Concerted catalytic and photocatalytic degradation of organic pollutants over CuS/g-C3N4 catalysts under light and dark conditions

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Highlights
- CuS/g-C3N4 composite catalysts were successfully fabricated.
- The optimal mass ratio of CuS in the composite was determined.
- Fenton-like catalytic and photocatalytic effects were combined for sewage purification.
- The continuous degradation of organic pollutants was achieved.

Abstract
Organic pollutants in industrial and agricultural sewage are a serious threat to the environment and human health. Achieving continuous photocatalytic degradation of organic pollutants under light and dark conditions would have exciting implications for practical sewage treatment. In this paper, CuS/g-C3N4 composite catalysts with CuS nanoparticles anchored on g-C3N4 sheets were successfully fabricated via a simple solvothermal reaction. The morphology, structure, optical absorption characteristics, electron–hole recombination rate, and degradation performance of the as-prepared CuS/g-C3N4 catalysts were investigated in detail. The results confirmed that the as-fabricated CuS/g-C3N4 catalysts exhibited high Fenton-like catalytic degradation efficiencies in the dark, and rapid concerted Fenton-like catalytic, direct H2O2 photocatalytic and CuS/g-C3N4 photocatalytic degradation activities under visible light. Thus, the as-fabricated CuS/g-C3N4 catalysts can degrade organic pollutants continuously during both day and night. These degradation properties, along with the simple catalyst fabrication process, will facilitate the practical application of this system in the continuous removal of organic pollutants.

Introduction
Sewage purification, especially the removal of organic molecular pollutants including dyes, pesticides, and plasticizers, has gained considerable attention owing to its great importance for ecological and human health [1]. To date, various methods, including adsorption [2–4], filtration [5], biodegradation [6], chemical catalysis [7], and photocatalysis [8,9], have been successfully developed for the removal of these organic pollutants. Among these methods, photocatalytic degradation has emerged as one of the most promising technologies because it is typically inexpensive and environmentally friendly, readily uses solar light, and does not generate secondary pollutants [8–10]. However, common photocatalysts, such as TiO2, ZnO, Fe2O3, SrTiO3, or other oxide-based species, show low or no catalytic activity in the absence of light, which greatly hinders their practical applicability for the continuous, around-the-clock degradation of organic pollutants [8–13]. Therefore, developing novel photocatalysts that are highly efficient in the absence of light is highly desirable.
light is a high priority, and would have great significance for achieving continuous catalytic degradation of organic pollutants.

Graphitic carbon nitride (g-C₃N₄) is a promising visible-light-driven photocatalyst with a narrow band gap of approximately 2.70 eV [14]. This material is composed of earth abundant elements and can be easily prepared by pyrolysis of nitrogen-rich precursors. However, because of fast charge recombination, the photocatalytic performance of g-C₃N₄ remains limited by its low efficiency. To improve the photocatalytic performance of g-C₃N₄, various strategies, such as metal/non-metal doping, noble metal deposition, or compositing with heterogeneous semiconductors [15,16], have been developed. These strategies readily promote charge separation and enhance photocatalytic activity. However, endowing the resultant g-C₃N₄-based photocatalysts with highly efficient catalytic activity without light is still challenging.

Copper sulfide (CuS) has been proven to be a suitable semiconductor for use in composites with g-C₃N₄ to obtain catalysts with enhanced photocatalytic activity [17,18]. For example, Yu et al. integrated g-C₃N₄ nanosheets with hexagonal CuS nanoplates to synthesize a g-C₃N₄-CuS nanocomposite photocatalyst and demonstrated that the prepared g-C₃N₄-CuS had a much higher hydrogen evolution rate (126.5 μmol·h⁻¹) than a pure g-C₃N₄ nanosheet under solar light [17]. Chen et al. also reported that a porous g-C₃N₄/CuS heterostructured photocatalyst exhibited enhanced photocatalytic performance towards the degradation of various organic dyes under visible light irradiation [18]. Note that CuS is not only a good co-photocatalyst, but also a Fenton-like catalyst, a type of catalyst that can effectively degrade a wide range of organic pollutants with the help of hydrogen peroxide (H₂O₂) with or without light [19,20]. The Fenton reaction is a catalytic process that generates hydroxyl radicals from H₂O₂ and the hydroxyl radical is a powerful oxidant that can oxidize organic molecules into lower-molecular-weight molecules or carbon dioxide and water [21]. Therefore, a composite of CuS and g-C₃N₄ may exhibit both enhanced photocatalytic activity and Fenton-like catalytic activity, and provide an alternative method for achieving continuous degradation of organic pollutants both with and without light.

