Enhanced Visible-Light-Induced Photocatalytic Performance of g-C₃N₄/ZnS/CuS Ternary Composite for Environmental Remediation

Ying Si*, Xiaoxian Zhang, Ping Li, Shuwang Duo#
Jiangxi Key Laboratory of Surface Engineering, Jiangxi Science and Technology Normal University, Nanchang, Jiangxi 330013, China

* 15736751035@163.com; # swduo@imr.ac.cn

Abstract: The inherent drawback of high photo-induced electron-hole pair recombination rate restricts the photocatalytic performances of graphitic carbon nitride (g-C₃N₄). Here, in this work, g-C₃N₄/ZnS/CuS ternary nanocomposites with different CuS concentration were successfully fabricated by a hydrothermal process and subsequent followed by a cation exchange reaction. The as-synthesized samples were characterized by the techniques of XRD, SEM, DRS, FT-IR and PL. Characterization results show a much more efficient electron-hole pair separation rate of g-C₃N₄/ZnS/CuS, the g-C₃N₄/ZnS/CuS (8%) sample shows the best photocatalytic performance for degradation of Rhodamine B (RhB), which is about 1.6 times higher than that of g-C₃N₄/ZnS and 6.2 times higher than that of pure g-C₃N₄, respectively. The high photodegraded activity is attributed to the important role of ZnS and CuS acted as electron co-catalysts, which retard the fast recombination of photo-generated holes and electrons, resulting in higher photodegraded activity than pure g-C₃N₄. Our research work indicates that the heterostructured formation of g-C₃N₄, ZnS and CuS is helpful for the fabrication of g-C₃N₄-based photocatalysts with enhanced visible light photocactivity.

1. Introduction
Owing to continuous increasing of environmental pollutants as the development of industry [1], development of green route to decompose these pollutants has becomes a hot research topic. So far, many methods have been reported to achieve the degradation of organic pollutants, including without limitation physical or chemical treatment, or biological technology. Among there ported methods, Solar-driven photocatalysis is widely considered as an efficient and environmentally friendly technology for completely degradation of organic pollutants [2]. In recent years, owing to the potential application value of semiconductor materials in the field of photocatalytic degradation, various semiconductor photocatalytic materials have been explored to especially obtain visible-light photocatalysts with efficient photodegradation activity [3-6].

Recently, graphitic carbon nitride (g-C₃N₄) has been widely considered to be a prominent photocatalyst candidate due to its excellent thermal and chemical stability, non-toxicity, visible-light response and low cost [7-9]. Nevertheless, the photocatalytic efficiency of pristine g-C₃N₄ is seriously limited by the rapid recombination rate of electron-hole pairs [10]. To reduce the undesirable recombination rate of photo generated electron-hole pairs and elevate photocatalytic efficiency, pristine g-C₃N₄ was coupled with all sorts of metal sulfides to form composites, which can promote the separation of photoreduced charge carriers, and consequently improve the photodegradation...
efficiency of g-C$_3$N$_4$ [11]. ZnS can rapidly generate charge carriers and has more negative CB position
than of g-C$_3$N$_4$, as a result, the g-C$_3$N$_4$/ZnS composite has been verified to exhibiting enhanced
photocatalytic efficiency under visible light irradiation [12-15]. However, the g-C$_3$N$_4$/ZnS composite
still possesses rapid recombination rate of photo generated electron-hole pairs [16], which may restrain
the photodegradation efficiency of g-C$_3$N$_4$/ZnS composite on a certain level. CuS is an important
semiconducting nanomaterial having direct band gap with good photosensitivity, excellent physical
and chemical stability [17]. Jiang et al. fabricated g-C$_3$N$_4$/ZnS/CuS heterojunctions through a
solvothermal process and subsequently a microwave (MW) assisted precipitation, which exhibited
substantially enhanced visible light photodegradation efficiency [18]. Nevertheless, the reported
methods typically involve a complicated preparation procedure, which possibly restrain the practical
applications. Therefore, the exploration of a simple and effective approach to prepare g-C$_3$N$_4$/ZnS/CuS
composite photocatalysts is still strongly desirable.

