***Facile fabrication of novel porous graphitic carbon nitride/copper
sulfide nanocomposites with enhanced visible light driven
photocatalytic performance***

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Abstract

In this work, a novel organic–inorganic heterostructured photocatalyst: porous graphitic carbon nitride (g-C₃N₄) hybrid with copper sulfide (CuS) had been synthesized via a precipitation-deposition method at low temperature for the first time. UV-Vis spectroscopy revealed the porous g-C₃N₄/CuS nanocomposites showed a strong and broad visible light absorption. Furthermore, the g-C₃N₄/CuS nanocomposites showed higher photocatalytic activity in the photodegradation of various organic dyes than that of pure g-C₃N₄ and CuS, and the selected sample of g-C₃N₄/CuS-2 exhibits the best photocatalytic activity under visible light. The good photocatalytic activity could be ascribed to the matching of the g-C₃N₄ and CuS band gap energies. Besides, photoluminescent spectra and photoelectrochemical measurements also proved that the CuS/g-C₃N₄ could greatly enhance the charge generation and suppress the charge recombination of photogenerated carriers. According to the experimental result, a possible photocatalytic mechanism has been proposed. Due to the high stability, the porous g-C₃N₄/CuS could be applied in the field of environmental remediation. Our work highlights that coupling semiconductors with well-matched band energies provides a facile way to improve the photocatalytic activity.

Keywords: g-C₃N₄, CuS, porous g-C₃N₄/CuS nanocomposite, heterojunction, semiconductor photocatalyst.

1. Introduction

In recent years, semiconductor photocatalysis has received considerable attention as a green technology for green energy production or water purification since Fujishima and Honda found that water could be split into hydrogen (H_2) using titanium dioxide (TiO_2) as photoanode [1-3]. Owing to its unique characteristics such as low cost, nontoxicity and high stability, TiO_2 has been considered as a most promising semiconductor [4]. However, the large band gap of TiO_2 (3.2 eV) restricts the absorption in the ultraviolet region, which accounts for only ~5 % of the entire solar spectrum [5]. Therefore, numerous visible light respond photocatalysts have attracted considerable attention to extend the light response range [6-9].

Graphitic carbon nitride ($g-C_3N_4$), with a narrow band gap of ~2.7 eV, is considered as a promising metal-free polymeric photocatalyst owing to its good thermal, chemical, photochemical stability and low cost in synthesis [10]. However, the photocatalytic activity of $g-C_3N_4$ is still restricted by the sunlight absorption and high recombination rate of photoinduced electron-holes. In order to overcome these drawbacks, several routes have been developed to further enhance the photocatalytic activity of $g-C_3N_4$, like doping some elements [11,12], loading some noble metal [13,14] or combining with heterogeneous semiconductors [15,16]. In particular, forming a heterojunction with $g-C_3N_4$, such as $g-C_3N_4/SrTiO_3$ [17], $g-C_3N_4/SnO_2$ [18], $g-C_3N_4/ZnO$ [19], $g-C_3N_4/TiO_2$ [20], $g-C_3N_4/CdS$ [21] and $g-C_3N_4/BiOBr$ [22], is an effective strategy to enhance the photocatalytic activity. Unfortunately, most of them either could not remarkable extend the optical absorption, or ignore the influence of

structure and morphology of g-C₃N₄ to the photocatalytic properties. As we know, bulk g-C₃N₄ exhibits low photocatalytic efficiency owing to its low surface area [23], by construction of porous or hierarchical nanostructures is considered as a quite promising strategy to achieve satisfactory catalytic efficiency as it could increase the active surface area of g-C₃N₄ [24].

On the other hand, nanostructured metal sulfide-based photocatalysts have attracted extensive attentions due to the ability at rapidly and efficiently remove organic pollutants in aqueous systems. Among them, copper sulfide (CuS), with a relatively narrow band gap, is a nontoxicity, good photosensitivity, and excellent physical and chemical stability, eco-friendly and economic suitable materials [25-27], which make it as a potential candidate for visible light photocatalysis. However, like most single semiconductor photocatalyst, high rate of electron-hole recombination greatly hinders its practical applications as photocatalysts.

