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Preparation of Zinc Sulfide Microspheres and Its Photocatalytic Activity on Antibiotics

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In this work, the zinc sulfide microspheres were prepared by hydrothermal synthesis method in the presence of polyvinylpyrrolidone as surfactants. The as-prepared zinc sulfide microspheres were characterized by X-ray diffraction, scanning electron microscopy, UV-VIS diffuse reflectance spectra and Fourier transform infrared. The results showed that the size of prepared particles uniform and dispersed well. The decgradation rate of the antibiotics pollutants ciprofloxacin and gatifloxacin were studied under UV and visible light irradiation. The photocatalytic experiments showed that the degradation rate of ciprofloxacin and gatifloxacin with the as-prepared zinc sulfidephotocatalysts were 75.31 % and 74.57 % under UV light irradiation 60 min, respectively. However,the degradation rate of ciprofloxacin and gatifloxacin are very low in the visible light.

Key Words: Zinc sulfide, Hydrothermal synthesis, Photocatalysis, Antibiotics.

INTRODUCTION

Antibiotics are used extensively in human and veterinary medicine. But, the residue of antibiotics leads to resistance of bacteria and hazards to teratogenic and carcinogenic as well as other animals[1,2]. Usually, it has residue in the environment and always results in environmental pollution. Antibiotics pollutants in aquatic environment and their potential ecological risks have drawn the global concerns because of their abundant and unsuitable usage in recent years. And it doesn't remove the antibiotics pollutants from environment with the current pollution treatment technology[3-5]. Semiconductor photocatalytic techniques to degraded organic pollutants in waste water has attracted increasingly attentions due to their operation flexible, energy effectiveness, wide application, non re-pollution and highly degradation efficiency, *etc*., thus it was used to treat waste water.

Among the most semiconductor, zinc sulfide (ZnS) is an important one with a large exciton binding energy (40 meV) and a small Bohr radius (2.4 nm), which has been considered to be a promising material for sensors, photocatalysts, *etc*.[6,7]. Zinc sulfide nanocrystals are good photocatalysts as a result of the rapid generation of electron-hole pairs by photoexcitation and the highly negative reduction potentials of excited electrons[8,9].

In this work, fluroquinolones antibiotics ciprofloxacin and gatifloxacin *i.e.*, are selected as main study object. The ciprofloxacin and gatifloxacin are the third generation broad-spectrum fluoroquinolone antimicrobial, which is active against both gram-positive and gram-negative bacteria and is often used to treat human or animal bacterial infections. It has been great concern to people due to the environmental pollution since its abundant usage. Therefore, the ZnS microspheres were prepared by hydrothermal synthesis method in presence of polyvinylpyrrolidone as surfactants, the photocatalystic activity of as-prepared ZnS microspheres was investigated by photocatalytic degradation of ciprofloxacin and gatifloxacin and the results suggested that the size of prepared particles uniform and dispersed well.

EXPERIMENTAL

Zinc acetate (CP), thiourea (CP), polyvinyl pyrrolidone (PVP, CP) and ethanol (CP) were all purchased from Shanghai Chemical Reagent Co. Ltd., and used as received. Ciprofloxacin and gatifloxacin were purchased by Shanghai Shunbo Biological Engineering Co. Ltd., deionized and doubly distilled water was used throughout this work.

Preparation of ZnS spheres photocatalysts: 0.02 mol $Zn(CH_3COO)_2$ and 0.04 mol NH_2CSNH_2 were added into distilled water and mixed uniformity. After stirring for 1.0 h, 0.05 g polyvinylpyrrolidone was added into the above mixture under continuous stirring 10 min. And then the mixed solution was transferred into a Teflon-lined stainless-steel autoclave. The Teflon-lined autoclave was sealed tightly and maintained

at 150 ºC for 24 h and then cooled to room temperature naturally. The white product obtained was separated by centrifugation and repeatedly washed with deionized water and ethanol for several times to remove impurities. Finally the sample was dried in a vacuum at 70 ºC for 12 h.