In this contribution, we adopted a facile approach for preparing g-C$_3$N$_4$/ZnS/CuS composite
photocatalyst by a hydrothermal method and subsequently a cation exchange reaction. The
morphology, microstructure and photocatalytic properties of the as-prepared photocatalyst was
comprehensively characterized by XRD, SEM, DRS, FT-IR and PL. Rhodamine B (RhB) was adopted
as the model to evaluate the photocatalytic efficiency of the photocatalyst. The g-C$_3$N$_4$/ZnS/CuS
composite photocatalyst exhibited enhanced visible-light photocatalytic efficiency than both pure-
g-C$_3$N$_4$ and g-C$_3$N$_4$/ZnS binary composite owing to the enhanced separation efficiency of photo-induced
electron-hole pairs in g-C$_3$N$_4$/ZnS/CuS composite.

2. Experimental

The starting materials were of analytical grade and employed without any purification. The fabrication
of g-C$_3$N$_4$/ZnS binary composite by a two-step procedure, g-C$_3$N$_4$ was first obtained by heat treatment
of melamine at 550°C for 2 h with a heating rate of 5°C/min in an alumina crucible under air
atmosphere [19]. Finally, then the pale-yellow product can be collected by mechanical grinding
treatment.

g-C$_3$N$_4$/ZnS composite was synthesized at a molar ratio of 1:1 by hydrothermal process as follows
[18]. Typically, thioacetamide, zinc acetate dehydrate and the precalculated g-C$_3$N$_4$ were added into
deonized water and stirred for 0.5h at ambient temperature. The obtained mixture was then transferred
into a stainless-steel Teflon-lined autoclave for hydrothermal treatment at 170°C for 5 h. Final g-
C$_3$N$_4$/ZnS was obtained by centrifugation and drying at 60 °C for one night.

g-C$_3$N$_4$/ZnS/CuS composite was further fabricated by a cation exchange reaction [20]. Typically,
the as-prepared g-C$_3$N$_4$/ZnS were dispersed in water and ultrasonicated for 30 min, then a certain
amount of Cu(NO$_3$)$_2$ aqueous solution was added dropwise into the mixture and the reaction
temperature was kept at 80°C for 6 h. Finally, the dark green powder was collected by centrifugation.
The CuS molar ratios were 3, 5 and 8 mol%, respectively.

The as-synthesized materials were characterized by X-ray diffraction (XRD, Shimadzu XRD-6100,
Japan), scanning electron microscopy (SEM, Zeiss Sigma, Germany), UV-Vis diffuse reflectance
spectra (DRS, lambda750), FT-IR (Spectrometer PerkinElmerSpectrum Two, USA) and
Photoluminescence spectra (PL, Zolix LSP-X500A).

The photocatalytic performance was evaluated by degrading of RhB (10 mg L$^{-1}$) in an optical
reactor. The visible light was provided by xenon lamp with a 420nm cut off filter. 4 ml of reaction
solution was taken out at 20 min intervals and followed by filtering with at0.22-μm microspore filter to
remove the photocatalyst. The RhB concentration can be analyzed by UV-vis spectrophotometer to
record the absorbance at 464 nm.