Hence, we take the structure g-C₃N₄ into account and report an in situ precipitation-deposition route to prepare a novel organic-inorganic hererostructured photocatalyst: porous g-C₃N₄ hybrid with CuS for the first time in this study. By this way, it not only improved the photogenerated charges, but also extended the optical absorption. The as-prepared porous g-C₃N₄/CuS exhibited an enhanced photocatalytic performance toward the degradation of various organic dyes than the individual g-C₃N₄ and CuS under visible light irradiation owing to its forming a heterojunction. Furthermore, the possible photocatalysis mechanism of the enhanced photocatalytic properties of g-C₃N₄/CuS also was discussed.

2. Experimental section

2.1 Chemicals

Urea (Sinopharm Chemical Reagent, AR grade 99.0 %), thioacetamide (Sinopharm Chemical Reagent, AR grade 99.0 %), copper nitrate trihydrate (Aladdin, AR grade 99.0 %), rhodamine B (RhB, Aladdin, AR grade), Methyl orange (MO, Aladdin, 96.0 %), all other reagents used in this work were analytically pure and used without further purification.

2.2 Preparation of porous g-C₃N₄/CuS nanocomposites

The porous g-C₃N₄ was prepared by direct heating of urea in a semi-closed alumina crucible under ambient pressure in air. In detail, 8 g of urea was pretreated at 80 °C for 24 h and then the as-prepared urea was calcined at 500 °C for 4 h with the heating rate of 2.3 °C/min. After calcination, the faint yellow product was further collected, washed with nitric acid, deionized water, ethyl alcohol and dried in 60 °C for one night.

The porous g-C₃N₄ hybrid with CuS was synthesized via a wet-chemical method at low temperature, as shown in scheme 1. In a typical experimental procedure, 100 mg g-C₃N₄ was mixed with 40 mL deionized water by ultrasonication for 30 mins to form a faint yellow suspension. The 2 mm (0.482 g) Cu(NO₃)₂·3H₂O was added to the above suspension with another 15 mins and the color of the suspension quickly changed to blue. After that, the above suspension was annealed at 60 °C with vigorous stirring. At the same time, 8 mm (0.600 g) thioacetamide (TAA) was dissolved in 20

mL deionized water to form a colorless solution. Subsequently, the TAA solution was quickly injected into blue suspension and the reaction contained for 10 mins. The mixture green black mixture precipitate was collected by centrifugation with deionized water and ethanol for 3 times, respectively. Finally the precipitate was dried at 60 °C for a night under vacuum. Products prepared with different amount of porous g-C₃N₄ (100, 200 and 300 mg) were labeled as g-C₃N₄/CuS-1, g-C₃N₄/CuS-2 and g-C₃N₄/CuS-3. For blank control experiments, pure CuS was also prepared by the procedure described above.

2.3 Characterization methods

The crystal structures of the samples were tested by X-ray diffraction (XRD, D/max 2550, Rigaku Corporation). The infrared spectrum of absorption was obtained by fourier transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Nicolet Corporation). The morphologies of the as-prepared samples were examined by emission scanning microscopy (SEM, Nova Nano SEM 230, FEI Electron Optics B.V) and field emission transmission electron microscopy (TEM, JEM-2100F, Japanese electronics co. LTD). Photoluminescence spectra of the photocatalysts were measured on a fluorescence spectrophotometer (PL, F-4600, Japan's Hitachi LTD). The UV-Vis spectra of the catalysts were obtained on a UV-Vis spectrometer (Evolution 220, Thermo Fisher Scientific). Surface chemical compositions and chemical status were analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha 1063, Thermo Fisher).

2.4 Photocatalytic experiments

The photocatalytic activity of porous g-C₃N₄/CuS nanocomposites samples were evaluated via photocatalytic decomposition of various organic dyes (RhB, MB) in an aqueous solution under visible-light irradiation ($\lambda \geq 420$ nm). Visible irradiation was obtained via a 300 W xenon lamp with a 420 nm cut-off filter. In each experiment, the photocatalysts of 10 mg was mixed with a 15 mL organic dyes aqueous solution (10 mg/L). Prior to irradiation, the suspensions were magnetically stirred in dark for 30 mins to obtain the absorption-desorption equilibrium between the photocatalyst and organic dye. At the photoreactions, the organic dye solution with photocatalyst was continuously stirred with magnetic stirred. And for irradiation time intervals of 15 mins, the 5 mL suspensions were sampled and centrifuged to remove the particles. The concentrations of RhB and MB were determined by recording the absorbance at the 554 nm and 665 nm via a UV-Vis spectrophotometer, respectively. After that, the organic dye aqueous solution was ultrasonic with the separated photocatalyst and the suspension was poured into the quartz glass vessel to begin the next run. Besides, the experiment of stability and main oxidative species in the photocatalytic process would be also carried out. And the experiment process would be described in detail subsequently.