In this study, CuS/g-C₃N₄ composite catalysts were fabricated and used to treat dye-containing sewage in the dark and under visible light irradiation to verify the above speculations. UV–vis and photoluminescence (PL) spectra showed broad visible light absorption and a low photoinduced carrier recombination rate. When used to degrade a dye-containing solution with the help of H₂O₂, the CuS/g-C₃N₄ catalysts exhibited high Fenton-like catalytic activity in the degradation of rhodamine B (RhB), 30 mg·L⁻¹ in the dark and excellent photocatalytic and Fenton-like catalytic activity under visible light. Moreover, the as-fabricated CuS/g-C₃N₄ may be a promising catalyst for achieving continuous catalytic activity in highly concentrated dye wastewaters, which would be of great use in practical applications.

**Experimental**

**Materials**

Melamine, copper (II) chloride dihydrate (CuCl₂·2H₂O), sodium dodecyl benzene sulfonate (SDBS), thioacetamide (TAA), anhydrous ethanol, ethylene glycol and RhB of analytical–reagent grade were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All reagents were used as received.

**Fabrication of the CuS/g-C₃N₄ catalysts**

The fabrication of the CuS/g-C₃N₄ catalysts is schematically illustrated in Fig. S1. Bulk g-C₃N₄ was fabricated by direct heating of melamine at 550 °C in air for 5 h at a heating rate of 5 °C·min⁻¹ from room temperature. CuS powder was prepared as follows: 0.341 g of CuCl₂·2H₂O and 0.025 g of SDBS were dissolved in 100 mL of deionized water. TAA (50 mL, 0.12 M) was added to the above solution. Then, the flask containing the solution was immersed in a constant temperature bath (100 °C) for 4 h. The dark product was washed repeatedly with ethanol and deionized water, and then oven-dried at 50 °C for 12 h.

The CuS/g-C₃N₄ catalysts were fabricated using a simple solvolothermal reaction. Typically, 0.5 g of g-C₃N₄ and 0.03 g of CuS were dispersed in 25 mL of glycol. After ultrasonic treatment for 30 min, the solution was stirred for 1 h to thoroughly mix the components. Then, the solution was sealed in a polytetrafluoroethylene (Teflon)-lined stainless-steel autoclave, and heated to 190 °C for 24 h. The product was washed repeatedly with ethanol and deionized water, and the CuS/g-C₃N₄ catalyst was collected. The same process was applied to obtain the other CuS/g-C₃N₄ catalysts with different CuS contents. The resultant CuS/g-C₃N₄ catalysts were labelled x%-CuS/g-C₃N₄, where x is the weight ratio of CuS to g-C₃N₄. In this work, catalysts with x values of 0, 2, 4, 6, 8, and 10 were prepared.

**Characterization**

The crystal structures of the samples were evaluated using a Rigaku D/MAX 2550 X-ray diffractometer with Cu Kα radiation (50 kV, 200 mA) (Rigaku Co., Tokyo, Japan). The morphology and elemental composition of each sample was determined using field-emission scanning electron microscopy (FESEM, JEOL JSM 6700F, Japan) and transmission electron microscopy (TEM, FEI Tecnai G2S-Twin, America). UV–vis diffuse reflectance spectroscopy (DRS) was performed using a SHIMADZU 2550 UV/vis spectrophotometer (Japan). The PL spectra of the photocatalysts were acquired on a fluorescence spectrophotometer (Fluoromax-4 HORIBA Jobin Yvon, America). The UV–vis spectra of the dye suspensions were obtained on a UV–vis spectrometer (TU-1901, Persee, Beijing, China).