Photocatalytic experiment: The photodegradation reaction of waste water including ciprofloxacin or gatifloxacin was carried out in a homemade photocatalytic reactor. The photochemical reactor contains 0.1 g catalyst and 100 mL of 20 mg/L aqueous solution of ciprofloxacin or gatifloxacin. After 20 min in the dark, it reached absorption balance, its initial absorbency was determined. The photocatalytic reaction was initiated by irradiating with different light source. The sampling analysis was conducted in 10 min interval. The photocatalytic degradation rate (DC) was calculated by the following formula: $DC = [(1-A_i/A_0)] \times 100\ \%$. Where A_0 is the initial absorbency of ciprofloxacin or gatifloxacin antibiotics solution which reached absorbance balance and Ai is the absorbance of reaction solution.

X-ray diffraction technique was used to characterize the crystal structure. In this work, XRD patterns were obtained with X' Pert MPD diffractometer (Philips, Holland) equipped with CuK_α radiation (40 kV, 30 mA). The 2θ scanning angle range was 10-80º with a step of 7º/min. The SEM images were examined with JSM-7001 F scanning electron microscopy (JEOL Ltd., Japan). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Nexus 470 FT-IR (America thermo-electricity company) in the range 4000-400 cm^{-1}, using KBr pellets. UV-VIS diffuse reflectance spectra (UV-VIS DRS) of photocatalyst powder was obtained for the dry-pressed disk samples using Specord 2450 spectrometer (Shimazu, Japan) equipped with the integrated sphereaccessory for diffuse reflectance spectra, using $BaSO_4$ as the reflectance sample.

RESULTS AND DISCUSSION

Characterization of ZnS spheres photocatalysts

UV-VIS DRS: Fig.1 showed the as-prepared sphere ZnS photocatalyst. It can be clearly seen that the photocatalyst has strong adsorption in the UV area, the band gap was evaluated of -3.32 eV, which correspond with the report of literature. Due to the as-prepared sphere ZnS photocatalyst process large Bohr radius than the ZnS particles and it did not has blue shift, namely it has no quantum size effect.

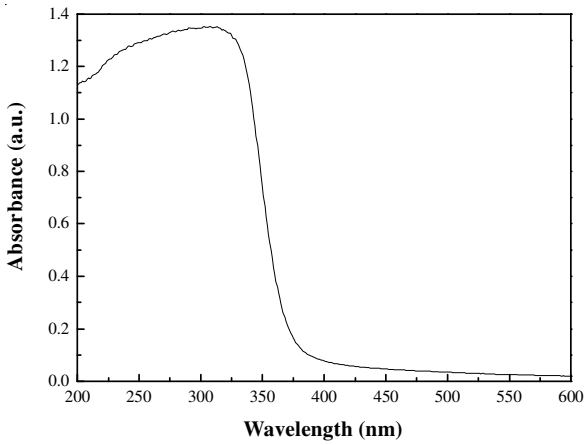


Fig. 1. UV-VIS of prepared ZnS

XRD: Fig. 2 showed the spectrum of XRD. From the spectrum, it can be found that the characterized speaks of -28º, 48º and 56º, which corresponded to the hexagonal crystalline model of ZnS. It indicates that the as-prepared photocatalyst process pure crystal.

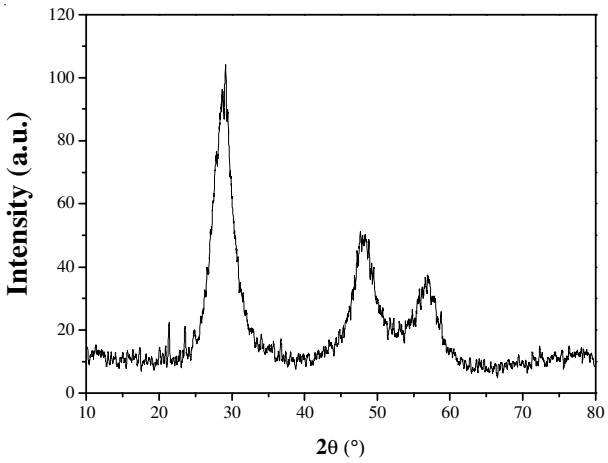


Fig. 2. XRD of prepared ZnS

FT-IR: Fig. 3 shows FT-IR of as-prepared spheres photocatalyst. It can be obviously found main peaks in the spectrum. The peaks of 3500 cm^{-1} and 1260 cm^{-1} were mainly caused by the -OH and O-H groups, which adsorbed on the surface of ZnS, it directs that the surface -OH groups were strongly binding Zn^{2+}. The peaks of 1400 cm^{-1} and 1610 cm^{-1} were the characterized peaks of C=O stretching vibration of symmetric and asymmetric, respectively. The peak of 617 cm^{-1} was contributed to the ZnS. It suggests that the more surface activated groups should be caused better photocatalytic activity.