2.5 Photoelectrochemical measurements

The electrochemical impedance spectroscopy (EIS) were measured on a CHI660E electrochemical workstation using a conventional three electrode system with the as-prepared photocatalyst coated on ITO conducting glass as a working electrode , a platinum foil as a counter electrode and Hg/Hg₂Cl₂/sat. KCl as a

reference electrode, respectively. The electrolyte was immersed in 0.1 M Na₂SO₄ aqueous solution. The working electrode was prepared as follows: 3 mg of the catalyst was dispersed in 50 uL ethanol and nafion (5 wt.% in mixture of lower aliphatic alcohols and water, contains 45% water, Aldrich) homogeneously under sonication for 30 mins to make slurry. The slurry was dip-coated on the conducting side of ITO glass and calcined at 200 °C for 1 h in a vacuum oven. The active area of the electrode was 1 cm². EIS were conducted over an amplitude of the applied sine wave potential of 5 mV and a frequency of 0.1–10⁶ Hz.

3. Results and discussion

3.1 Characterization of g-C₃N₄/CuS nanocomposites

Typical X-ray diffraction of porous g-C₃N₄, CuS, and porous g-C₃N₄/CuS nanocomposites was shown in Fig. 1. The results indicated that the photocatalysts were well crystallized without other impurities. All the peaks in the pure CuS could be assigned to hexagonal phase (JCPDS card No. 06-0464). The pattern of pure g-C₃N₄ displayed a typical feature of two peaks at 13.2° and 27.4° which can be indexed as (110) and (002) diffractions, corresponding to the periodic array of the in-planar tri-s-triazine and the inter-plannar stacking of aromatic systems, respectively. Compared with the pure g-C₃N₄, the main characteristic diffraction peaks of g-C₃N₄/CuS nanocomposites did not obviously change after CuS being hybridized with g-C₃N₄. Meanwhile typical crystalline of CuS obviously emerged in all

nanocomposites. These results indicated that the CuS was successfully hybrid with g-C₃N₄ by the present synthetic route.

The components of as-prepared composite catalysts were further confirmed by FT-IR. Here the as-prepared sample of g-C₃N₄/CuS-2 was chosen as the example to represent the g-C₃N₄/CuS nanocomposites. As showed in Fig. 2, the FTIR spectra of the porous g-C₃N₄, CuS and g-C₃N₄/CuS-2 nanocomposites. In the FTIR spectra of pure g-C₃N₄, a series of peaks located between 1200 cm⁻¹ and 1500 cm⁻¹ could be attributed to the typical stretching vibration of CN heterocycles. The peaks at 1630 cm⁻¹ and 3150 cm⁻¹ could be attributed to C=N stretching vibration modes and indicatives of NH stretching vibration modes, respectively. Besides, the peak at 808 cm⁻¹ was belonging to the s-triazine ring modes. In the spectra of CuS, the peak at 613 cm⁻¹ was orientated to the vibration of Cu-S bands and the peak at 1627 cm⁻¹, 3450 cm⁻¹ and 1100 cm⁻¹ could be ascribed to the hydroxyl groups of hydrated oxide surface and TAA on the surface of CuS, respectively [28]. Furthermore, all characteristic absorption peaks of g-C₃N₄ and CuS appeared in the g-C₃N₄/CuS, which is well in accordance with the XRD analysis and indicated that there was no structural change of g-C₃N₄ in the preparation process.

