Synergistically homogeneous-heterogeneous Fenton catalysis of trace copper ion and g-C₃N₄ for degradation of organic pollutants

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ABSTRACT

Using the bulk g-C₃N₄ as a precursor, four g-C₃N₄ nanosheets were further prepared by ultrasonic, thermal, acid, and alkali exfoliation. The structures of these materials were characterized by various techniques such as X-ray powder diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, energy dispersive X-Ray spectroscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy. The synergistical Fenton catalysis of these materials with Cu²⁺ was evaluated by using rhodamine B as a simulated organic pollutant. The results showed that there existed a significant synergistical Fenton catalysis between Cu²⁺ and g-C₃N₄. This synergistic effect can be observed even when the concentration of Cu²⁺ was as low as 0.064 mg L⁻¹. The properties of g-C₃N₄ strongly influenced the catalytic activity of the Cu²⁺/g-C₃N₄ system. The coexistent of Cu²⁺ and the alkali exfoliated g-C₃N₄ showed the most excellent catalytic activity. Hydroxyl radicals as oxidizing species were confirmed in the Cu²⁺/g-C₃N₄ system by electron paramagnetic resonance spectrum. The synergistic catalysis may be attributed to the easier reduction of Cu²⁺ adsorbed on the g-C₃N₄.

This study provided an excellent Fenton catalytic system, and partly solved the rapid deactivation of heterogeneous Fenton catalysts caused by the leaching of metal ions.

Key words: advanced oxidation process, copper, heterogeneous Fenton catalyst, synergistical catalysis, g-C₃N₄

HIGHLIGHTS

- There exists a significant synergistical Fenton catalysis between trace Cu²⁺ and g-C₃N₄.
- The Cu²⁺ concentration is lower than the maximum acceptable limit in drinking water.
- This study partly solved the rapid deactivation caused by the leaching of metal ions.
- This study reminds researchers to pay attention to the possible synergistic catalysis between leached ions and supports.
INTRODUCTION

Directly discharging of wastewaters containing refractory organics, such as dyes, phenols, drugs, and insecticides, seriously threatens the safety of environment. Economically treating these wastewaters is still a difficult task. Among various treating strategies based on physical, chemical, and biological principles, advanced oxidation processes (AOPs) are the most attractive techniques, because these processes generate strongly oxidizing radical species (primarily HO·) affording potentials of destroying the refractory pollutants to non-toxic small molecules like water, carbon dioxide, and inorganic salts. One of the AOPs, the classical homogeneous Fenton process, which activates H₂O₂ generating HO· through the redox cycle of Fe²⁺/Fe³⁺, has been extensively studied and commercially applied (Lin et al. 2020). However, some defects existing in this process increase the operating costs. For example, the pH should be controlled at about 3, thus the wastewater has to be acidified before treatment and neutralized before discharge. This process also products large amounts of iron sludge requiring further disposal. To overcome these defects, increasing attentions have been paid to heterogeneous Fenton systems, i.e. using solid Fe-containing materials as catalysts to activate H₂O₂. In recent decades, many iron compounds and supported iron materials as heterogeneous Fenton catalysts have been studied (Zhu et al. 2019). Meanwhile, other metals including Ag, Al, Ce, Co, Cr, Cu, Mn, and Ru as catalytically active species in heterogeneous Fenton systems have also received attentions (Bokare & Choi 2014). Among these metals, copper is the most important non-iron active species studied both in homogeneous and heterogeneous Fenton systems, because copper shows higher catalytic activity than other metals in a wide pH range (Bokare & Choi 2014; Gu et al. 2019). The Cu(II)-catalyzed Fenton reaction was generally considered to be based on the redox cycle of Cu (I)/Cu (II) to activate H₂O₂, similar to the redox cycle of Fe²⁺/Fe³⁺ (Nichela et al. 2013).