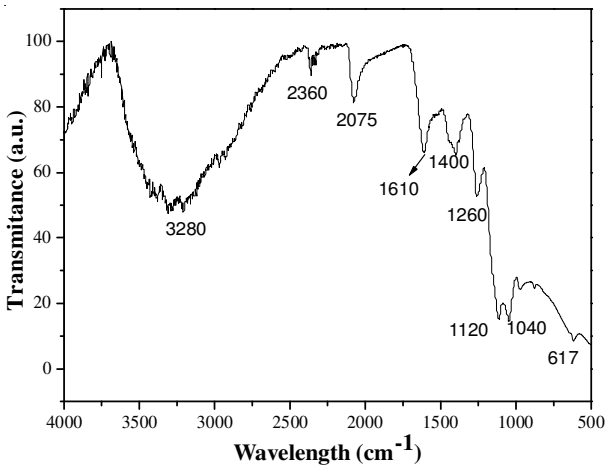


Fig. 3. FT-IR of prepared ZnS sample

Fig. 4 shows the SEM image of as-prepared ZnS spheres photocatalyst. From the image, it can be clearly seen that the ZnS spheres photocatalysts were well dispersed and the ZnS sphere particle-sized of 1-3 μm. It directs that the hydrothermal method could be used to prepare the spherical uniformity and regularity of better photocatalysts. It suggests that the photo-catalytic rate should not be influenced by the sample.

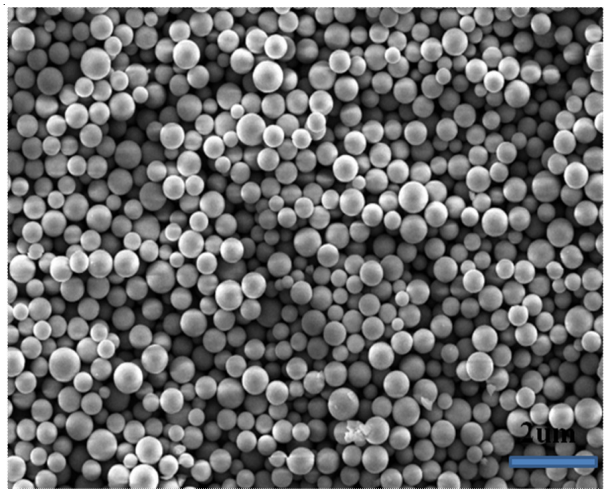
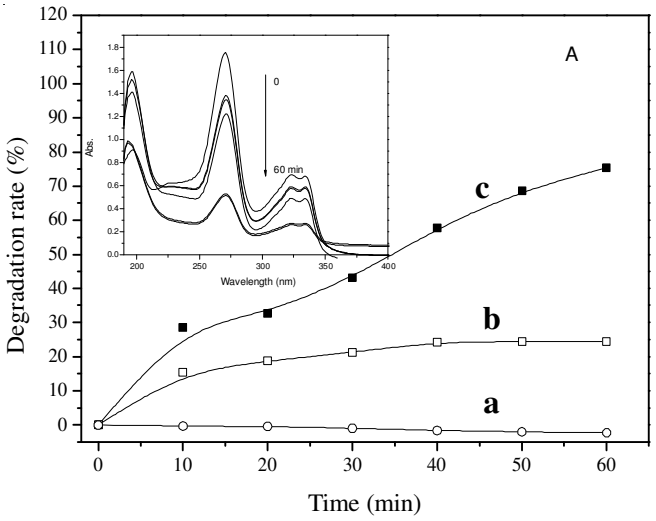