The chemical valence state and bond configuration of novel g-C₃N₄/CuS heterojunctions was analyzed by X-ray photoelectron spectrum. As shown in Fig. 3, the survey spectrum, C, N, S, Cu and O were detected in the sample of g-C₃N₄/CuS-2, and the O on the surface of the g-C₃N₄/CuS-2 was came from the adsorption of oxygen from the atmosphere. Besides, the Cu, S and N were only detected in the

spectra of g-C₃N₄ and CuS, respectively. These results were well in accordance with the chemical composition of the as-prepared sample, which also confirmed by the XRD and FTIR analysis. The high resolution X-ray photoelectron spectra of C 1s were shown in Fig. 3b. CuS showed only one peak at 284.8 eV, which could be assigned to the external hydrocarbon contamination. While in the spectra of g-C₃N₄ and g-C₃N₄/CuS-2 had the other peak at around 288.2 eV and 288.6 eV were came from the N-C=N in its chemical bone structure, which indicated the existence of g-C₃N₄. Besides, the C 1s binding energy of g-C₃N₄/CuS-2 was slightly higher than that of g-C₃N₄. In the N 1s high resolution XPS spectra of g-C₃N₄, several peak at 398.8 eV, 399.8 eV, 400.9 eV and 404.6 eV which could be ascribed to N (C-N=C) groups (sp² bonded), tertiary nitrogen N-(C)₃ groups, C-N-H amino groups and the charging effects, respectively. Notably, the N 1s binding energy of g-C₃N₄/CuS-2 was slightly higher than that of g-C₃N₄, which is similar to the C 1s peak of N-C=N groups at 288.3 eV. Meanwhile, combined with the slight shift in the C 1s and N 1s spectra, the result represented the interactions between CuS and g-C₃N₄ [29], which may be the chemical bonds of Cu-S-N or Cu-S-C. In comparison, the Cu 2p_{3/2} and Cu 2p_{1/2} peaks of CuS appeared at 932.8 eV and 952.7 eV, respectively, which were highly than the corresponding binding energy of g-C₃N₄/CuS-2 at 932.1 eV and 952.0 eV, respectively. And the S 2p_{3/2} and S 2p_{1/2} peaks at CuS and g-C₃N₄/CuS-2 had the same shift tendency. Based on above analysis, with the combination of XRD, FTIR investigation, the conclusion indicated that the g-C₃N₄/CuS was not only a physical mixture but also with interactions between CuS and g-C₃N₄.

The morphology and structure of as-prepared samples were investigated via scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM images (Fig. 4) implied that the pure CuS was small nanosheets with severely agglomerated. It was obvious that the g-C₃N₄ was wrinkled sheet-like structure and has smooth surface. By the wet-chemical method to prepare g-C₃N₄/CuS nanocomposites, the surface of g-C₃N₄ would be rough and CuS nanosheets would decorate on somewhere of the surface of g-C₃N₄. Besides, the agglomeration of CuS on the surface would be alleviated with the content of g-C₃N₄ increased. It was observed the presence of g-C₃N₄ does not affect after the hybridization with CuS. The microstructure of as-prepared samples was further investigated via TEM (as shown in Fig. 5). It was obvious that the g-C₃N₄ showed a number of mesopores, and the porous structure would serve as support to bind CuS in the nanocomposites. The CuS nanosheets were severely aggregated. In the TEM images of g-C₃N₄/CuS nanocomposites, as shown in Fig.5 c, d, e, the two phases of CuS and g-C₃N₄ were contacted form closely an interface, which is favorable for the charge transfer between g-C₃N₄ and CuS. And by hybridize CuS nanosheets with the porous g-C₃N₄, the CuS would be deposited on the surface of g-C₃N₄ with good dispersion. The uniform distribution on the surface indicated that surface of CuS was lowered down with the interaction with g-C₃N₄. From the HR-TEM of g-C₃N₄/CuS-2, it was hard to found the clear lattice fringe of g-C₃N₄ for the two-dimensional ordering was weak [30]. The clear lattice fringe presented in the Fig. 5e was 0.289 nm, which could be assigned to the (103) planes of CuS. Obviously, the composite of g-C₃N₄/CuS was in hybrid state

rather than a physical mixture of two separate phases of g-C₃N₄ and CuS. This result indicated that g-C₃N₄/CuS nanocomposites in structure are heterogeneous.