Leaching of metal ions is a fatal disadvantage of these solid catalysts (Zhu et al. 2019). This leaching not only leads to catalyst deactivation rapidly, but also raises the question whether the sites of the Fenton reaction are metal ions in the solid phase or the leached metal ions dissolved in the homogeneously aqueous phase. Obviously, it is a vital work to identify the Fenton catalysis through homogeneous or heterogeneous mechanism (Kuan et al. 2015). Some studies showed that the Fenton catalysis was attributed to homogeneous mechanism of the leached metal ions from solid catalysts, some studies suggested that the catalysis depended on the combination of homogeneous and heterogeneous mechanism. However, most studies using solid catalysts simply assumed that the Fenton reaction proceeded through heterogeneous routes. Some studies carried out experiments to ascertain the presence of heterogeneous mechanism. The approaches employed included (i) checking the catalytic activity of filtrates; (ii) adjusting solutions at alkaline/near-neutral pH to prevent metal ions leaching; (iii) comparing pollutant degradation kinetics in homogeneous and heterogeneous Fenton systems; and (iv) analysing the concentration of leached metal ions. When the concentration of the metal ions was found to be small, the reaction was assumed through a heterogeneous route (Kuan et al. 2015).
Kuan et al. (2015) studied the Fenton oxidation of 4-chlorophenol in the presence of FeOx/TiO2 or CuFe2O4 as a catalyst. Using inductively coupled plasma-optical emission spectroscopy (ICP-OES) in combination with pH monitoring and ultraviolet-visible spectroscopy (UV-vis), they monitored the degradation of 4-chlorophenol over the two Fenton heterogeneous systems. The results showed that these two systems proceeded predominantly through a homogeneous route via dissolved metal ions from the solid catalysts, and sub-ppm levels of Fe and Cu ions dissolved from the solid phases were sufficient to explain the observed 4-chlorophenol degradation rates. They also pointed out that above four approaches employed to ascertain the presence of heterogeneous catalytic routes cannot exclude the homogeneous Fenton route in the presence of solid catalysts.

Another problem ignored by researchers is the possible interaction between dissolved metal ions and solid catalyst supports. It has been reported that carbon materials as supports can significantly accelerate the reduction of Fe(III) to Fe(II), the rate-limiting step in the heterogeneous Fenton reaction, resulting in the enhancement of the decomposition of H2O2 and the production of HO· (Zhu et al. 2020a, 2020b). Obviously, a reasonable guess can be proposed that the carbon supports may also adsorb the dissolved metal ions such as Fe3+ and Cu2+ and promote their reduction, thus enhance the Fenton catalytic activities. That is to say, there may be synergistic catalysis between metal ions and carbon supports. This point, as far as we know, has not been reported. In fact, carbon material can be used not only as supports of heterogeneous Fenton catalysts, but also as heterogeneous Fenton catalysts (Navalon et al. 2011). Carbon materials as heterogeneous Fenton catalysts on their own have received increasing interests in recent years, because there is no the defect of metal ion leaching in this kind of metal free catalysts. Carbon materials studied as heterogeneous Fenton catalysts included activated carbon, carbon black, biochar, carbon nanotube, carbon xerogel, glycerol-based carbon, carbon quantum dot, graphite, graphene, etc. Among these carbon materials, graphene, a famous 2D carbon material, has attracted the most intensive attention. Graphene, graphene oxide, and reduced graphene oxide were all studied as heterogeneous metal-free catalysts for Fenton processes (Zhu et al. 2020a, 2020b).

Graphitic carbon nitride (g-C3N4) is another famous 2D carbon material, which has similar structure with graphene. g-C3N4 materials were mainly used as photocatalysts (Li et al. 2020a, 2020b), and also used as catalyst supports, including as heterogeneous Fenton catalyst supports (Ding et al. 2019; Wang & Nan 2020). Recently, we reported the performance of g-C3N4 as a heterogeneous Fenton catalyst for the first time (Zhu et al. 2020a, 2020b). We found that even unmodified g-C3N4 prepared by the conventional urea pyrolysis was still an effective heterogeneous Fenton catalyst over a wide pH range. However, the catalytic activity of the g-C3N4 was not high at room temperature. In this paper, we, using rhodamine B as a simulated organic pollutant, studied the synergistically homogeneous-heterogeneous Fenton catalysis of trace Cu2+ and g-C3N4. The results showed that the Fenton catalytic activity in the coexistence of Cu2+ and g-C3N4 was much higher than that in the existence of Cu2+ or g-C3N4 alone. When g-C3N4 nanosheets replacing the convenient bulk g-C3N4, excellent catalytic activity can be observed.

