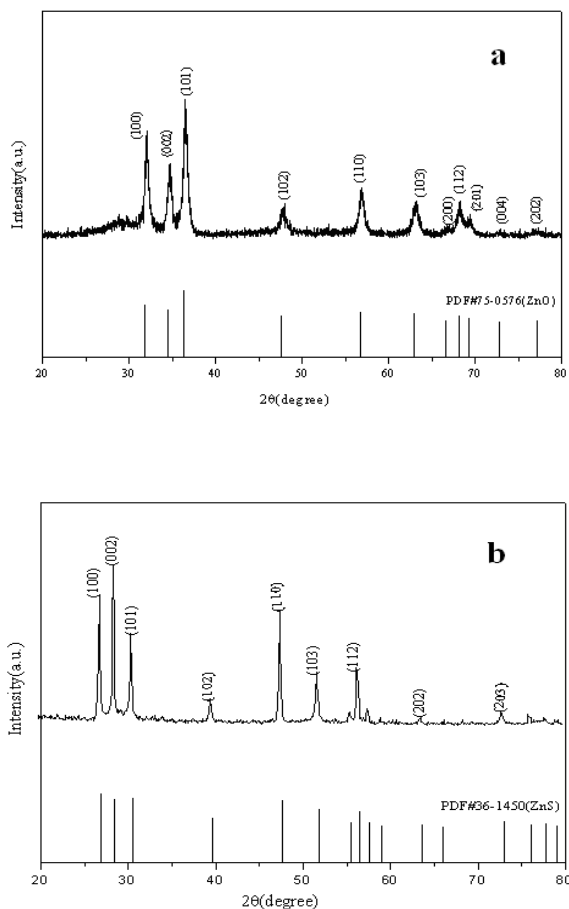


Fig. 2. XRD patterns of the ZnO nanofibers(a) and ZnS nanofibers(b).

3.2 SEM analysis

The morphology of the obtained samples was investigated by SEM. As is shown in Fig.3, three images showed good fiber morphology. Fig. 3(a) showed that the average diameter of the nanofibers was 320 ± 33 nm, and the surface was very smooth and even. Fig. 3(b) indicated that the average diameter of the nanofibers declined to 180 ± 26 nm, and became coarser and thinner after calcination due to the decomposition of PVP and nitrate at 700°C . Fig. 3(c) revealed that the average diameter of the nanofibers increased to 200 ± 79 nm owing to vulcanization reactions of ZnO and CS_2 , but still demonstrated good fibrous morphology.

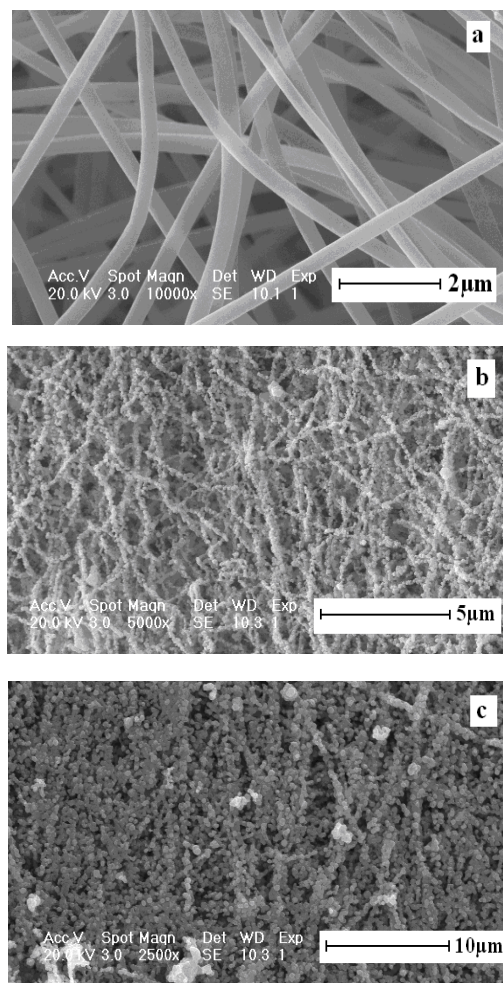


Fig. 3. SEM images of the PVP/Zn(NO₃)₂ composite nanofibers(a), ZnO nanofibers(b) and ZnS nanofibers(c).