The specific surface areas as well as the pore size distributions were investigated by N₂ adsorption-desorption isotherm analysis. As shown in Fig. 6, the as-prepared samples of g-C₃N₄ and g-C₃N₄/CuS-2 exhibited type-IV isotherms with a hysteresis loop, and the BJH pore size distribution indicated the existence of mesopores. The g-C₃N₄ and g-C₃N₄/CuS-2 composites had a broad pore-size distribution from 2 nm to about 80 nm and the most probable mesoporous diameter was about 3.818 nm and 3.726 nm, respectively. The mesopores could be ascribed to the wrinkled sheet-like structure and obvious porous structure as shown in SEM and TEM. The BET surface and pore volume of pure g-C₃N₄ and CuS was 61.269 m²/g, 0.143 cc/g and 9.568 m²/g, 0.0528 cc/g, respectively. But for g-C₃N₄/CuS-2, the BET surface and pore volume is 42.230 m²/g and 0.095 cc/g, respectively, which was in between g-C₃N₄ and CuS. This results indicated that the CuS was anchor on the surface of g-C₃N₄ and some mesopores may obstructed by CuS. While could not dramatically decrease the BET surface compared with g-C₃N₄, and it still contain the porous structure.

The optical absorption property of the as-prepared samples was studied by UV-Vis diffuse reflectance spectroscopy. As shown in Fig. 7, the pure g-C₃N₄ has a good photoabsorption performance in the visible light region. For the CuS, it has a wide absorption range from 200 nm to 800 nm, this may owe to its intrinsic green black color. The absorption intensity of the nanocomposites increased in the visible light region with the increasing content of CuS, which implies that the introduction of

CuS could favor the visible light absorption. Besides, the absorption edge of g-C₃N₄/CuS shifted to longer wavelengths as the content of CuS increased. The band gap energie of semiconductors were estimated by kubelka-munk transformation [31]:

$$\alpha h\nu = A (h\nu - E_g)^{n/2} \quad (1)$$

where α , h , ν , and A are the absorption coefficient, Planck constant, light frequency, and a constant. Besides, the n depends on the characteristics of the transition in a semiconductor. As previous report, the n values of g-C₃N₄ and CuS was 4 and 1 [32,33]. Thus, as shown in Fig. 7b, c the band gap values of g-C₃N₄ and CuS were estimated to 2.69 eV and 1.86 eV, respectively. In addition, the potentials of valance band (E_{VB}) and conduction band (E_{CB}) of a semiconductor material could be calculated via the following empirical equations [34]:

$$E_{VB} = X_{semiconductor} - E^e + 0.5E_g \quad (2)$$

$$E_{CB} = E_{VB} - E_g \quad (3)$$

where E_{VB} is the valence band edge potential, $X_{semiconductor}$ is the electronegativity of the semiconductor, E^e is the energy of free electrons vs. hydrogen (about 4.5 eV/NHE) and E_{CB} is the conduction band edge potential. The bandgap of g-C₃N₄ and CuS was estimated at 2.69 eV and 1.86 eV, respectively. The $X_{semiconductor}$ values of g-C₃N₄ and CuS are 4.64 eV and 5.27 eV, respectively. The E_{VB} and E_{CB} potential s of g-C₃N₄ and CuS could be calculated using eqn (2)-(3), which the E_{VB} , E_{CB} of g-C₃N₄ and CuS are 1.56 eV/NHE, -1.13 eV/NHE and 1.70 eV/NHE, -0.16 eV/NHE, respectively.