**Catalytic activity**

To assess the catalytic ability of the CuS/g-C₃N₄ catalysts, a RhB solution was catalytically degraded at room temperature in the dark and under visible light (300 W Xe lamp, λ > 420 nm). Typically, 40 mg of the CuS/g-C₃N₄ catalyst was added to 100 mL of a 30 mg·L⁻¹ RhB solution, and the suspension was stirred in the dark for 30 min to establish the adsorption–desorption equilibrium between RhB and the CuS/g-C₃N₄ catalyst. Then, 0.5 mL of 30% hydrogen peroxide (H₂O₂) was added to initiate the reaction both in the dark and under visible light. The concentration of the suspension was analysed every 10 min by a UV–vis spectrophotometer. The reproducibility of the results was evaluated by repeating the experiments at least three times, first for 30 min in the dark, and then for 30 min under visible light. The same test procedures were applied to all control experiments and experiments using different amounts of H₂O₂ or different amounts of 6%-CuS/g-C₃N₄. Considering the major role of CuS in the Fenton degradation reaction in the dark, we performed a comparative experiment with the same content of CuS, namely, 40 mg of 6%-CuS/g-C₃N₄ and 2.4 mg of pure CuS, to compare the Fenton catalytic capacities of pure CuS and 6%-CuS/g-C₃N₄ in the dark.

To verify the continuous catalytic activity of the CuS/g-C₃N₄ catalysts in highly concentrated dye wastewater in the absence and presence of light, 40 mg of the 6%-CuS/g-C₃N₄ catalyst was added to 150 mL of a 150 mg·L⁻¹ RhB solution, and the suspension was stored in the dark for 30 min. Then, 0.5 mL of H₂O₂ was added to initiate the reaction, and the solution was held in the dark for 1 h. The reaction was then continued under visible light for an additional
The concentration of the suspension was analysed every 20 min. Then, 0.5 mL of H₂O₂ was added to the remaining suspension to restart the reaction cycle. This reaction process was maintained for three cycles.

Results and discussion

Characteristics of the CuS/g-C₃N₄ catalysts

The CuS/g-C₃N₄ catalysts were fabricated by a simple solvothermal reaction of bulk g-C₃N₄ and CuS powder. Fig. 1 shows the X-ray diffraction (XRD) patterns of pure CuS, pure g-C₃N₄ and the x%-CuS/g-C₃N₄ composites, where x is the weight ratio of CuS to g-C₃N₄. Two main peaks appear for pure g-C₃N₄ and all the CuS/g-C₃N₄ composites. The distinct peaks at 13.1° and 27.4° can be readily indexed as the (1 0 0) and (0 0 2) crystal planes of g-C₃N₄, respectively (JCPDS, no. 87-1526) [22,23]. In addition, there are several small peaks at 29.2°, 31.7°, 32.7°, 47.9°, 52.8° and 59.4° for the CuS/g-C₃N₄ composites, which are consistent with those of pure CuS and can be indexed as the (1 0 2), (1 0 3), (1 0 6), (1 1 0), (1 0 8), and (1 1 6) crystal planes of CuS (JCPDS, no. 06-0464) [19,20]. With increasing CuS content, the diffraction peaks of CuS become more intense.

The structures of the bulk g-C₃N₄, CuS powder and the as-fabricated CuS/g-C₃N₄ catalysts are presented in Fig. 2. The CuS powder is a flower-like aggregate composed of two-dimensional nanoplates. Taking 6%-CuS/g-C₃N₄ as an example, the sheet-like catalysts took on a sheet-like morphology with anchored nanoparticle clusters. Interestingly, the flower-like CuS particles can be transformed into CuS nanoparticles during the solvothermal process, generating a higher BET surface area and more mesopores [18,25,26]. In addition, CuS nanoparticles were anchored on the exfoliated g-C₃N₄ sheets during the solvothermal process, which may improve the dispersion of CuS nanoparticles and enhance the interface between the CuS nanoparticles and the g-C₃N₄ sheets. Higher BET specific surface areas and more mesopores can improve the adsorption rate and adsorption capacity of a catalyst and provide more active sites, leading to higher catalytic capacities. Thus, it can be inferred that the catalytic capacity of the CuS/g-C₃N₄ composites is determined not only by their CuS content but also by their BET surface area and pore volume.