**METHODS**

**Materials**

Urea was purchased from Tianjin Fengchuan Chemical Reagent Co., Ltd (Tianjin, China). Methanol, absolute alcohol, Cu(NO3)2·3H2O, KOH, HCl (56%), H2SO4 (98%), NaOH, ethylenediamine tetraacetic acid (EDTA), rhodamine B (RhB), isopropanol, and H2O2 (30%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). These reagents were of analytical grade and were used without further purification.

**Preparation of bulk g-C3N4**

The bulk g-C3N4 was synthesized by the conventional urea pyrolysis (Liu et al. 2011; Zhu et al. 2020a, 2020b). Urea was dried at 80 °C for 1 h in a crucible with a cover. Then the crucible was heated to 580 °C with the heating rate of about 3 °C min−1 in a Muffle furnace, and remained at 580 °C for 3 h. The product was washed successively with 0.1 mol L−1 HCl, deionized water, and absolute alcohol until the filtrate was neutral. Lastly, the wet sample was dried in a vacuum freeze dryer for 10 h.

**Preparation of ultrasonic exfoliated g-C3N4**

The bulk g-C3N4 of 0.1 g was dispersed in 100 mL methanol. The mixture was treated by ultrasonic for 4 h using a JN-5200DT sonicator (Ningbo Jiangnan Instrument Factory, China) working at 40 kHz and 200 w. The product was separated by centrifugation, washed to be neutral, and dried at 105 °C (Zhao et al. 2014).
Preparation of thermal exfoliated g-C₃N₄
The nanosheet was prepared by thermal oxidation etching of the bulk g-C₃N₄ in air (Niu et al. 2012). The bulk g-C₃N₄ in a crucible was heated to 580 °C with a heating rate of 5 °C min⁻¹ and kept at 580 °C for 2 h.

Preparation of acid exfoliated g-C₃N₄
The bulk g-C₃N₄ of 2 g was dispersed in 40 mL H₂SO₄ (98%). The mixture was stirred at room temperature for 8 h, and then slowly poured into 200 mL deionized water. The temperature of the mixture increased rapidly, and the color changed from yellow to light yellow. After ultrasonic treatment for 4 h, the product was separated by centrifugation, washed to be neutral, and dried at 105 °C (Xu et al. 2013).

Preparation of alkaline exfoliated g-C₃N₄
The colloidal of g-C₃N₄ nanosheet was obtained by exfoliating the bulk g-C₃N₄ in KOH aqueous solution (Li et al. 2017). The bulk g-C₃N₄ of 0.5 g was dispersed in 40 mL KOH aqueous solution of 5 mol L⁻¹. The mixture was stirred at 80 °C for 12 h. In this period the mixture gradually became a transparent colloid. After centrifuging the colloid to remove little residue, the restacked g-C₃N₄ was obtained by adding HCl solution to the transparent colloid. The product was washed with water and dried at 60 °C.

Characterization of g-C₃N₄
Powder X-ray diffraction (XRD) data were collected on a Bruker D8 Advance diffractometer with Cu Kα radiation. Fourier transform infrared (FTIR) spectra were obtained on a WQF-510 infrared spectrophotometer (Beijing Rayleigh Analytical Instrument Corp., China) using the KBr disc method. Scanning electron microscope (SEM) images were recorded on a JEOL JSM-7500F electron microscope. Transmission electron microscopy (TEM) images were obtained using a Tecnai G2F20 S-Twin TMP electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo Scientific-Excab 250XI electron spectrometer. The electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EMX Plus EPR spectrometer. DMPO was used as a radical trapping agent.