3.2 Photocatalytic study of of g-C₃N₄/CuS nanocomposites

The photocatalytic activities of as-prepared samples were evaluated via the

degradation of various organic dyes: rhodamine B (RhB) and methylene blue (MB) under visible light irradiation (> 420 nm). Prior to irradiation, the suspensions were magnetically stirred in dark for 30 mins to obtain the absorption-desorption equilibrium between the photocatalyst and organic dye. As shown in Fig. 8, the decrease in the concentration of RhB and MB was faster and more prominent with g-C₃N₄/CuS nanocomposites than the pure g-C₃N₄ or CuS under same experimental conditions. As shown in Fig. 8a, RhB aqueous solutions under the visible light irradiation was stable, and about 5 % and 40 % RhB was decomposed for pure g-C₃N₄ and CuS. While all the g-C₃N₄/CuS nanocomposites showed an obviously enhance photocatalytic activities than pure g-C₃N₄ and CuS, especially the g-C₃N₄/CuS-2 showed the highest photodegradation ratio after 60 mins, about 99.6 % RhB was decomposed. Furthermore, as the CuS content in the hybrid nanocomposites increases, the photocatalytic activity of the g-C₃N₄/CuS composites first increased, and then decreased. This kind of phenomenon was due to the increase mount of CuS, g-C₃N₄ would be cover or coated by CuS, which would damage the porous structure and dramatically decrease the specific surface areas. Besides, when the experimental data to the very low initial concentrations of the substrates, the photocatalytic oxidation of organic pollutants follows Langmuir Hinshelwood kinetics [35]:

$$-dc/dt = kc \quad (4)$$

In addition, it can be integrated as a pseudo first-order equation as following:

$$\ln(C/C_0) = -kt \quad (5)$$

where k is kinetic rate constants, which related to the reaction temperature, PH and

photocatalytic activity increases with increasing this value (k). And in our experiment we maintained constant temperature of reaction and PH of solution, so the k is only related to the photocatalytic activity. The kinetic rate constants of the samples were obtained by plotting $\ln(C_0/C)$ with the visible light irradiation time (minute), which is shown in Fig. 8b. The apparent rate constants calculated were 0.063% min^{-1} , 0.768% min^{-1} , 2.799% min^{-1} , 5.548% min^{-1} and 4.018% min^{-1} for g-C₃N₄, CuS, g-C₃N₄/CuS-1, g-C₃N₄/CuS-2 and g-C₃N₄/CuS-3, respectively. Among them, the apparent rate of g-C₃N₄/CuS-2 was 5.548% min^{-1} , which was about 88 times and 7.2 times that of over the g-C₃N₄ and CuS, respectively. Besides we also studied the photocatalytic activities of MB. As shown in Fig 8d, e. for degradation of MB, the as-prepared samples had the same laws. The g-C₃N₄/CuS nanocomposites showed an enhanced photocatalytic activity than pure g-C₃N₄ and CuS. Furthermore, about the 99.8 %, 20 % and 30 % MB was decomposed within 120 mins over the g-C₃N₄/CuS-2, g-C₃N₄ and CuS, respectively. For the kinetic rate constants the g-C₃N₄/CuS-2 was 3.57% min^{-1} which is 21 times and 10.2 times than pure g-C₃N₄ and pure CuS (As shown in Fig. 8e, f).

The stability of photocatalyst is one of the most important parts for its practical application. To study the stability of the as-prepared samples, the used g-C₃N₄/CuS-2 was collected by high-speed centrifugation (12000 r/min). The product of centrifuge was washed with alcohol and deionized water for several times and then dried in 60 °C for a night. And the collected sample was examined in the same RhB, MB degradation experiment like mentioned above without any treatment. As shown in Fig. 9, the photodegradation rate and decomposed rate remained the similar level after

three runs, which indicated that the g-C₃N₄/CuS could maintain a high photostability. Furthermore the XRD patterns、XPS spectrum and TEM images of the g-C₃N₄/CuS-2 nanocomposites after the successive experimental was presented in Fig. 10. It can be seen that the structure of g-C₃N₄/CuS-2 was consistent with original g-C₃N₄/CuS-2. Especially there is no obvious change after recycling reaction as shown in XPS spectrum and TEM images. These results demonstrated that phase structure and composite structure of g-C₃N₄/CuS-2 was highly stable. Therefore, the g-C₃N₄/CuS nanocomposites can be used efficiently as the photocatalysis in the area of environmental protection.

3.3 Possible photocatalytic mechanism of g-C₃N₄/CuS nanocomposites

It is well known that the organic dyes are decomposed via the oxidative species in the photodegradation process. In order to further investigate the primary active species involved in the process and possible photodegradation mechanism, the effects of scavengers on the degradation of RhB, MB over g-C₃N₄/CuS-2 was examined. Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), benzoquinone (BQ) and tert-butyl alcohol (TBA) used as the scavenger of hole (h⁺), superoxide radical (•O²⁻) and hydroxyl radical (•OH), respectively [36-38]. As shown in Fig. 11a, with the presence of 1 mol.L⁻¹ EDTA-2Na, BQ and TBA, the degradation of RhB under visible irradiation significantly decreased. These results showed the significant difference with the different scavengers were added, which indicated that the h⁺, •O²⁻ and •OH were the active species for the degradation of RhB. Besides, the same experiment for degradation of MB had the similar results (as shown in Fig. 11b).