3.3 EDS analysis

In order to further confirm the component of nanofibers, the samples were characterized by EDS, as shown in Fig. 4. The EDS analysis results from Fig.4(a) showed that there were four prominent peaks, which were caused by C,N,O,Zn elements. Au peak results from the conductor film plated on the surface of the samples for SEM observation. It was suggested that the sample was PVP/Zn(NO₃)₂ composite nanofibers. The EDS analysis results from Fig. 4(b) revealed that the samples were composed of O and Zn elements. It confirmed that the samples were ZnO nanofibers. Fig. 4(c) demonstrated that the peak of O element disappeared and one new peak appeared, which was caused by S element. This indicated that pure ZnS nanofibers were formed.

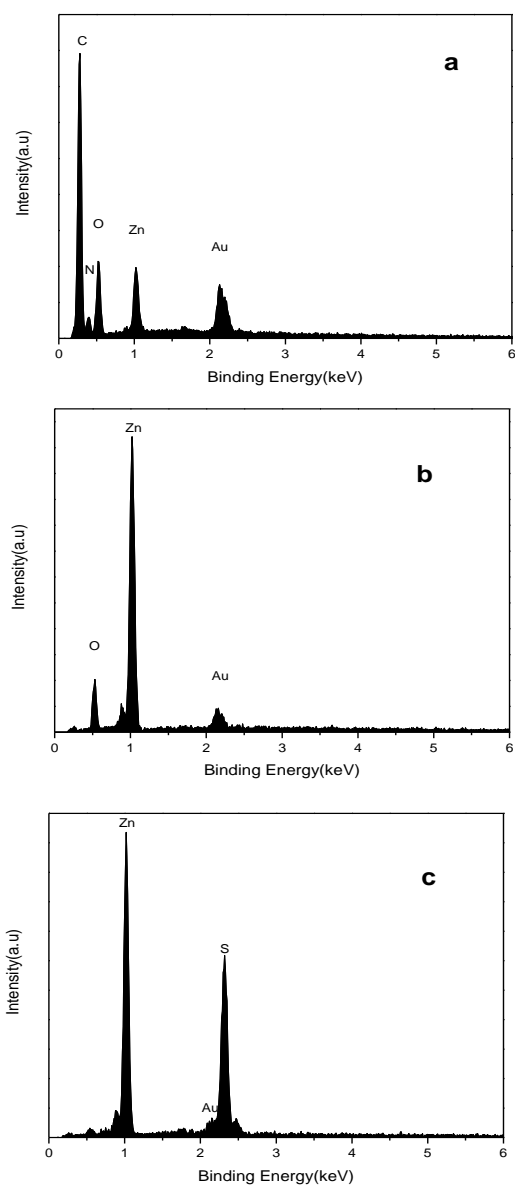


Fig. 4. EDS images of the PVP/Zn(NO₃)₂ composite nanofibers(a), ZnO nanofibers(b) and ZnS nanofibers(c).

3.4 Photocatalytic Degradation of RHB

In the course of experiment, ZnO nanofibers and ZnS nanofibers were used as photocatalysts, RHB was used as degradation target, and the photocatalytic degradation effects of two kinds of nanofibers on RHB were systematically investigated. The experiment process is as follows: firstly, diluted RHB solution was prepared by mixing 5ml RHB solution of 1.0×10^{-4} mol/L with 95ml deionized water into two beakers, respectively, and a small amount of solution was taken out in advance for the test of initial data. Secondly, 0.05g ZnO nanofibers was added into one of the above beakers, and 0.05g ZnS nanofibers was added into the other. Thirdly, the two beakers of solution were dispersed by ultrasound for 10min, and stirred by magnetic force for 10min at room temperature,

and then the two beakers were subjected to irradiation under UV light(500W). At last, 15ml degradation solution was taken out at regular intervals of 10min and the UV-vis absorption spectras of supernatant after centrifugation were measured.

Fig. 5 showed time-dependent UV-vis absorption spectra of RHB with ZnO nanofibers(a) and ZnS nanofibers(b) as photocatalysts exposed to UV light. As shown in Fig. 5, the maximum absorption band of the two kinds of solution was declined gradually with the increasing of the irradiation time. Therefore, ZnS nanofibers and ZnO nanofibers have evident photocatalytic degradation effect on RHB when exposed to UV light and the photocatalytic degradation effect of ZnS nanofibers was better than that of ZnO nanofibers.