Catalytic degradation of RhB
Typically, 100 mL RhB solution with a concentration of 50 mg/L was used as simulated wastewater to evaluate the catalytic performance of the studied systems. The degradation of RhB was carried out in a glass reactor of 250 mL immersed in a constant temperature water bath with magnetic stirring. The initial solution pH was adjusted using a small amount of 0.1 mol L⁻¹ HCl or 0.1 mol L⁻¹ NaOH solution. After adding the g-C₃N₄ and Cu²⁺ solution into the RhB solution, the mixture was stirred for 50 min to achieve adsorption-desorption equilibrium. Then the reaction was started by adding a certain amount of H₂O₂ solution. Unless otherwise specified, the reaction temperature was 25 °C, the initial pH was 9, the amount of g-C₃N₄ was 0.2 g L⁻¹, the concentration of Cu²⁺ was 0.64 mg L⁻¹, and the initial concentration of H₂O₂ was 50 mmol L⁻¹. At predetermined time intervals, a 4 mL reaction solution was taken out. After immediate centrifugation, the concentration of RhB was analyzed at 554 nm using an INESA 722G spectrophotometer. The decolorization efficiency of the dye was calculated based on the residual concentration. The UV-vis absorption spectra of the reaction solution were recorded by using a Shimadzu UV-2600 spectrophotometer.

To study the effect of variables on the degradation, the experiments were repeated under different initial pH values, g-C₃N₄ dosages, Cu²⁺ concentrations, H₂O₂ concentrations, dye concentrations and temperatures. As comparison, Cu²⁺ can be replaced by Ni²⁺, Zn²⁺, Fe²⁺, or Fe³⁺. EDTA or Fe(III)-EDTA can also be added to the reaction system to study their effects. The degradation of various other dyes was also carried out under the typical condition. The free radical capture experiment was carried out under the typical condition but adding isopropanol into degradation solution to 60 mmol L⁻¹.

RESULTS AND DISCUSSION
Characterization of bulk g-C₃N₄ and g-C₃N₄ nanosheets
The XRD patterns of the prepared bulk g-C₃N₄ and g-C₃N₄ nanosheets are shown in Figure 1. The crystal structure of the bulk g-C₃N₄ was verified by its XRD data (Liu et al. 2011). The sharp peak at 27.5° was indicative of the graphitic stacking structure, which was indexed as (002). The calculated stacking distance of aromatic units is 0.324 nm. A weak peak at 12.8° was attributed to the in-planar repeating unit, which was indexed as (100). Compared with the bulk g-C₃N₄, the XRD pattern of the sample prepared by ultrasonic exfoliation almost did not change, indicating that this g-C₃N₄ sample still remained larger.
size after the ultrasonic treatment. For the sample prepared by the thermal exfoliation, the sharp peak slight shifted from 27.5° to 27.7°, and the calculated stacking distance of aromatic units decreased to 0.322 nm, indicating that the thermal treatment resulted in a more condensed packing of g-C$_3$N$_4$ (Niu et al. 2012). After the acid exfoliation, the XRD peak at 27.5° obviously decreased and widened, and the peak at 12.8° almost disappeared, showing the formation of nano-sized ultrathin nanosheet (Xu et al. 2013).

The alkali treatment of the bulk g-C$_3$N$_4$ resulted in a transparent colloidal. This was significantly different from the above bulk and exfoliated g-C$_3$N$_4$ those particles are visible to the naked eye. The sample of alkali exfoliation used to be characterized came from restacking of the dissolved g-C$_3$N$_4$ nanosheet by adding HCl. From its XRD pattern it can be found that this re-stacked material still presented the typical structural features of g-C$_3$N$_4$. However, the peak at 27.5° obviously decreased, and the peak at 12.8° substantially shifted to 10.3°, indicating this material had a larger ‘hole to hole’ distance compared with the other g-C$_3$N$_4$ samples (Li et al. 2017).

