Hydrothermal synthesis of Cu-doped ZnS for enhanced photocatalytic degradation of tetracycline under the visible light

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Abstract. Undoped and Cu-doped ZnS were successfully synthesized by hydrothermal method. X-ray diffraction, Fourier transform infrared spectrometer, scanning electron microscope, transmission electron microscopy and UV-vis spectrophotometer were used to characterize the synthesized products. Characterization results indicated that Cu has been successfully doped into ZnS, and the doped material was smaller and had looser surface. In addition, the band gap was decreased from 3.50 eV to 2.27 eV through doping of Cu. Photocatalytic degradation of tetracycline confirmed the superiority of Cu-doped ZnS compared with ZnS, and the electron paramagnetic resonance and quenching experiment were used to investigate the photocatalytic mechanism. ·OH was regarded as the dominant species for tetracycline oxidation degradation. The effects of tetracycline concentration and catalyst dosage were further studied. Also, the good stability of Cu-doped ZnS was demonstrated via the 5-cycle test.

Keywords: Cu-doped ZnS, photocatalysis, degradation, tetracycline.

1. Introduction
As a common antibiotic, tetracycline has been widely used to treat infectious diseases of human and animal [1]. However, tetracycline is difficultly absorbed by organisms, and then mostly expelled through feces and urine [2], hence the possibility of release into various environmental media was significantly improved. The most serious threat of tetracycline in environment is the production of multi-resistant bacterial strains. Unfortunately, the elimination of tetracycline by conventional water treatment methods is ineffective, as a result, tetracycline can still be detected in surface water, drinking water and sludge [3]. Therefore, it is essential to develop the technologies for efficient degradation of tetracycline in water.

Semiconductor photocatalysis plays an important role in treating pollutions. In recent years, transition metal sulfides, especially ZnS, possess the special photocatalytic performance for the highly negative potential of conduction band electrons [4]. However, the band gap of pure ZnS is extremely wide (about 3.54 eV), meaning it cannot be effectively activated except by ultraviolet light. This disadvantage limits the sunlight utilizing ability of ZnS [4, 5]. Transition metals can be used to dope ZnS in order to enhance its photocatalytic performance [6]. Pourreteda et al. suggested that the enhancement mechanism by doping transition metals are the suppression on the recombination of photogenerated carrier charge as well as the formation of suitable band gap and conduction band [7].
Cu is a common transition metal element and Cu ion has a similar ionic radius (0.74 Å) with Zn ion (0.72 Å) [8]. In this case, the forming energy and lattice distortion of Cu doping into ZnS may be relatively low, leading to the good stability [9]. ZnS and Cu-doped ZnS have been synthesized via various methods (chemical precipitating, sonochemical, Successive Ion Layer Absorption and Reaction (SILAR), etc.) and applied for degradation of organics under visible light [10-12]. Previous researches suggested that Cu-doped ZnS commonly revealed the better photocatalytic performance than pure ZnS. Nevertheless, there has rarely been a systematic study about the degradation of tetracycline by Cu-doped ZnS in the presence of visible light yet, which inspires us to investigate the feasibility of Cu-doped ZnS mediated tetracycline removal under visible light.

In this work, firstly, hydrothermal method was used to produce ZnS and Cu-doped ZnS materials. Then the resultants were characterized by different techniques. The photocatalytic performances of two materials were systematically investigated through the degradation experiments of tetracycline under visible light. EPR analysis and quenching experiments were conducted to reveal possible active species and reaction mechanism. This study may provide the insight into Cu-doped ZnS based photocatalytic systems for environmental remediation.

2. Experimental

2.1. Chemicals
All analytically pure ZnCl₂, Cu(NO₃)₂, ethanol, tetracycline and other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd, and deionized water was used throughout the experiments.

Synthesis of samples
NaCl (0.08 mol/L) was dissolved in the solution containing ethanol and ethylene glycol, and then the mixed solution was treated ultrasonic at 50 KHz for 2 hours. After that, ultrasonic treatment was used to dissolve the thiourea (0.016 mol/L) into the solution and then stirred for 2 hours. The solution was heated at 160 °C for 16 hours. ZnS could be obtained from the solution after centrifuging, washing and drying.

The prepared sample (0.15 g) was dissolved with ethanol (50 mL) by ultrasonic treatment at 50 KHz for 2 hours, and CuSO₄ (0.05 g) was dissolved with ethanol (20 mL) by the same method. After mixed these two solutions and stirred for 2 hours, the solution was then heated at 80 °C for 4 hours. Then Cu-doped ZnS nanoparticles could be obtained by the same experimental procedures of obtaining ZnS.