3. Results and Discussion

X-ray diffraction (XRD) measurements are first applied to examine the crystalline phase and phase
purity of the as-prepared samples in this study. Figure 1a shows XRD spectra of pure g-C$_3$N$_4$, ZnS,
g-C$_3$N$_4$/ZnS binary composite, and g-C$_3$N$_4$/ZnS/CuS ternary composite with different CuS concentration.
Obiously, pure $g$-C$_3$N$_4$showstwo characteristic peaks, which located at 13.0° and 27.4°, corresponding to the (100) and (002) diffraction planes, respectively [21]. For pure ZnS, six main diffraction peaks at 28.7°, 33.3°, 47.7°, 56.5°, 69.7° and 77.0° are presented, which can be indexed to (111), (200), (220), (311), (400) and (331) diffraction planes of cubic ZnS according to JCPDS card (No. 05-0566), respectively. The characteristic peak of $g$-C$_3$N$_4$ (27.4°) is very close with that of ZnS (28.7°). In addition, the peak intensity of CuS is weak and inconspicuous in the XRD spectra, which is probably attributed to its relatively low concentration and crystallinity, or high dispersion in the system [20]. EDS (Figure 1b) analysis further confirms that $g$-C$_3$N$_4$/ZnS/CuS ternary composite mainly consist of C, N, Zn, S and Cu elements. These results of XRD and EDS indicate the successful fabrication of the target product.

![Figure 1](image-url)

**Figure 1.** XRD spectra (a) of the pristine $g$-C$_3$N$_4$, ZnS, $g$-C$_3$N$_4$/ZnS, and $g$-C$_3$N$_4$/ZnS/CuS with different CuS concentration, (b) EDS spectrum of $g$-C$_3$N$_4$/ZnS/CuS(8%), respectively.

The Fourier transform infrared spectroscopy (FT-IR) is performed to further verify the existence of $g$-C$_3$N$_4$ in the composite photocatalysts. Figure 2 shows the FT-IR patterns of pristine-$g$-C$_3$N$_4$, $g$-
C$_3$N$_4$/ZnS and g-C$_3$N$_4$/ZnS/CuS composites with various CuS content ratios. In the pure g-C$_3$N$_4$, the peak at about 810 cm$^{-1}$ is related to the bending vibration characteristic of heptazine units. The spectral band at the 1200-1600 cm$^{-1}$ is attributed to the typical tensile pattern of the aromatic CN heterocycles, while, the broad band around 3200 cm$^{-1}$ is assigned to the stretching vibration mode of a mine groups [22]. The main characteristic peaks of g-C$_3$N$_4$ can be clearly seen in binary and ternary composite photocatalysts, which have no obvious change after combination with ZnS and CuS. The results illustrate that the structure of g-C$_3$N$_4$ can be well maintained in the composites.

![Figure 2. FT-IR spectra of the pristine g-C$_3$N$_4$, ZnS, g-C$_3$N$_4$/ZnS and g-C$_3$N$_4$/ZnS/CuS with different CuS concentration.](image1)

![Figure 3. UV-vis diffuse reflectance spectra of the pristine g-C$_3$N$_4$, ZnS, g-C$_3$N$_4$/ZnS, and g-C$_3$N$_4$/ZnS/CuS with different CuS concentration.](image2)

The UV-vis diffuse reflectance spectra (DRS) are utilized to measure the optical absorbance of g-C$_3$N$_4$, ZnS, g-C$_3$N$_4$/ZnS, and g-C$_3$N$_4$/ZnS/CuS composite photocatalyst, which are shown in Figure 3. Obviously, it could be seen that ZnS exhibits absorption in the UV region due to its intrinsic bandgap absorption. However, for g-C$_3$N$_4$/ZnS, the absorption shifts significantly to visible light region and its
adsorption at wavelength \(<400\) nm becomes greater than g-C_3N_4. After loading CuS, the absorption in the visible light region is further enhanced with the increasing concentration of CuS, displaying that g-C_3N_4/ZnS/CuS has best visible-light absorption capability than g-C_3N_4/ZnS, especially when the load ratio of CuS is 8%, which is maybe attributed to the fabrication of the g-C_3N_4/ZnS/CuS heterojunction. The enhanced adsorption capability is responsible for the improvement the visible-light utilization efficiency and consequently results in enhancement of the visible-light-induced photodegradation efficiency.