The structures of the prepared bulk g-C$_3$N$_4$ and g-C$_3$N$_4$ nanosheets were further characterized by FTIR (Figure 2). The results indicated that all the prepared exfoliated samples preserved main structure of the bulk g-C$_3$N$_4$ (Liu et al. 2011; Sudhaik et al. 2018). The wide band between 3,000 and 3,500 cm$^{-1}$ was attributed to the uncondensed amino N–H stretching vibration. The strong bands at 1,630, 1,569, 1,454, and 1,395 cm$^{-1}$ were assigned to the stretching vibration of heptazine-
derived repeating units. The bands at 1,313 and 1,229 cm\(^{-1}\) corresponded to the stretching vibration of connected units of N–(C)\(_3\) or C–NH–C. The sharp band at 808 cm\(^{-1}\) represented the out-of-plane bending vibration of heptazine rings. However, there were some additional bands appearing in the alkali exfoliated sample. These bands could be attributed to the oxygen-containing groups generated from the alkali treatment of g-C\(_3\)N\(_4\). The band at about 3,400 cm\(^{-1}\) could be assigned to the absorbed or substituted OH groups. The shoulder band at about 1,700 cm\(^{-1}\) indicated the formation of C=O group. The bands at 451, 600, 732, 782, 829, 944, and 1,163 cm\(^{-1}\) may be related to the bending vibration of oxygen-containing groups. In addition, the band at 808 cm\(^{-1}\), which represented the out-of-plane bending vibration of heptazine rings, shifted slightly to 782 cm\(^{-1}\).

The morphology of the g-C\(_3\)N\(_4\) samples is shown in Figure 3. The as-prepared bulk g-C\(_3\)N\(_4\) showed loose aggregation of thin sheets. Its specific surface area was measured as about 77 m\(^2\) g\(^{-1}\), near the values of g-C\(_3\)N\(_4\) prepared by using similar methods (Liu et al. 2011; Sudhaik et al. 2018). All of the four exfoliated g-C\(_3\)N\(_4\) samples generally showed the stacking structure of nanosheets, although their morphologies were different. In addition, the thin chiffon-like nanosheets can be observed from the TEM image of the re-stacked sample of the alkali exfoliated g-C\(_3\)N\(_4\).

In view of the fact that the alkali exfoliated g-C\(_3\)N\(_4\) exhibited the best catalytic performance among the prepared g-C\(_3\)N\(_4\) samples (see below), XPS technique was employed to further detect the changes of surface groups. As shown in Figure 4, the survey scan showed that the bulk g-C\(_3\)N\(_4\) was composed primarily of carbon and nitrogen. The very weak O1s peak commonly observed in XPS spectra of g-C\(_3\)N\(_4\) may come from adsorbed oxygen. However, in the survey scan of the alkali exfoliated g-C\(_3\)N\(_4\), the C1s and N1s peaks decreased significantly, meanwhile, an obvious enhanced O1s peak can be observed, indicating that the treatment of alkali exfoliation resulted in partial destruction of the g-C\(_3\)N\(_4\) structure and formation of oxygen-containing groups. The high-resolution spectrum of O1s showed the deconvoluted three peaks at 531.8, 532.7, and 533.8 eV, being attributed to oxygen of O=C, O–C and O–H, respectively. Accordingly, two new C1s peaks at 286.1 eV and 289.0 eV attributed to carbon of O–C and O=C–O, respectively, can be deconvoluted from the C1s high-resolution spectrum of the alkali exfoliated g-C\(_3\)N\(_4\) (Pisanu et al. 2018). Meanwhile, the deconvoluted peak corresponded to sp\(^2\)-bonded carbon (N–C= N) decreased significantly and shifted slightly from 288.0 eV to 288.6 eV. The weak peak at 284.8 eV, which was attributed to graphitic carbon and usually appeared on the XPS characterization for g-C\(_3\)N\(_4\), also decreased. The high-resolution spectrum of N1 s showed that the deconvoluted three peaks at 398.6, 400.2, and 401.3 eV, which could be attributed to sp2 hybrid nitrogen (C–N=C), tertiary nitrogen (N–(C)\(_3\)), and amino groups with a hydrogen atom (C–N–H), respectively, still existed after the treatment of alkali exfoliation. The peak deconvoluted at 399.6 eV was attributed to the new N-containing group resulted from the alkali treatment.