The optical absorption characteristics and electron–hole recombination rate of the as-prepared CuS, g-C₃N₄ and CuS/g-C₃N₄ catalysts were studied by UV–vis DRS and PL spectroscopy, respectively. As shown in Fig. 4a, pure g-C₃N₄ shows a fundamental absorption edge at approximately 455 nm in the visible light region. The corresponding band gap energy (E$_g$) was calculated to be 2.73 eV ($E_g = 1240/\lambda$, $\lambda$ is the absorption wavelength), which is very close to the reported value for g-C₃N₄ nanosheets [27]. Pure CuS has a wide absorption range of 300 to 800 nm, which is in good agreement with its intrinsic green-black colour. The absorption edge of pure CuS is at approximately 900 nm, and the corresponding band gap energy is 1.38 eV. In addition, the potentials of the valance band (E$_{vb}$) and conduction band (E$_{cb}$) of a semiconductor can be calculated via the following empirical equations [18]:

$$E_{vb} = X_{semiconductor} - E^* + 0.5E_g$$

(1)

$$E_{cb} = E_{vb} - E_g$$

(2)

where $X_{semiconductor}$ is the electronegativity of the semiconductor, and $E^*$ is the energy of free electrons vs. hydrogen (approximately 4.5 eV/NHE). The $X_{semiconductor}$ values of g-C₃N₄ and CuS are 4.64 eV and 5.27 eV, respectively. The band gap energies ($E_g$ values) of g-C₃N₄ and CuS were estimated at 2.73 eV and 1.38 eV, respectively. The E$_{vb}$ and E$_{cb}$ potential of s of g-C₃N₄ and CuS could be calculated to be 1.51 eV/NHE and −1.22 eV/NHE and 0.83 eV/NHE and −0.55 eV/NHE, respectively.
When CuS is added, the resulting \( x\%\text{-CuS/g-C}_3\text{N}_4 \) composites show better visible light absorption. The absorption edges of 2\%\text{-CuS/g-C}_3\text{N}_4, 4\%\text{-CuS/g-C}_3\text{N}_4, 6\%\text{-CuS/g-C}_3\text{N}_4, 8\%\text{-CuS/g-C}_3\text{N}_4, \) and 10\%\text{-CuS/g-C}_3\text{N}_4 had shifted to 506, 546, 569, 650 and 753 nm, and the corresponding band gap energies were 2.45, 2.27, 2.18, 1.91 and 1.65 eV, respectively. Smaller band gaps mean the less...
energy is required to induce efficient electron transfer. Moreover, the electron–hole recombination rates of the as-prepared g-C_3N_4 and CuS/g-C_3N_4 catalysts were investigated by PL spectroscopy (Fig. 4b). The PL peaks of x%-CuS/g-C_3N_4 were blueshifted relative to that of bulk g-C_3N_4. The blueshift can presumably be attributed ascribed to the decrease in the conjugation length and the strong quantum confinement effect due to the few-layer structure of the g-C_3N_4 nanosheets. This result further verified that the melanin-derived bulk g-C_3N_4 was exfoliated into thin-layered g-C_3N_4 during the solvothermal process. Similar observations have been reported in other studies [25,28]. A lower PL peak intensity indicates a lower electron–hole recombination rate and a higher electron-transfer rate [17]. The as-obtained x%-CuS/g-C_3N_4 composites show lower peak intensities than pure g-C_3N_4, suggesting that the CuS nanoparticles anchored on the surface of g-C_3N_4 could efficiently transfer the electrons generated from g-C_3N_4 [16]. A lower electron–hole recombination rate can be achieved by increasing the CuS content. Therefore, the good suppression of recombination and good visible light absorption of x%-CuS/g-C_3N_4, as well as the high BET specific surface area, would contribute to their better photocatalytic activity towards organic pollutants in sewage under visible light. With the addition of the Fenton-like catalytic activities of CuS [19,20], the as-obtained CuS/g-C_3N_4 catalysts were expected to achieve continuous degradation of organic pollutants both with and without light.

Degradation performance of the CuS/g-C_3N_4 catalysts

The degradation performance of the CuS/g-C_3N_4 catalysts towards organic pollutants was evaluated by decomposing RhB with the help of H_2O_2 in the dark and under visible light. First, the degradation behaviors of x%-CuS/g-C_3N_4 composites were investigated under visible light. As shown in Fig. 5a, the time profiles of C/C_0, where C_0 and C represent the initial and reaction concentrations of the RhB solution, respectively, indicate that for all samples, the CuS/g-C_3N_4 catalysts exhibited higher degradation activity than pure CuS and g-C_3N_4, which confirms that the interaction between CuS and g-C_3N_4 could successfully suppress electron–hole recombination and improve the photocatalytic activity. Among the catalysts, 6%-CuS/g-C_3N_4 shows the best degradation performance; it degraded approximately 95% of the RhB in 60 min. The corresponding degradation rate constants (k) were calculated assuming a pseudo-first-order reaction based on ln(C_0/C) = kt (Fig. 5b). The rate constant with 6%-CuS/g-C_3N_4 is 0.04924 min\(^{-1}\), which is greater than that of each of the other catalysts. These results confirm that there is an optimal content of CuS in the composite, which in this work is 6%, that provides the best degradation performance. Thus, the following discussion will focus on the 6%-CuS/g-C_3N_4 catalyst.