2.2. Characterization
X-ray diffraction (XRD-6100, Shimadzu, Japan) was used to test the crystal structure of the product by a Cu Ka radiation (λ=0.154178nm) with the scan range of 2θ = 20-80°. The chemical structure of the product was analyzed by a Nicolet NEXUS 670 FT-IR (Thermo Nicolet Corporation, VA, USA). The microstructure was observed by the scanning electron microscope (SEM, S4800, Hitachi, Japan) and transmission electron microscopy (TEM, JEM-2100UHR, Hitachi, Japan). Optical property was studied by UV-vis spectrophotometer (TU-1901, Beijing Purkinje General, China). The electron paramagnetic resonance (EPR) analysis was carried out with Bruker A300 spectrometer. 5,5-dimethylpyrroline-oxide (DMPO) was used to capture active radicals.

2.3. Photocatalytic performance of Cu doped and Cu-doped ZnS
The degradation experiments of tetracycline were performed in the Model XPA-VII photocatalytic reactor. Catalyst (0.4 g/L) was added into the tetracycline solution to prepare the solution for photocatalysis experiments, followed by ultrasonic treatment (15 minutes) and continuous stirring (30 minutes) before reaction. The reaction was initiated by the irradiation with a 300W xenon lamp fitted with a filter (> 420 nm). At given interval, 5 mL sample was taken out and the supernatant was isolated by centrifugal separator. The concentration of tetracycline was determined by UV-vis spectrophotometer at 357 nm.
3. Result and discussion

3.1. Characterization of catalyst

Fig. 1 (a) illustrates the XRD patterns of as-prepared samples. Three distinct diffraction peaks at 27.96°, 46.92° and 56.04° can be ascribed to the (110), (220) and (311) crystal surfaces of ZnS with cubic zinc blende structure (JCPDS card, NO.05-0566) [13]. Compared with ZnS samples, the (110) peak of Cu-doped ZnS becomes obviously broadened and weakened, indicating the decline of crystalline degree owing to the doping of Cu [14]. Meanwhile, the peaks of Cu-doped ZnS exhibit slight shift to the high angle. It could be ascribed to the contraction of ZnS crystal lattice caused by Cu$^{2+}$, with a smaller radius, replacing Zn$^{2+}$ [15].

Fig. 1 (b) shows the FT-IR spectra of ZnS and Cu-doped ZnS. Compared with ZnS, the peak of ZnS at 1108 cm$^{-1}$ splits into two peaks at 1126 cm$^{-1}$ and 1056 cm$^{-1}$ because of the doping of Cu [14]. And the peak at 606 cm$^{-1}$ is ascribed to the stretching vibration of Cu-S, which proves that Cu successfully doped into ZnS by replacing part of Zn ions [16].

The results of UV-vis spectrophotometer are shown in Fig 1 (c). Only one obvious absorption region below 380 nm can be observed in ZnS, whereas an strong absorption band at 220 - 850 nm appears in Cu-doped ZnS, implying the potential absorption of visible light. Moreover, the band gap energies of ZnS (3.50 eV) and Cu-doped ZnS (2.27 eV) are respectively estimated by Tauc's relation, as shown in Fig 1 (c).

Fig. 1 (d-f) are SEM and TEM images of ZnS and Cu-doped ZnS. The average particle sizes of ZnS and Cu-doped ZnS are 1 μm and 700 nm respectively. It is significant that the shape of ZnS nanomaterial is well spherical with good uniformity and regularity. Because of the doping of Cu, ZnS becomes looser and has bigger surface area, which might have positive effect on the photocatalytic property.
Fig. 1 (a) XRD patterns, (b) FT-IR spectra, (c) UV-vis reflection spectra and calculated bandgap diagrams for ZnS and Cu-doped ZnS, (d-f) SEM and TEM images of ZnS and Cu-doped ZnS.

3.2. Photocatalytic performance

In order to study the photocatalytic performance, ZnS and Cu-doped ZnS were used for the degradation of tetracycline. The results are shown in Fig. 2 (a). Only 5.9% tetracycline was removed by ZnS. In contrast, Cu-doped ZnS was better in photocatalytic degradation, leading to the final removal efficiency of 77%. The phenomenon was consistent with above characterization result that Cu-doped ZnS performed a better visible light absorption than ZnS. Meanwhile, the relatively rapid removal of tetracycline may be related to some reactive species formed during the photocatalytic reaction.

3.3. Possible photocatalytic mechanism

The photocatalytic reaction mechanism is well known that the electrons of the valence band (VB) move to the conduction band (CB) by photoexitation, as a result of the formation of electron-hole pairs (Eq. (1)). Then the ·O₂⁻ and ·OH are generated by the reaction of electrons and h⁺ respectively (Eq. (2-3)), which were indeed detected by the EPR in Fig. 2 (b-c). Moreover, ·O₂⁻ could also transformed into ·OH through several steps (Eq. (4-5)). ·OH is the highly reactive species degrading tetracycline [17-19].
However, it is easy for electron and hole to recombine (Eq. (6)) [20], which could ultimately limit the formation of ·OH.