Figure 3 | SEM images of (a) bulk g-C\(_3\)N\(_4\) and g-C\(_3\)N\(_4\) nanosheets prepared via (b) ultrasonic, (c) thermal, (d) acid, and (e) alkali exfoliation; (f) TEM image of alkali exfoliated g-C\(_3\)N\(_4\).
Synergistic catalysis between Cu$^{2+}$ and bulk g-C$_3$N$_4$

The existence of synergistic catalysis between Cu$^{2+}$ and g-C$_3$N$_4$ was firstly proved by using the bulk g-C$_3$N$_4$ (Figure 5). At pH 5 and 50 °C, the bulk g-C$_3$N$_4$ alone showed only weak catalytic activity, and the decolorization efficiency was only about 20% in 140 min, and the catalytic activity of Cu$^{2+}$ with the concentration as low as 0.064 mg L$^{-1}$ was nearly same to that of the bulk g-C$_3$N$_4$. However, when the two coexisted, the catalytic activity was obviously improved. In this case the decolorization efficiency was more than 60% in 140 min, clearly showing the synergistic catalysis between the two.

Further increasing the concentration of Cu$^{2+}$ to 0.64 mg L$^{-1}$, the catalytic activity of Cu$^{2+}$ was obviously improved, and the dye degradation efficiency reached about 60% in 140 minutes. However, when this Cu$^{2+}$ coexisted with the bulk g-C$_3$N$_4$, the decolorization efficiency reached more than 90% in the same period, showing excellent catalytic performance. Moreover, this Cu$^{2+}$ concentration is even lower than the maximum acceptable limit of Cu$^{2+}$ concentration in drinking water. The discharge of wastewater containing Cu$^{2+}$ with this concentration should not cause environmental pollution. The higher concentration of Cu$^{2+}$ would conceal the synergistic effect because of its obvious catalytic activity (Figure S1). Moreover, the discharge of Cu$^{2+}$ with high concentration will cause environmental pollution.

The synergistic catalysis at different pH was investigated by using the bulk g-C$_3$N$_4$ (Figure 6). The results showed that there was synergistic catalysis in the range of pH 3–9. In particular, at pH 5 the synergistic effect was most obvious. In the alkaline condition, the catalytic activity of single Cu$^{2+}$ was higher than that of the bulk g-C$_3$N$_4$, partially concealing the synergistic effect.

It should be pointed out that although the above investigation doubtlessly proved that there was a synergistic effect between Cu$^{2+}$ and the bulk g-C$_3$N$_4$, higher catalytic activity emerged only at higher temperature. At room temperature the catalytic activity was relatively low. For example, at 50 °C, the degradation efficiency reached more than 90% in 140 min, while at...
30 °C, it was only about 40% (Figure S2). This may be due to the lack of active sites provided by the bulk g-C3N4. Therefore, we prepared four g-C3N4 nanosheets via various exfoliations and studied their synergistic catalysis with Cu2⁺ to expectantly obtain high catalytic activity at room temperature.