The enhanced photocatalytic activity can be ascribed to the formation of heterojunction between g-C₃N₄ and CuS. Based on the experimental and estimated results, a possible visible light photocatalytic mechanism of g-C₃N₄/CuS nanocomposites was proposed in Fig. 12. The positions of the E_{VB} and E_{CB} of CuS matched well with the E_{VB} and E_{CB} of g-C₃N₄. When the g-C₃N₄/CuS heterojunction under the irradiation of visible light, both g-C₃N₄ and CuS could photoinduced the electron and hole. Since, the E_{VB} of g-C₃N₄ is more negative than that of CuS, the photoinduced hole on the valence band of CuS would easily transfer to the g-C₃N₄ valence band. Furthermore, as the E_{CB} of CuS is more negative than that of g-C₃N₄, the photoinduced electron on the conduction band of g-C₃N₄ would easily transfer to the CuS conduction band, which would restrain the photoinduced electron-holes recombination. Due to the standard reduction potential of 2.72 eV/NHE ($\bullet\text{OH}$, $\text{H}^+/\text{H}_2\text{O}$) and 2.38 eV/NHE ($\bullet\text{OH}/\text{OH}^\cdot$), the E_{VB} level of g-C₃N₄ (1.57 eV/NHE) is not high enough to produce $\bullet\text{OH}$. The hole on the valence band of g-C₃N₄ could directly react with organic pollutants. Furthermore, compared with the standard reduction potential of -0.33 eV/NHE ($\text{O}_2/\bullet\text{O}^{2-}$), the electron on the conduction band of g-C₃N₄ (-1.13 eV/NHE) could react with O₂ to form $\bullet\text{O}^{2-}$ radicals, however the electron on the conduction band of CuS (-0.16 eV/NHE) could not produce the $\bullet\text{O}^{2-}$ radicals. While the electron on the conduction band of CuS is high enough to react with O₂ to generate H₂O₂ for the reduction potential of O₂/H₂O₂ is 0.695 eV/NHE. This possible photocatalytic mechanism of g-C₃N₄/CuS was also proved by using scavenger method before.

In order to prove the possible photocatalytic mechanism, the PL spectra of g-C₃N₄ and g-C₃N₄/CuS-2 nanocomposites was obtained. The intensity of PL is associated to the photoinduced carries recombination in semiconductor. As shown in Fig. 13a, the PL spectra of as-prepare samples were obtained with an excitation wavelength of 365 nm at room temperature. The PL intensity of g-C₃N₄ is higher than that of g-C₃N₄/CuS-2 in 440 nm, which proved that the g-C₃N₄/CuS-2 had a lower photoinduced carrier recombination rate that come from the efficient transfer of photoinduced eletron-holes between the interface of g-C₃N₄ and CuS.

EIS measurement is an available method to investigate the charge transfer resistance and the separation efficiency of the photoinduced charge carriers. The smaller diameter implies the lower impedance and faster interface charge transfer. As shown in Fig. 13b, the diameter for arc radius of the g-C₃N₄/CuS-2 electrode was smaller than that of the g-C₃N₄ indicated that the synergistic effect between g-C₃N₄ and CuS indeed exist, which could effectively promote the separation and transfer of photogenerated electron hole pairs, resulting in enhancing photocatalytic activity. The EIS results further confirmed that the separation and transfer of photoinduced carriers were more efficient in the g-C₃N₄/CuS-2, which accorder with that obtained by the PL spectra.