Fig. 4. SEM of prepared ZnS

Photocatalytic activity on antibiotics

Photo-degradation of ciprofloxacin and gatifloxacin with UV light: The process of photo-degradation of ciprofloxacin and gatifloxacin with UV light was listed in Fig. 5(A). The results show that ZnS spheres has low adsorption on ciprofloxacin and gatifloxacin under no UV light irradiation, which corresponding to the curve of Fig. 5(A and B) b. It was mainly due to that the surface physical adsorption of micro-ZnS spheres and the adsorptive rate could reach 24.4 % and 24.37 % in 60 min, respectively, but the adsorption gone to saturation at 40 min. The ciprofloxacin was degraded only under UV light irradiation and the degradation rate corresponding to the curve of Fig. 5(A) a. It can be found that the degradation rate was negative, the reason mainly due to the self-polymerization of ciprofloxacin when the UV light irradiation ciprofloxacin solutions. But the degradation rate of gatifloxacin could reach 19.12 % under the same condition. It directs that the UV light can also achieve degradation gatifloxacin. When the ciprofloxacin and gatifloxacin solutions were degraded with micro-ZnS spheres and UV light irradiation, the photo-degradation rate was obviously improved, which corresponding to the curve of Fig. 5(A and B) c. The photo-degradation rate could reach 75.31 % and 74.57 % in 60 min, respectively. It directs that micro-ZnS spheres photocatalyst possess higher photocatalytic activity under UV light irradiation, due to the micro-ZnS spheres belong to wide band gaps semiconductor materials which activated with UV light.

Photo-degradation of ciprofloxacin and gatifloxacin with visible light: In order to investigate the photocatalytic activity of ZnS spheres on antibiotics under visible light, the photo-degradation of antibiotics solutions processes were carried out under visible light irradiation. The results followed in Fig. 6. It can be clearly seen that the photo-degradation rates were low. It reached 35.47 % (a) and 43.21 % (b) in 60 min under visible light irradiation and considered the self-adsorption of micro-ZnS spheres, the photocatalytic activity and mineralization showed very lowness. The reasons mainly depend on the micro-ZnS spheres photocatalysts which belong to the wide band gap semiconductor. The electrons transition of conduct band can be activated by UV light and generated the pairs of electrons/holes.



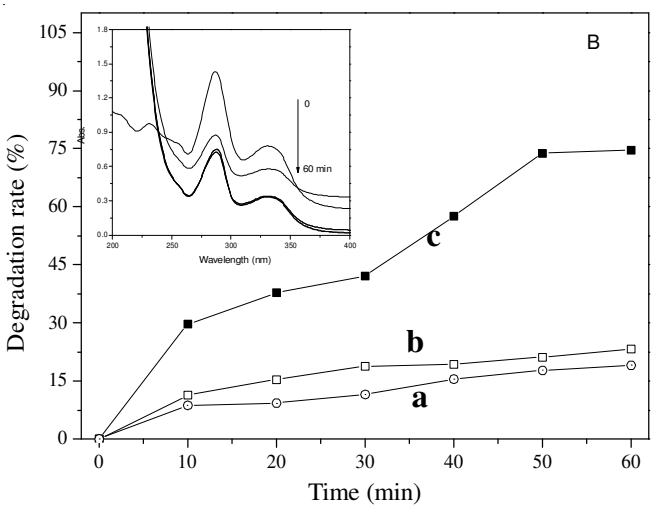


Fig. 5. Degradation of ciprofloxacin (A) and gatifloxacin (B) with ZnS under UV light irradiation

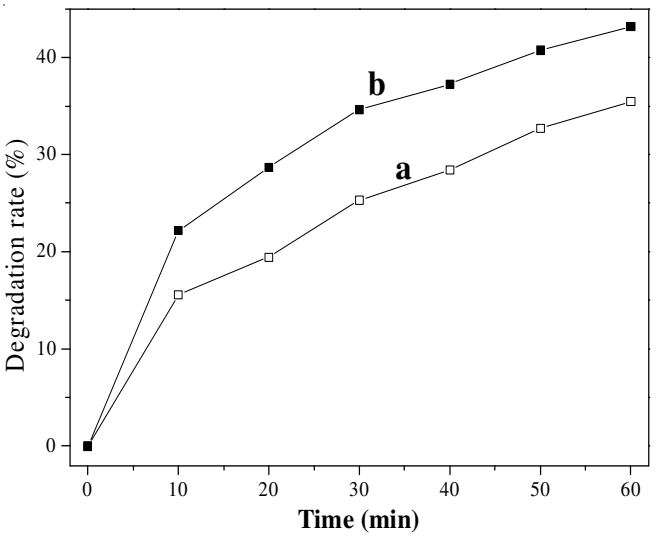


Fig. 6. Degradation of ciprofloxacin and gatifloxacin with ZnS under visible light irradiation

