

## Synergistically homogeneous-heterogeneous Fenton catalysis of trace copper ion and g-C<sub>3</sub>N<sub>4</sub> for degradation of organic pollutants

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### ABSTRACT

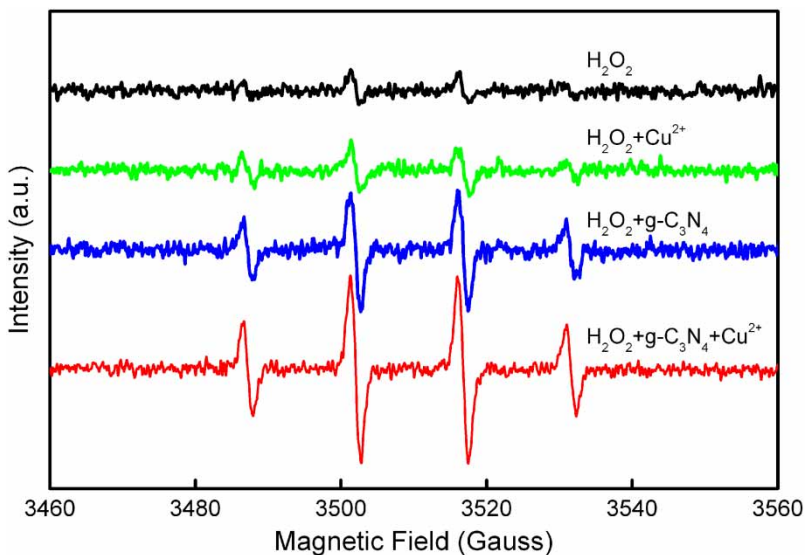
Using the bulk g-C<sub>3</sub>N<sub>4</sub> as a precursor, four g-C<sub>3</sub>N<sub>4</sub> nanosheets were further prepared by ultrasonic, thermal, acid, and alkali exfoliation. The structures of these materials were characterized by various techniques such as X-ray powder diffraction, Fourier transform 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 Cu<sup>2+</sup> was evaluated by using rhodamine B as a simulated organic pollutant. The results showed that there existed a significant synergistical Fenton catalysis between Cu<sup>2+</sup> and g-C<sub>3</sub>N<sub>4</sub>. This synergistic effect can be observed even when the concentration of Cu<sup>2+</sup> was as low as 0.064 mg L<sup>-1</sup>. The properties of g-C<sub>3</sub>N<sub>4</sub> strongly influenced the catalytic activity of the Cu<sup>2+</sup>/g-C<sub>3</sub>N<sub>4</sub> system. The coexistent of Cu<sup>2+</sup> and the alkali exfoliated g-C<sub>3</sub>N<sub>4</sub> showed the best catalytic activity. Hydroxyl radicals as oxidizing species were confirmed in the Cu<sup>2+</sup>/g-C<sub>3</sub>N<sub>4</sub> system by electron paramagnetic resonance spectra. The synergistic catalysis may be attributed to the easier reduction of Cu<sup>2+</sup> adsorbed on the g-C<sub>3</sub>N<sub>4</sub>. 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-C<sub>3</sub>N<sub>4</sub>

### HIGHLIGHTS

- There exists a significant synergistical Fenton catalysis between trace Cu<sup>2+</sup> and g-C<sub>3</sub>N<sub>4</sub>.
- The Cu<sup>2+</sup> 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.

## GRAPHICAL ABSTRACT



## INTRODUCTION

Direct 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  $\text{HO}\cdot$ ) affording the potential for transforming 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  $\text{H}_2\text{O}_2$  generating  $\text{HO}\cdot$  through the redox cycle of  $\text{Fe}^{2+}/\text{Fe}^{3+}$ , has been extensively studied and commercially applied (Lin *et al.* 2020). However, some problems 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 produces large amounts of iron sludge, requiring further disposal. To overcome these difficulties, increasing attention has been paid to heterogeneous Fenton systems, i.e. using solid Fe-containing materials as catalysts to activate  $\text{H}_2\text{O}_2$ . In recent decades, many iron compounds and supported iron materials as heterogeneous Fenton catalysts have been studied (Zhu *et al.* 2019). In addition, other metals including Ag, Al, Ce, Co, Cr, Cu, Mn, and Ru as catalytically active species in heterogeneous Fenton systems have also received attention (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 over 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  $\text{H}_2\text{O}_2$ , similar to the redox cycle of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  (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 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 have suggested that the catalysis depended on the combination of homogeneous and heterogeneous mechanisms. However, most studies using solid catalysts simply assumed that the Fenton reaction proceeded through heterogeneous routes. Some studies have carried out experiments to ascertain the presence of heterogeneous mechanisms. 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) analyzing the concentration of leached metal ions. When the concentration of the metal ions was found to be small, the reaction was assumed to be through a heterogeneous route (Kuan *et al.* 2015).