4. Conclusions

In conclusion, the novel porous g-C₃N₄/CuS nanocomposites were successfully prepared via an in situ precipitation-deposition route. By introduction of g-C₃N₄, CuS

would uniformly distribute on the surface of g-C₃N₄ and avoid severe agglomeration. The UV-vis spectra showed that the g-C₃N₄/CuS nanocomposites were able to absorb visible light. Compared with the pure g-C₃N₄ and CuS, the photocatalytic activity of the as-prepared g-C₃N₄/CuS was dramatically increased for RhB and MB photodegradation under visible light irradiation ($\lambda \geq 420$ nm). The enhanced photocatalytic activity of the g-C₃N₄/CuS could be ascribed to the formation of a heterojunction, which improved the efficient transfer of photoinduced electron-holes between the interface of g-C₃N₄ and CuS. Such a facile route may help to provide an idea for the design or fabricate other efficient g-C₃N₄ based photocatalysts for pollutants removal.

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FIGURE CAPTIONS

Scheme 1 Schematic representation of the deposition of CuS nanoplates on the porous g-C₃N₄ sheet.

Figure 1 XRD patterns of g-C₃N₄, CuS and g-C₃N₄/CuS nanocomposites.

Figure 2 FT-IR spectra of g-C₃N₄, CuS and g-C₃N₄/CuS-2.

Figure 3 (a) Survey spectra of g-C₃N₄, CuS and g-C₃N₄/CuS-2, high-resolution XPS spectra of (b) C 1s; (c) N 1s; (d) Cu 2p; (e) S 2p.

Figure 4 SEM images of (a) CuS, (b) g-C₃N₄ and (c) g-C₃N₄/CuS-1, (d) g-C₃N₄/CuS-2 and (e) g-C₃N₄/CuS-3 nanocomposites.

Figure 5 TEM images of (a) CuS, (b) g-C₃N₄ and (c) g-C₃N₄/CuS-1, (d) g-C₃N₄/CuS-2, (e) g-C₃N₄/CuS-3 nanocomposites and (f) HR-TEM image of g-C₃N₄/CuS-2.

Figure 6 (a) The N₂ adsorption-desorption isotherms of g-C₃N₄, CuS and g-C₃N₄/CuS nanocomposites, pore size distributions of (b) g-C₃N₄ and (c) g-C₃N₄/CuS-2.

Figure 7 (a) UV-Vis absorption spectra of g-C₃N₄, CuS and g-C₃N₄/CuS nanocomposites, (b) plot of $(Ah\nu)^{1/2}$ versus energy (h ν) for the band gap energy of g-C₃N₄, (c) the plot of $(Ah\nu)^2$ versus energy (h ν) for the band gap energy of CuS.

Figure 8 (a) Degradation rate of RhB under visible-light irradiation (> 420 nm) without catalyst and in the presence of g-C₃N₄, CuS and g-C₃N₄/CuS nanocomposites,

(b) a natural logarithm C/C_0 fitting curves of all samples (RhB), (c) the value of the rate constant k of the photodegradation of RhB in the presence of as-prepared samples, (d) Degradation rate of MB under visible-light irradiation (> 420 nm) without catalyst and in the presence of g-C₃N₄, CuS and g-C₃N₄/CuS nanocomposites, (e) a natural logarithm C/C_0 fitting curves of all samples (MB), (f) the value of the rate constant k of the photodegradation of MB in the presence of as-prepared samples, error bars were based on the standard deviations of three parallel experiments.

Figure 9 (a) Cycle runs of g-C₃N₄/CuS-2 for degradation of RhB under visible light irradiation ($\lambda > 420$ nm), (b) the degradability distributions of each run under visible-light irradiation for 60 mins (RhB), (c) Cycle runs of g-C₃N₄/CuS-2 for degradation of MB under visible light irradiation ($\lambda > 420$ nm), (d) the degradability distributions of each run under visible-light irradiation for 120 mins (MB).

Figure 10 (a) XRD patterns, (b) XPS spectrums and (c) TEM images of the g-C₃N₄/CuS-2 nanocomposites before and after the successive experimental.

Figure 11 Effects of different scavengers on degradation of (a) RhB and (b) MB over g-C₃N₄/CuS-2, error bars were based on the standard deviations of three parallel experiments.

Figure 12 Schematic illustration of the possible photocatalytic mechanism.

Figure 13 (a) PL spectra of g-C₃N₄ and g-C₃N₄/CuS-2 nanocomposites, (b) EIS Nyquist plots of g-C₃N₄ and g-C₃N₄/CuS-2.

Scheme 1

Fig. 1

Fig. 2

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Fig. 12

Fig. 13

TOC/Graphical abstract