Photocatalytic mechanism on ciprofloxacin: According to the activated process of semiconductor, ZnS spheres the photo-degradation of antibiotics are shown in Fig. 7. First, ZnS was activated under UV light irradiation and generated

electrons/holes pairs. Second, the electrons/holes transferred to the surface of ZnS. And the electrons could be oxidated by the surface traps. The holes could oxide the hydroxyl of solution and form the activated hydroxyl free radical. Last, the $OH^{\bullet}$ can enhance the ciprofloxacin hydroxylation and cause ciprofloxacin decarboxylation reaction, further piperazine ring cleavage and mineralization, finally the structure of ciprofloxacin was destroyed and degraded.

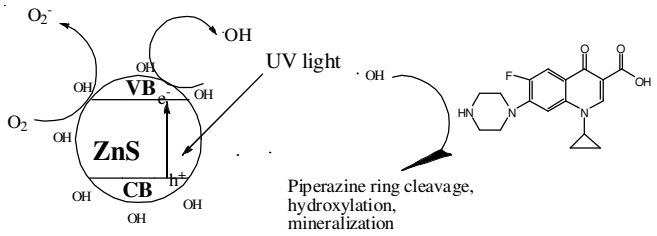


Fig. 7. Scheme of degradation ciprofloxacin with ZnS photocatalyst

Conclusion

Zinc sulfide microspheres were prepared by hydrothermal synthesis method in the presence of polyvinylpyrrolidone as surfactants and the results suggested that the size of prepared particles uniform and dispersed well. The degradation rates of the antibiotics pollutants ciprofloxacin and gatifloxacin were studied under UV light based on the basis of this prepared method. The experimental results showed that the degradation rates on ciprofloxacin and gatifloxacin with the prepared ZnS photocatalysts were 75.31 % and 74.57 % under UV light irradiation 60 min, respectively. However,the degradation rate on ciprofloxacin and gatifloxacin are very low under the visible light irradiation. Thus, it needs to further study the modified methods to enhance the photocatalytic activity of ZnS in visible light range.

REFERENCES

1. F. Tamtam, F. Mercier, B. Le Bot, J. Eurin, Q.T. Dinh, M. Clément and M. Chevreuil, *Sci Total Environ.*, **393**, 84 (2008).
2. R.H. Lindberg, P. Wennberg, M.I. Johansson, M. Tysklind and B.A.V. Andersson, *Environ. Sci. Technol.*, **39**, 3421 (2005).
3. B. Halling-Sørensen, S. Nors-Nielsen, P.F. Lanzky, F. Ingerslev, H.C. Holten-Lützhøft and S.E. Jørgensen, *Chemosphere*, **36**, 357 (1998).
4. A.M. Jacobsen, B. Halling-Sørensen, F. Ingerslev and S.H. Hansen, *J. Chromatogr. A*, **1038**, 157 (2004).
5. S.W. Yang and K. Carlson, *Water Res.*, **38**, 3155 (2004).
6. W. Yu, P.F. Fang and S.J. Wang, *Appl. Surf. Sci*., **255**, 5709 (2009).
7. C. Wang, Y.H. Ao, P.F. Wang, S.H. Zhang, J. Qian and J. Hou, *Appl. Surf. Sci.*, **256**, 4125 (2009).
8. L.W. Yin, Y. Bando, J.H. Zhan, M.S. Li, and D. Golberg, *Adv. Mater*., **17**, 1972 (2005).
9. L.H. Dong, Y. Chu, Y.P. Zhang, Y. Liu and F.Y. Yang, *J. Colloid Interf. Sci.*, **308**, 258 (2007).