Fabrication of CdS/ZnS/g-C₃N₄ Composites for Enhanced Visible-Light Photocatalytic Degradation Performance

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Abstract. Constructing a heterojunction is an ideal way to modify the photocatalytic efficiency of semiconductor photocatalysts. In this paper, CdS/ZnS/g-C₃N₄ (CZG) ternary composites with different mass ratio of CdS (10%, 20%, 30%) were prepared by cation exchange method using as-synthesized ZnS/g-C₃N₄ and Cd(NO₃)₂·6H₂O as the starting materials. The composition and optical properties were investigated by XRD and photoluminescence spectra (PL). The results showed the ternary heterojunctions possessed faster photo-induced electrons/holes separation efficiency. The photocatalytic experiments exhibited that the obtained ternary composite materials exhibited enhanced visible-light photodegradation efficiency for the degradation of MO aqueous solution. Among the ternary composite materials, the CZG-10% composite displayed the highest photocatalytic performance of 68.52%. The enhanced photodegradation efficiency could be ascribed to the reasonable design of the heterojunction.

1. Introduction
Currently, environmental crisis resulted from organic contaminants in water environment has caused a serious threat to human existence, ecological environment, and sustainable development. Photocatalysis is widely accepted as a potential strategy to solve the terrible environmental issues, because of its high efficiency, low cost, and no secondary pollution [1]. Since reported in 2009, graphite-phase carbon nitride (g-C₃N₄) has drawn much interest due to its advantages of low cost, wide source and easy synthesis. Nowadays, it has been widely applied to decompose water to produce hydrogen and photo-degradation of organic pollutants under visible-light illumination [2, 3].

Simple-phase g-C₃N₄ exhibits good physicochemical stability, suitably optical band gap, and the ability of absorbing visible light. However, pure g-C₃N₄ has a relative wide band gap, which results in the low visible-light utilization rate [4]. Besides, pure g-C₃N₄ can only absorb sunlight with a wavelength less than 460 nm, and shows low photo-induced e/ h⁺ pairs separation rate, which seriously limit its practical applications [5]. Constructing heterojunction is considered as a most promising method to obtain reduced optical band gap and improved photo-induced e/ h⁺ pairs separation efficiency [6]. The ZnS/g-C₃N₄ heterojunction prepared by using ZIF-8 as a template is indeed confirmed to show enhanced MO photodegradation activity under visible light irradiation, the enhanced performance is mainly attributed to the matched band energy position of ZnS and g-C₃N₄, and thus obtaining the enhanced electron/hole pairs transfer and separation efficiency [7, 8]. Nevertheless, the e/ h⁺ pairs recombination efficiency is still high. Therefore, further enhancing the photo-induced electrons/holes separation efficiency is of great significance for the higher photodegradation efficiency.
Because of its narrow band gap (~2.4 eV), unique photoelectric properties, good stability, CdS has broad application prospects in the photocatalytic treatment of wastewater [9]. It is promising to obtain faster electron-hole recombination rate by further coupling ZnS/g-C3N4 and CdS [10, 11]. In this contribution, we prepared CZG ternary composites based on a simple cation exchange reaction. The composition and photochemical properties of the as-prepared photocatalyst were investigated by XRD and PL. MO was used as the simulated pollutant to evaluate the photodegradation performance. The CZG composites exhibited enhanced visible-light photocatalytic efficiency than binary composite owing to the improved photo-induced charge carriers separation efficiency.

2. Experimental Section

2.1. Materials
Melamine, 2-methylimidazole (2-MI), Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), Thioacetamide (TAA), Ethanol, Methanol (CH₃OH), Cd(NO₃)₂·6H₂O, and Methyl orange (MO) were purchased and used directly. The deionized water was used throughout the process.

2.2. Instrumentation
XRD (Shimadzu, Japan) was used to investigate the compositions and phase structure. PL spectra were obtained using an Omni-PL (Zolix, China) spectrometer with an excitation wavelength of 325 nm.

2.3. Synthesis of g-C₃N₄ [12]
Pure g-C₃N₄ was fabricated using a two-step thermal treatment. Typically, a certain amount of melamine was placed into a muffle furnace, and then treated at 550 °C for 2 h. Moreover, the as-obtained yellow bulk g-C₃N₄ was further treated under the similar conditions. The obtained white g-C₃N₄ nanosheets were grind into powder for following synthesis.

2.4. Synthesis of ZnS/g-C₃N₄ [13]
In a typical experiment, a certain amount of Zn(NO₃)₂·6H₂O and 2-MI were dispersed in methanol by ultrasound. After the mixture was aged for a day, the obtained ZIF-8 was collected by centrifugation. The as-obtained g-C₃N₄, calculated amount of ZIF-8 and 0.376 g TAA were dispersed into 60 mL absolute alcohol, and transferred into a 100 mL poly tetra fluoroethylene autoclave, and then the mixture was heated at 90 °C for 1 h. Finally, the product was obtained by centrifugation.