The effects of the amounts of H_2O_2 and the catalyst (6%-CuS/g-C_3N_4) on the catalytic degradation of RhB under visible light were also investigated. As shown in Fig. 6a and b, when the amount of H_2O_2 was varied from 0.1 to 0.5 mL, the RhB degradation efficiency increases rapidly from 55% to 95%, but when the amount is increased further (to 0.9 mL), the efficiency remains almost unchanged. This phenomenon is similar to what is seen in other organic pollutant degradation systems under light [29,30]. At low H_2O_2 concentrations, the improvement in efficiency is mainly due to the OH radicals generated from H_2O_2 under light irradiation and the fact that H_2O_2 is a good electron acceptor [31,32]. At high H_2O_2 concentrations, the excess H_2O_2 molecules scavenge the valuable OH species, leading to a slight decrease in the efficiency [33]. Thus, the optimal amount of H_2O_2 for the catalytic degradation of RhB under visible light is 0.5 mL. The relationship between the degradation efficiency and the amount of 6%-CuS/g-C_3N_4 catalyst is shown in Fig. 6c and d. In 60 min, the degradation efficiency increases rapidly from 55% to 95% when the amount of catalyst is increased from 20 to 40 mg, and the efficiency decreases slightly (to 89%) when the amount of catalyst is increased further to 60 mg. It is generally accepted that increasing the catalyst loading would increase the light absorption and pollutant adsorption, leading to improved catalytic activity. However, a further increase in the catalyst loading may cause light scattering and screening effects, which would reduce the specific activity [34,35]. In addition, aggregation of the catalyst may also reduce the catalytic activity [35]. Thus, in this work, the optimal amount of the 6%-CuS/g-C_3N_4 catalyst to achieve the best degradation performance was found to be 40 mg.

To further understand the catalytic mechanism of the 6%-CuS/g-C_3N_4 catalyst and the potential for around-the-clock catalytic activity, comparative experiments on the degradation of RhB in the dark were conducted. Considering the major role of CuS in the Fenton degradation reaction in the dark, we performed a comparative experiment using the same CuS content, namely, 40 mg of 6%-CuS/g-C_3N_4 compared with 2.4 mg of pure CuS. As shown in Fig. 7a, the 6%-CuS/g-C_3N_4 catalyst shows high catalytic efficiency in decomposing RhB with the help of H_2O_2 in the dark. The catalyst can degrade approximately 74% of the RhB in 60 min. Pure g-C_3N_4 shows no catalytic activity, and pure CuS degrades approximately 46% of the RhB in 60 min. CuS catalysts have been demonstrated to be highly efficient Fenton-like reagents [19,20]. OH was generated from the degradation of H_2O_2 in the presence of a CuS catalyst, and the highly reactive OH could oxidize the organic pollutant (RhB) into smaller molecules (CO_2, H_2O, etc.). The 6%-CuS/g-C_3N_4 catalysts were investigated by PL spectroscopy on the 6%-CuS/g-C3N4 catalyst.

**Fig. 5.** (a) The degradation of RhB monitored at normalized concentration change (C/C_0) vs. irradiation time (t) and (b) reaction rate constants associated with RhB degradation.
catalyst may promote similar Fenton-like degradation reactions in the current work, and the improved catalytic activity may be due to the good dispersion of CuS nanoparticles anchored on the g-C3N4 nanosheets and the interface between the CuS nanoparticles and g-C3N4 sheets. Accordingly, the Fenton-like reaction mechanism can be described as follows [19,20]:

\[
\begin{align*}
\text{Cu}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{H}^+ + \text{CuOOH}^+ \\
\text{CuOOH}^+ & \rightarrow \text{HOO}^- + \text{Cu}^+ \\
2\text{HOO}^- & \rightarrow 2\text{OH}^- + \text{O}_2 \\
\text{Cu}^+ + \text{H}_2\text{O}_2 & \rightarrow \text{Cu}^{2+} + \text{OH}^- + \text{OH}^-
\end{align*}
\]

\[\text{RhB} + \text{OH}^- \rightarrow \text{R}^- + \text{H}_2\text{O} \tag{7}\]

\[\text{R}^- + \text{O}_2 \rightarrow \text{degraded products} \tag{8}\]