Kuan *et al.* (2015) studied the Fenton oxidation of 4-chlorophenol in the presence of  $\text{FeO}_x/\text{TiO}_2$  or  $\text{CuFe}_2\text{O}_4$  as a catalyst. Using inductively coupled plasma-optical emission spectroscopy (ICP-OES) in combination with pH monitoring and ultra-violet-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 the 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  $\text{H}_2\text{O}_2$  and the production of HO $\cdot$  (Zhu *et al.* 2020a). Obviously, a reasonable guess can be proposed that the carbon supports may also adsorb the dissolved metal ions such as  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  and promote their reduction, thus enhancing 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 interest in recent years, because there is no problem of metal ion leaching in this kind of metal-free catalysts. Carbon materials studied as heterogeneous Fenton catalysts have included activated carbon, carbon black, biochar, carbon nanotube, carbon xerogel, glycerol-based carbon, carbon quantum dots, graphite, graphene, etc. Among these carbon materials, graphene, a well known 2D carbon material, has attracted the most intensive attention. Graphene, graphene oxide, and reduced graphene oxide have been all studied as heterogeneous metal-free catalysts for Fenton processes (Zhu *et al.* 2020b).

Graphitic carbon nitride (g- $\text{C}_3\text{N}_4$ ) is another well known 2D carbon material, which has a similar structure as graphene. g- $\text{C}_3\text{N}_4$  materials were mainly used as photocatalysts (Li *et al.* 2020), 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- $\text{C}_3\text{N}_4$  as a heterogeneous Fenton catalyst for the first time (Zhu *et al.* 2020b). We found that even unmodified g- $\text{C}_3\text{N}_4$  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- $\text{C}_3\text{N}_4$  was not high at room temperature. In this study, we used rhodamine B as a simulated organic pollutant, and investigated the synergistically homogeneous-heterogeneous Fenton catalysis of trace  $\text{Cu}^{2+}$  and g- $\text{C}_3\text{N}_4$ . The results showed that the Fenton catalytic activity in the presence of both  $\text{Cu}^{2+}$  and g- $\text{C}_3\text{N}_4$  was much higher than that in the presence of  $\text{Cu}^{2+}$  or g- $\text{C}_3\text{N}_4$  alone. When g- $\text{C}_3\text{N}_4$  nanosheets replaced the convenient bulk g- $\text{C}_3\text{N}_4$ , excellent catalytic activity can be observed.

## METHODS

### Materials

Urea was purchased from Tianjin Fengchuan Chemical Reagent Co., Ltd (Tianjin, China). Methanol, absolute alcohol,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , KOH, HCl (36%),  $\text{H}_2\text{SO}_4$  (98%), NaOH, ethylenediamine tetraacetic acid (EDTA), rhodamine B (RhB), isopropanol, and  $\text{H}_2\text{O}_2$  (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- $\text{C}_3\text{N}_4$

The bulk g- $\text{C}_3\text{N}_4$  was synthesized by conventional urea pyrolysis (Liu *et al.* 2011; Zhu *et al.* 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 a heating rate of about 3 °C  $\text{min}^{-1}$  in a muffle furnace, and remained at 580 °C for 3 h. The product was washed successively with 0.1 mol  $\text{L}^{-1}$  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- $\text{C}_3\text{N}_4$

The bulk g- $\text{C}_3\text{N}_4$  of 0.1 g was dispersed in 100 mL methanol. The mixture was treated with ultrasound 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 neutrality, and dried at 105 °C (Zhao *et al.* 2014).

### Preparation of thermal exfoliated g-C<sub>3</sub>N<sub>4</sub>

The nanosheet was prepared by thermal oxidation etching of the bulk g-C<sub>3</sub>N<sub>4</sub> in air (Niu *et al.* 2012). The bulk g-C<sub>3</sub>N<sub>4</sub> in a crucible was heated to 580 °C with a heating rate of 5 °C min<sup>-1</sup> and kept at 580 °C for 2 h.

### Preparation of acid exfoliated g-C<sub>3</sub>N<sub>4</sub>

The bulk g-C<sub>3</sub>N<sub>4</sub> of 2 g was dispersed in 40 mL H<sub>2</sub>SO<sub>4</sub> (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 ultrasound treatment for 4 h, the product was separated by centrifugation, washed to neutrality, and dried at 105 °C (Xu *et al.* 2013).