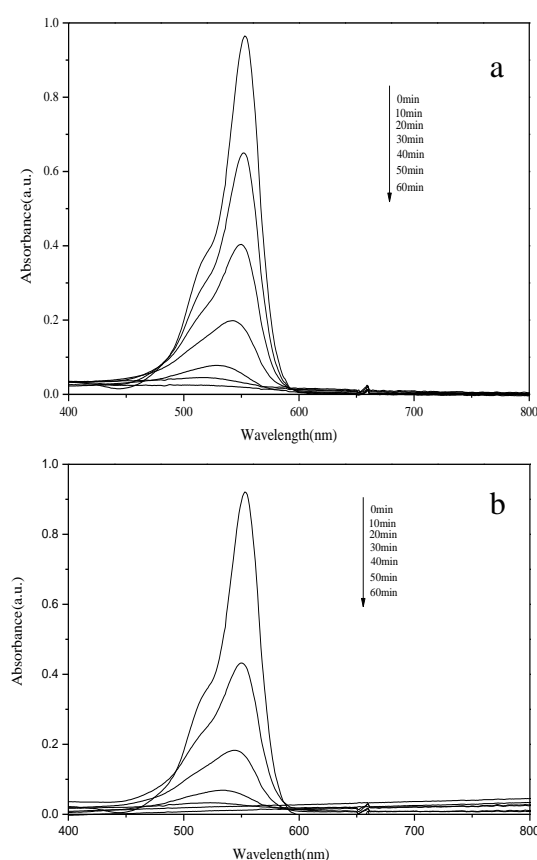


Fig. 5. Time-dependent UV-vis absorption spectra of RHB with ZnO nanofibers(a) and ZnS nanofibers(b) as photocatalysts.

As indicated in Fig. 6, after UV irradiation for 60min, the photocatalytic degradation rate of ZnO nanofibers on RHB reached up to 97.1%, and the photocatalytic degradation rate of ZnS nanofibers on RHB reached up to 98.8%. The photocatalytic degradation effect of ZnS nanofibers was better than that of ZnO nanofibers. It was further confirmed that the prepared ZnS nanofibers had outstanding photocatalytic property.

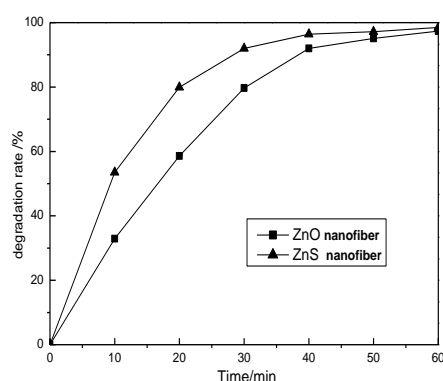


Fig. 6. Photocatalytic degradation rate of RHB with ZnO nanofibers and ZnS nanofibers as photocatalysts exposed to UV light.

4. Conclusions

PVP/Zn(NO₃)₂ precursor composite nanofibers were successfully fabricated by electrospinning, and ZnO nanofibers were synthesized by calcining the precursor composite nanofibers at 700°C for 2h, and then ZnS nanofibers were obtained by vulcanization reaction of ZnO nanofibers and CS₂ at 800°C for 1h.

XRD revealed that ZnO nanofibers and ZnS nanofibers were hexagonal crystal system in structure. SEM micrographs indicated that the samples showed good fiber morphology. Moreover, the average diameter of the PVP/Zn(NO₃)₂ precursor composite nanofibers was 320±33nm, and the surface was smooth and even. The average diameter of the ZnO nanofibers declined to 180±26nm, and became coarser and thinner after calcination. The average diameter of ZnS nanofibers increased to 200±79nm, but still showed good fibrous morphology. The synthesis of PVP/Zn(NO₃)₂ composite nanofibers, ZnO nanofibers and ZnS nanofibers were further confirmed by EDS.

The photocatalytic degradation effect of ZnS nanofibers was better than that of ZnO nanofibers, and the photocatalytic degradation rate of ZnS nanofibers on rhodamine B reached up to 98.8% after UV irradiation for 60min. Therefore, ZnS nanofibers have outstanding photocatalytic property.

Acknowledgments

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