2.5. Synthesis of CdS/ZnS/g-C₃N₄
Typically, 0.2 g ZnS/g-C₃N₄ was dispersed in 10 mL deionized water, and then a certain molar amount of Cd(NO₃)₂·6H₂O was added to the above mixture. After stirring for 30 minutes, the suspension was kept in an oil bath at 80°C for 6 h. Subsequently, it was collected by centrifugation, washed with water and ethanol three times, separately. Finally, several CdS/ZnS/g-C₃N₄ composites with different mass ratios of CdS (10%, 20%, 30%) were prepared, and recorded as CZG-X% (X=10, 20, 30).

2.6. Evaluation of Photocatalytic Performance
The evaluation of photocatalytic activity of the obtained sample was performed by using a 500 W Xenon lamp as the light source and MO as the simulated pollutant. Typically, 50 mg as-obtained samples were completely added into 50 mL MO aqueous solution (10 mg/L), and stirred for 1 h in the dark to realize the adsorption-desorption equilibrium. After the start of irradiation, 4 mL of reaction solution at every 20 min intervals was taken out and filtered to measure the absorbance at 464 nm on a UV-Vis spectrophotometer.
3. Results and Discussion

X-ray diffraction (XRD) is firstly used to determine the composition and phase purity of the as-prepared samples. As shown in figure 1, for g-C_3N_4, two obviously characteristic peaks can be fitted located at 13.7° and 27.4°, respectively, which correspond to (100) and (002) crystal planes (JCPDF No. 87-1526) [14]. Simultaneously, the two characteristic peaks of g-C_3N_4 appear in all other samples. Additionally, it can be observed that the peaks at 47.1° and 58.2° appear in the composite materials, which are ascribed to the characteristic peaks of the (220) and (311) diffraction planes of cubic ZnS (JCPDF No. 05-0566) [15], separately. Both ZnS/g-C_3N_4 and CZG ternary composites only display the characteristic peaks of g-C_3N_4 and ZnS without impurity phases, nevertheless, the typical diffraction peaks located of CdS are not enough strong to be clearly observed.

![XRD spectra of g-C_3N_4, ZnS/g-C_3N_4, and ternary composites.](image)

As we all know, PL spectra are usually used to analyse the photo-induced carrier separation efficiency of photocatalysts. Figure 2 shows the PL spectra of ZnS/g-C_3N_4 and CZG ternary composites with different mass ratios of CdS. After coupling ZnS/g-C_3N_4 and CdS, the CZG ternary composites shows obvious fluorescence quenching compared with ZnS/g-C_3N_4. The fluorescence quenching can be attributed to the reduced recombination rate of light-induced e/h^+ pairs in the composite systems, and thus improving the photocatalytic activity. When the mass proportion of CdS in the ternary composites is 10%, the PL intensity is lowest, indicating that the photocatalytic performance may be obtained using CZG-10% as photocatalyst.

![PL spectra of ZnS/g-C_3N_4, CZG-20%, CZG-30%, and CZG-10%.](image)
In order to further verify the photocatalytic performance towards to MO, the ZnS/g-C₃N₄ and CZG ternary composites with different ratios of CdS were used as the photocatalysts. It can be seen from figure 3 that MO is difficult to be degraded in the absence of photocatalysts, indicating that the self-degradation of MO is negligible under experimental conditions. After adding the ZnS/g-C₃N₄ binary composite to the system, it can be seen that 60.25% MO is degraded within 160 min. After coupling ZnS/g-C₃N₄ and CdS, more obvious photodegradation activities are observed for CdS/ZnS/g-C₃N₄, among them, CZG-10% shows the highest photocatalytic performance of 68.52%, which are consistent with the PL test results.

In order to investigate the potential practical application, it is necessary to carry out the consecutive four times recycling experiments [16]. As shown in figure 4, after every cycle experiment, the degradation efficiency of MO only shows slight decrease. The result illustrates that CZG-10% possesses excellent stability in the process of photodegraded reaction, which is beneficial for the practical application of photocatalysts.
In order to further understand the reaction kinetics in the experimental process, the reaction rate constants of ZnS/g-C$_3$N$_4$ and CZG ternary photocatalysts were calculated through the following equation:

$$-\ln(C/C_0) = kt$$

Here, $C_0$ and $C$ are the equilibrium content of MO and the actual content of MO at a given time $t$. The relationship between MO content and time is shown in figure 5. Under visible light, the ternary CdS/ZnS/g-C$_3$N$_4$ composites showed higher degradation rate than binary ZnS/g-C$_3$N$_4$ composite. The photocatalytic rate constant of CZG ternary and ZnS/g-C$_3$N$_4$ composites for the photodegradation process can be figured out from the slope of the kinetic diagram, among them, it can be observed that CZG-10% displayed the highest reaction rate constant.

![Figure 5. Relationship between photocatalytic degradation rate of MO and time in the presence of different photocatalysts.](image)

**4. Conclusions**

In summary, CZG ternary composites with different mass proportions of CdS were prepared by simple cation exchange reaction. Under simulated experimental conditions, the ternary composites displayed enhanced the photocatalytic degradation efficiency of MO compared with the binary composite. The enhanced photocatalytic performance is attributed to the fabrication of a heterojunction among CdS, ZnS and g-C$_3$N$_4$ based on their well-matched band structure, and thus photo-generated $e^-/h^+$ pairs can be better separated. Here, the construction of CZG ternary composites has a good effect on the photodegradation of organic pollutants.

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