Synergistic catalysis between Cu2⁺ and g-C3N4 nanosheets

Figure 7 and S3 show the catalytic activities of the g-C3N4 samples with and without Cu2⁺ at pH 9 and 25 °C. In the absence of Cu2⁺, the Fenton catalytic activity of the g-C3N4 nanosheets prepared by different methods was obviously higher than that of the bulk g-C3N4. When each nanosheet separately coexisted with Cu2⁺, the synergistic catalysis was more significant than that of the Cu2⁺ and bulk g-C3N4 system. In particular, the alkali exfoliated g-C3N4 and Cu2⁺ system exhibited most excellent catalytic performance. The dye degradation efficiency reached about 97% in 10 min at room temperature, which was much...
better than that of the Cu$^{2+}$ and bulk g-C$_3$N$_4$ system. Even if the concentration of Cu$^{2+}$ was reduced to 0.064 mg L$^{-1}$, the mixed system still showed fairly good catalytic activity. The degradation efficiency of the dye reached 75% in 10 min and 90% in 60 min (Figure 8).

The effect of pH value on the catalytic performance of the alkali exfoliated g-C$_3$N$_4$ and Cu$^{2+}$ system was also investigated (Figure 9). It was found that the catalytic activity was excellent in the range of pH 7–9. The activity decreased when pH dropped below 6. In fact, the restacked product of the alkali exfoliated g-C$_3$N$_4$ could dissolve in water in alkaline condition, forming a transparent solution. This may be one of the reasons for its high activity. When the pH value decreased, the system was turbid, indicating the precipitation of g-C$_3$N$_4$ via restacking.

The alkali exfoliated g-C$_3$N$_4$ and trace Cu$^{2+}$ constituted an excellent synergistic catalytic system. This system still showed high degradation efficiency for RhB under the condition of low g-C$_3$N$_4$ dosage (0.05 g L$^{-1}$), low concentration of H$_2$O$_2$ (5 mmol L$^{-1}$), and higher dye concentration (100 mg L$^{-1}$). It also performed well in degradation of various other dyes (Figure S4). Compared with recently reported catalysts for heterogeneous Fenton degradation of RhB, this synergistic system displayed quite excellent catalytic activity, as shown in Table S1.
Possible mechanism

Hydroxyl radicals (HO·) generated by activating H₂O₂ as oxidizing species were confirmed in the Cu²⁺/g-C₃N₄ system by the characteristic ESR spectrum of DMPO-OH spin adduct (Figure 10). As controlled experiments, a very weak signal can be observed in the presence of H₂O₂ alone without Cu²⁺ and g-C₃N₄, it may be owing to the decomposition of H₂O₂ caused by impurities. In the presence of Cu²⁺, the signal was slightly enhanced, indicating that the low concentration Cu²⁺ had only a weak ability to activate H₂O₂. In the presence of the alkali exfoliated g-C₃N₄, the signal became stronger, indicating that the alkali exfoliated g-C₃N₄ had obvious Fenton catalytic activity. However, in the presence of Cu²⁺ and the alkali exfoliated g-C₃N₄, the signal significantly enhanced, obviously indicating that the Cu²⁺ and the alkali exfoliated g-C₃N₄ had a synergistic Fenton catalytic effect. From the UV-vis spectra of the reaction solution in Figure S5, it can be found that the structure of the xanthene-conjugated chromophore (554 nm) of the RhB molecule was destructed quickly by hydroxyl radicals.

Figure 9 | Effect of pH on synergetic catalysis.

Figure 10 | EPR spectra of DMPO-OH in various system.
That HO· was the major reactive oxidizing species was further supported by a scavenging experiment of free radicals. The addition of isopropanol, a HO· scavenger, in the Cu²⁺ and the alkali exfoliated g-C₃N₄ system significantly decreased the degradation of RhB (Figure S6).