\[ X + \text{hv} \rightarrow X (e_{CB}^- + h_{VB}^+) \]  
\[ e_{CB}^- (X) + O_2 \rightarrow \cdot O_2^- \]  
\[ h_{VB}^+ (X) + H_2O \rightarrow \cdot OH + H^+ \]  
\[ H^+ + \cdot O_2^- \rightarrow \cdot OOH \]  
\[ e_{CB}^- + H^+ + \cdot OOH \rightarrow H_2O_2 \rightarrow 2 \cdot OH \]  
\[ e_{CB}^- (X) + h_{VB}^+ (X) \rightarrow X \]

In Cu-doped ZnS, Cu has the ability to trap the electron or hole causing the fewer probability for electron-hole recombination (Eq. (7-10)) [21]. Combined with the result of the quenching test, which used ethylene diamine tetraacetic acid (EDTA) as the scavenger, the photocatalytic elimination efficiency declined dramatically from 69.0% to 17.6% (Fig. 2d). It can be inferred that because EDTA had the ability to catch holes [22], the generation of ·OH was limited, leading to the decrease of photocatalytic degradation.

\[ \text{Cu}^{n+} + e^- \rightarrow \text{Cu}^{(n-1)+} \] (Reduction)  
\[ \text{Cu}^{(n-1)+} + O_2 \rightarrow \text{Cu}^{n+} + \cdot O_2^- \]  
\[ \text{Cu}^{n+} + h^+ \rightarrow \text{Cu}^{(n+1)} \] (Oxidation)  
\[ \text{Cu}^{(n+1)} + \text{OH}^- \rightarrow \text{Cu}^{n+} + \cdot OH \]

3.4. Effect of pollutant concentration on photocatalytic degradation efficiency

Tetracycline with different concentrations (5, 10, 20, 25 mg/L) was respectively used to investigate the corresponding effect. As shown in Fig. 2 (e), the removal efficiency rose up with the increase of concentration from 5 to 20 mg/L, and the optimum abatement (88.8 %) was achieved when the concentration was 20 mg/L. However, the degradation rate decreased once concentration reached 25 mg/L. These phenomena might be due to the reasons as follows. Cu-doped ZnS with abundant active sites could trigger enough reactive species for the degradation of tetracycline at relatively low concentration, in this case, more tetracycline might facilitate the contact with catalyst surface for a better degradation. However, at a high concentration, incoming visible light would be blocked by lots of tetracycline absorbed onto catalyst, leading to the limited photocatalytic degradation reaction.

3.5. Effect of catalyst dosage on photocatalytic degradation efficiency

Varying catalyst dosages (0.2, 0.3, 0.4 and 0.5 g/L) were designed to investigate how catalyst concentrations affect photocatalytic performance, as shown in Fig. 2 (f). It is obvious that with the increase of Cu-doped ZnS dosage, the degradation of tetracycline was constantly accelerated. When the dosages was 0.2 g/L, the removal efficiency was minimum (61.8%) but still over 50%. With the further addition of concentration, degradation effect were all higher than 80%, especially at 0.5 g/L, the best performance was obtained and 95.1% tetracycline was completely removed. Certainly, more catalysts would provide with more active sites for the better utilization of light energy.
Fig. 2 (a) Photocatalytic degradation of tetracycline by ZnS and Cu-doped ZnS, (b-c) EPR spectra of \( \cdot \text{O}_2^\cdot \) and \( \cdot \text{OH} \) in presence of Cu-doped ZnS and visible light, (d) Photocatalytic degradation of tetracycline by Cu-doped ZnS with and without EDTA, (e) Photocatalytic degradation of tetracycline by Cu-doped ZnS under different pollutant concentrations, (f) Photocatalytic degradation of tetracycline by Cu-doped ZnS under different catalyst dosages. Experimental conditions: \([\text{tetracycline}] = 25 \text{ mg/L (a), 10 mg/L (d), 20 mg/L (f), [catalyst]} = 0.4 \text{ g/L (a-e)\.}

3.6. The stability of Cu-doped ZnS
The stability of photocatalyst is worth research toward practical application. Therefore, five-cycle photocatalysis experiments were carried out, and result was illustrated in Fig. 3. After recycling for 5 times, there was only a slight decrease of removal efficiency from 88.8\% to 84.8\%, which may be caused by the mass loss of catalyst. It is apparent that Cu-doped ZnS has a great long-term stability that is favorable to practical application.
Fig. 3 Cycle runs for the degradation of TC. Experimental conditions: [tetracycline] = 20 mg/L, [catalyst] = 0.4 g/L.

4. Conclusion
In this study, ZnS and Cu-doped ZnS were successfully synthesized by hydrothermal method and employed under visible light for tetracycline degradation. Characterization and degradation results suggested that Cu-doped ZnS owned better photocatalytic activity. In the presence of visible light, 0.5 g/L Cu-doped ZnS can be effectively stimulated and remove 95.1% tetracycline within 2.5 h. Furthermore, the excellent stability of Cu-doped ZnS was demonstrated by the cycling experiments. Through the EPR analysis and quenching experiment, ·OH can be deduced as the dominate species for tetracycline oxidation degradation. In general, Cu-doped ZnS is a highly potential photocatalyst for degradation of tetracyline in water.

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