In the absence of H2O2, the 6%-CuS/g-C3N4 catalyst shows no catalytic activity. Thus, in this work, the addition of H2O2 is regarded as the start of the degradation reaction. Furthermore, H2O2 alone, in the absence of the catalyst, cannot degrade the RhB solution in the dark (Fig. 7b). Photolysis of H2O2 can slowly produce reactive OH·, leading to a low degradation efficiency of 5% in 60 min under visible light [36].

\[\text{H}_2\text{O}_2 \rightarrow 2\text{OH}^- \tag{9}\]

Thus, three degradation pathways exist under visible light, namely, the Fenton-like degradation reaction, the direct H2O2 photocatalytic degradation reaction and the CuS/g-C3N4 photocatalytic degradation reaction.

Studies have shown that CuS/g-C3N4 composites are efficient photocatalysts for pollutant degradation and water splitting [17,18]. Under visible light, both CuS and g-C3N4 could photoinduce electron–hole pairs [Eqs. (10) and (11)]. The conduction band (CB)/valence band (VB) potentials of CuS and g-C3N4 are −0.55/+0.83 and −1.22/+1.51 eV, respectively. The CB of g-C3N4 is more negative than that of CuS, so the photoinduced electrons \(e^- (g-C_3N_4)\) in the CB of g-C3N4 could easily transfer to the CB of CuS. Due to the standard reduction potentials of \(-0.33\ \text{eV/NHE (O}_2/\text{O}_2^-\) and \(-0.22\ \text{eV/NHE (H}_2\text{O}_2/\text{OH}^-/\text{OH}^+\)\), electrons in the conduction band of CuS (−0.55 eV/NHE) and g-C3N4 (−1.22 eV/NHE) could react with O2 to form ‘O2 radicals [Eqs. (12) and (13)] and react with H2O2 to form OH· and OH− radicals [Eqs. (14) and (15)]. These photogenerated oxidant species (OH· and ‘O2) have a high oxidative capacity to degrade organic pollutants [Eq. (16)] [37]. At the same time, the holes in the VB of g-C3N4 and CuS could be directly consumed by reactions with organic pollutants [Eqs. (17) and (18)] [18]. A schematic illustration of the possible photocatalytic mechanism is shown in Fig. 7c.

\[
\begin{align*}
\text{CuS}^{-} + h^+ (\text{CuS}) + e^- (\text{CuS}) \\
g (g\text{-C}_3\text{N}_4) + h^+ (g\text{-C}_3\text{N}_4) + e^- (g\text{-C}_3\text{N}_4) \\
e^- (g\text{-C}_3\text{N}_4) + \text{O}_2 \rightarrow \cdot \text{O}_2^- \\
e^- (\text{CuS}) + \text{O}_2 \rightarrow \cdot \text{O}_2^- \\
e^- (g\text{-C}_3\text{N}_4) + \text{H}_2\text{O}_2 \rightarrow \cdot \text{OH}^- + \cdot \text{OH}^- \\
e^- (\text{CuS}) + \text{H}_2\text{O}_2 \rightarrow \cdot \text{OH}^- + \cdot \text{OH}^- 
\end{align*}
\]
\[ \mathrm{O}_2^- \text{ or OH}^+ + \text{RhB} \rightarrow \text{degraded products} \quad (16) \]

\[ \mathrm{h}^+ (\mathrm{g-C}_3\mathrm{N}_4) + \text{RhB} \rightarrow \text{degraded products} \quad (17) \]

\[ \mathrm{h}^+ (\mathrm{CuS}) + \text{RhB} \rightarrow \text{degraded products} \quad (18) \]