As mentioned above, homogeneous Cu²⁺ as a Fenton catalyst has been extensively studied. It is generally believed that the activation of H₂O₂ to generate HO· is through Cu²⁺/Cu⁺ redox cycle mechanism, similar to Fe³⁺/Fe²⁺ cycle. However, if the Cu²⁺ concentration is as low as less than 1 mg L⁻¹, its catalytic activity is difficult to detect. For the Cu²⁺ and g-C₃N₄ system we can reasonably speculate that Cu²⁺, which adsorbed on the g-C₃N₄, was the active sites of the Fenton catalysis. Mainly in these sites H₂O₂ was activated to generate HO·. The catalysis of the unabsorbed homogeneous Cu²⁺ in the aqueous phase can be ignored due to the very low concentration. The catalysis of the g-C₃N₄ itself may only contribute a little to the dye degradation. Other ions with the same concentration, such as Ni²⁺, Zn²⁺, even Fe²⁺, the classical Fenton catalyst, did not enhance the catalytic activity of the bulk g-C₃N₄. Adding these ions to the Cu²⁺ and bulk g-C₃N₄ system also did not influence the catalytic activity (Figure S7).

It should be pointed out that the adsorbed Cu²⁺ is different from the supported Cu²⁺. The existence of adsorbed Cu²⁺ depends on the dissolved Cu²⁺ in the solution. To examine the speculation, we carried out several preliminary experiments. We measured the aqueous equilibrium concentration of Cu²⁺ in the Cu²⁺ and bulk g-C₃N₄ system and found that it was obviously lower than its initial concentration. The bulk g-C₃N₄ was separated from the equilibrium system, washed with water, and dried, then used to catalytically degrade the dye without adding additional Cu²⁺. It was found that this g-C₃N₄ performed obviously higher activity than the original g-C₃N₄, but lower activity than the Cu²⁺ and bulk g-C₃N₄ system (Figure S8). This implied that there existed absorbed Cu²⁺ on the separated g-C₃N₄. We also added EDTA into the Cu²⁺ and alkali exfoliated g-C₃N₄ system and found that the synergistical effect of Cu²⁺ completely disappeared due to the formation of stable Cu-EDTA complex. However, when adding more stable Fe-EDTA complex in the system, the catalytic activity was not influenced due to in this case EDTA did not react with Cu²⁺. As a control, the replacing of Cu²⁺ by Fe³⁺ with the same concentration did not accelerate the Fenton catalytic activity of the g-C₃N₄ (Figure 11).

Previous results have shown that the properties of g-C₃N₄ strongly affected the catalytic activity of the Cu²⁺/g-C₃N₄ system. The role of g-C₃N₄ may not only be used as adsorbent to enrich Cu²⁺. Its conductivity and surface groups may contribute to the reduction of Cu²⁺, which is the rate control step of Fenton reaction. These problems need to be further studied.

CONCLUSIONS

There may exist synergistic catalysis between the metal ions leached from the heterogeneous Fenton catalysts and the supports. This problem seems to have been ignored in the relevant research. This study, may be for the first time, confirmed that there existed a significant synergistical Fenton catalysis between trace Cu²⁺ and g-C₃N₄. The properties of g-C₃N₄...
strongly influenced the catalytic activity of the Cu\(^{2+}\)/g-C\(_3\)N\(_4\) system. The coexist of Cu\(^{2+}\) and the alkali exfoliated g-C\(_3\)N\(_4\) showed the most excellent catalytic activity. The synergistic catalysis may be attributed to the easier reduction of Cu\(^{2+}\) adsorbed on the g-C\(_3\)N\(_4\). The discharge of Cu\(^{2+}\) with the concentration below 1 mg L\(^{-1}\) would not threaten the safety of water environment. This study partly solved the rapid deactivation of heterogeneous Fenton catalysts caused by the leaching of metal ions, also reminds researchers to pay attention to the possible synergistic catalysis between leached Cu\(^{2+}\) and carbon supports when using copper supported on carbon materials as heterogeneous Fenton catalysts. The recovery of the g-C\(_3\)N\(_4\) nanosheets is still a problem. An obvious strategy is to combine g-C\(_3\)N\(_4\) with magnetic materials, thus the catalyst can be recovered by magnetic separation. In addition, the discussion of the mechanism in this study is still superficial, further in-depth exploration is necessary.

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CONFLICT OF INTEREST
There are no conflicts to declare.

DATA AVAILABILITY STATEMENT
All relevant data are included in the paper or its Supplementary Information.

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