It is well known that photoluminescence (PL) spectroscopy analysis is a common method to investigate the photogenerated electron-hole pair separation and recombination behavior of photocatalysts. Figure 4 presents the PL spectra of the pristine g-C_3N_4, g-C_3N_4/ZnS, and g-C_3N_4/ZnS/CuS composite with an excitation wavelength of 325 nm, respectively. Pristine g-C_3N_4 exhibited a strong peak at around 450 nm, yet the introducing of ZnS causes a slight decrease of PL peak intensity, and the intensity further decreases drastically with the increasing load ratio of CuS, which indicates that the separation rate order of photo-generated e^-h^+ pairs should be pure g-C_3N_4<g-C_3N_4/ZnS<g-C_3N_4/ZnS/CuS. This result provides a direct evidence for synergistic effect among g-C_3N_4, ZnS and CuS, making the photogenerated electrons from g-C_3N_4 transfer to ZnS and CuS, thus significantly promote the charge separation, which consequently leads to the enhancement of photocatalytic efficiency.

![Figure 4. Photoluminescence spectra of the pristine g-C_3N_4, g-C_3N_4/ZnS and g-C_3N_4/ZnS/CuS with different CuS concentration.](image)

To further prove the enhanced visible-light photodegradation efficiency of the g-C_3N_4/ZnS/CuS composite, the photocatalytic degradation of RhB in aqueous solution under visible light irradiation using no catalyst, pure g-C_3N_4, ZnS, g-C_3N_4/ZnS and g-C_3N_4/ZnS/CuS with different CuS concentration as photocatalyst are shown in Figure 5. It can be seen that the concentration of RhB shows no obvious change in the absence of catalyst. Individual ZnS has no response to the visible light due to inherent wide band gap, and consequently presents inconspicuous visible light photocatalytic efficiency. Pristine g-C_3N_4 with a narrowband gap also exhibits weak photodegradation efficiency for RhB under visible light irradiation. Nevertheless, the photodegradation efficiency using g-C_3N_4/ZnS composite increases to 26.35% compared with that of pristine g-C_3N_4 within 120 min under visible light irradiation. Moreover, after CuS is further loaded on g-C_3N_4/ZnS, the RhB photodegradation...
efficiency increases drastically with the increasing load ratio of CuS, which indicates that a synergistic effect exists in among g-C3N4, ZnS and CuS within the ternary composite. When CuS load ratio increases to8%, the g-C3N4/ZnS/CuS composite shows the highest degradation rate constant, which is about 6.2 times and 1.6 times higher than that of pristine g-C3N4 and g-C3N4/ZnS, respectively.

![Figure 5. Photocatalytic performances of the pristine g-C3N4, ZnS, g-C3N4/ZnS and g-C3N4/ZnS/CuS with different CuS concentration for the degradation of RhB (10 mg/L) under visible light irradiation.](image)

4. Conclusion
In summary, g-C3N4/ZnS/CuS composite were easily fabricated through hydrothermal process and further cation exchange reaction between ZnS and Cu2+ ions in aqueous solution. Systematic optical measures and photocatalytic experiments for pristine g-C3N4, ZnS, g-C3N4/ZnS and g-C3N4/ZnS/CuS show the as-prepared g-C3N4/ZnS/CuS composites exhibit wider adsorption edge for visible light, lower charge recombination rate and enhanced photocatalytic activity for RhB compared with the corresponding single- and two-component systems due to the synergetic effect in the ternary composite. Under visible light irradiation, when the concentration of CuS in the ternary composite is 8%, g-C3N4/ZnS/CuS shows the significantly enhanced degradation efficiency, which is about 6.2 times higher than that of pristine g-C3N4 and 1.6 times higher than that of g-C3N4/ZnS, respectively. To sum up, the synthesized g-C3N4/ZnS/CuS composite can be utilized as an effective visible-light photocatalyst for environmental remediation.

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