The enhanced CuS/g-C_3N_4 photocatalytic degradation reaction, in combination with the Fenton-like degradation reaction and the direct H_2O_2 photocatalytic degradation reaction, is responsible for the good degradation performance of the CuS/g-C_3N_4 catalysts towards organic pollutants. Notably, these three degradation pathways may have synergistic effects on the degradation of RhB under visible light, further enhancing the photocatalytic activity of this system. Assuming that these reactions occur separately, the Fenton-like reaction of 6%-CuS/g-C_3N_4 with H_2O_2 in the dark can be considered analogous to the Fenton-like reaction under light. Both the Fenton-like degradation reaction and the direct H_2O_2 photocatalytic degradation reaction can be approximated as pseudo-first-order reactions based on \( \ln(C_0/C) = kt \) (Fig. 7d). The rate constants of the Fenton-like reaction and direct H_2O_2 photocatalytic reaction are 0.02347 (k1) and 0.00249 (k2) min\(^{-1}\), respectively. The total rate constant is 0.04924 min\(^{-1}\) (k). Thus, the rate constant of the 6%-CuS/g-C_3N_4 photocatalytic degradation reaction can be calculated to be 0.02328 min\(^{-1}\) (k). The proportional distribution of the different degradation pathways is shown in the pie chart in Fig. 7e. Thus, the good degradation performance of 6%-CuS/g-C_3N_4 under visible light may arise from the combined advantages of (1) the synergistic effects of the Fenton-like reaction, direct H_2O_2 photocatalytic reaction and CuS/g-C_3N_4 photocatalytic degradation reaction, (2) the enhanced charge separation efficiency caused by the CuS-g-C_3N_4 heterojunction owing to interfacial electron and hole transfer between CuS and g-C_3N_4 and (3) the high BET surface area of 6%-CuS/g-C_3N_4.
The stability of a catalyst is one of the most important indicators of its practical applicability. The stability of the as-fabricated 6%-CuS/g-C3N4 was investigated by recycling 6%-CuS/g-C3N4 in repeated degradation experiments with and without light, and the results are shown in Fig. 7f. 6%-CuS/g-C3N4 maintains a similar level of catalytic activity after three reaction cycles, which indicates that 6%-CuS/g-C3N4 has good photochemical stability. Furthermore, SEM images of 6%-CuS/g-C3N4 before and after the recycling experiments are shown in Fig. S4. There are no obvious changes after the recycling reaction, which further indicates the high stability of the as-fabricated CuS/g-C3N4 catalyst.

Because the as-fabricated CuS/g-C3N4 catalysts exhibited high catalytic degradation activity both in the dark and under visible light, CuS/g-C3N4 is expected to be a promising catalyst for achieving continuous degradation of organic pollutants in the presence and absence of light. A controlled experiment on degradation of RhB at a high concentration (150 mg L⁻¹) was conducted in the dark and under visible light to verify the continuous catalytic activity of the 6%-CuS/g-C3N4 catalyst. As shown in Fig. 8a, the RhB in the solution was degraded continuously during three dark–light cycles. The catalyst degraded approximately 97% of the RhB in 360 min. In contrast to the reported around-the-clock photocatalysts that can store some photoexcited charge carriers (e⁻/h⁺) while under illumination and release them in the dark to achieve catalytic activity even in the dark [11,38–40], the photocatalysts described in this work demonstrate that combining a Fenton-like reaction and a photocatalytic reaction can also be a promising alternative strategy for designing and constructing new types of continuous photocatalysts for practical applications (Fig. 8b).

Conclusions

CuS/g-C3N4 composite catalysts with CuS nanoparticles anchored on g-C3N4 sheets were successfully fabricated via a simple solvothermal reaction. UV–vis and PL spectroscopy indicated that the CuS/g-C3N4 composites have good visible light absorption and can efficiently transfer photoinduced electron–hole pairs at the interface between CuS and g-C3N4, which can improve its photocatalytic activity towards organic pollutants in sewage under visible light. In addition, the as-fabricated CuS/g-C3N4 composites exhibit efficient Fenton-like catalytic activity, and they can degrade organic pollutants in the dark with the help of H2O2. Therefore, by combining the enhanced photocatalytic activity and Fenton-like catalytic activity, as well as the direct H2O2 photocatalytic reaction, the as-fabricated CuS/g-C3N4 composite catalyst system could continuously degrade organic pollutants in the absence and presence of light. Moreover, this finding, which is based on Fenton-like and photocatalytic reactions, may serve as a general strategy for fabricating new types of continuous photocatalysts for practical applications.

Conflicts of interest

The authors have declared no conflict of interest.

Compliance with Ethics Requirements

This article does not describe any studies with human or animal subjects.

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Appendix A. Supplementary material

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