### Preparation of alkali exfoliated g-C<sub>3</sub>N<sub>4</sub>

The colloidal g-C<sub>3</sub>N<sub>4</sub> nanosheet was obtained by exfoliating the bulk g-C<sub>3</sub>N<sub>4</sub> in KOH aqueous solution (Li *et al.* 2017). The bulk g-C<sub>3</sub>N<sub>4</sub> of 0.5 g was dispersed in a 40 ml KOH aqueous solution of 5 mol L<sup>-1</sup>. 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 small amounts of residue residue, the re-stacked g-C<sub>3</sub>N<sub>4</sub> was obtained by adding HCl solution to the transparent colloid. The product was washed with water and dried at 60 °C.

### Characterization of g-C<sub>3</sub>N<sub>4</sub>

Powder X-ray diffraction (XRD) data were collected on a Bruker D8 Advance diffractometer with Cu K $\alpha$  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 scanning 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-Escalb 250XI electron spectrometer. The electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EMX Plus EPR spectrometer. 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) was used as a radical trapping agent.

### Catalytic degradation of RhB

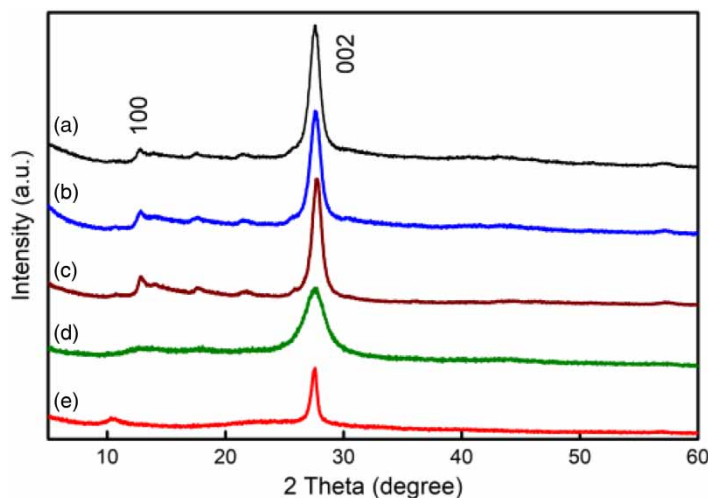
Typically, 100 mL RhB solution with a concentration of 50 mg/L was used as simulated wastewater to evaluate the catalytic performance of the studied systems. The degradation of RhB was carried out in a glass reactor of 250 mL immersed in a constant temperature water bath with magnetic stirring. The initial solution pH was adjusted using a small amount of 0.1 mol L<sup>-1</sup> HCl or 0.1 mol L<sup>-1</sup> NaOH solution. After adding the g-C<sub>3</sub>N<sub>4</sub> and Cu<sup>2+</sup> solution into the RhB solution, the mixture was stirred for 30 min to achieve adsorption–desorption equilibrium. Then the reaction was started by adding a certain amount of H<sub>2</sub>O<sub>2</sub> solution. Unless otherwise specified, the reaction temperature was 25 °C, the initial pH was 9, the amount of g-C<sub>3</sub>N<sub>4</sub> was 0.2 g L<sup>-1</sup>, the concentration of Cu<sup>2+</sup> was 0.64 mg L<sup>-1</sup>, and the initial concentration of H<sub>2</sub>O<sub>2</sub> was 50 mmol L<sup>-1</sup>. 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-C<sub>3</sub>N<sub>4</sub> dosages, Cu<sup>2+</sup> concentrations, H<sub>2</sub>O<sub>2</sub> concentrations, dye concentrations and temperatures. As a comparison, Cu<sup>2+</sup> could be replaced by Ni<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>2+</sup>, or Fe<sup>3+</sup>. 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 typical conditions. The free radical capture experiment was carried out under typical conditions, but adding isopropanol into the degradation solution to 60 mmol L<sup>-1</sup>.

## RESULTS AND DISCUSSION

### Characterization of bulk g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> nanosheets

The XRD patterns of the prepared bulk g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> nanosheets are shown in Figure 1. The crystal structure of the bulk g-C<sub>3</sub>N<sub>4</sub> 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-C<sub>3</sub>N<sub>4</sub>, the XRD pattern of the sample prepared by ultrasonic exfoliation almost did not change, indicating that this g-C<sub>3</sub>N<sub>4</sub> sample still remained as a

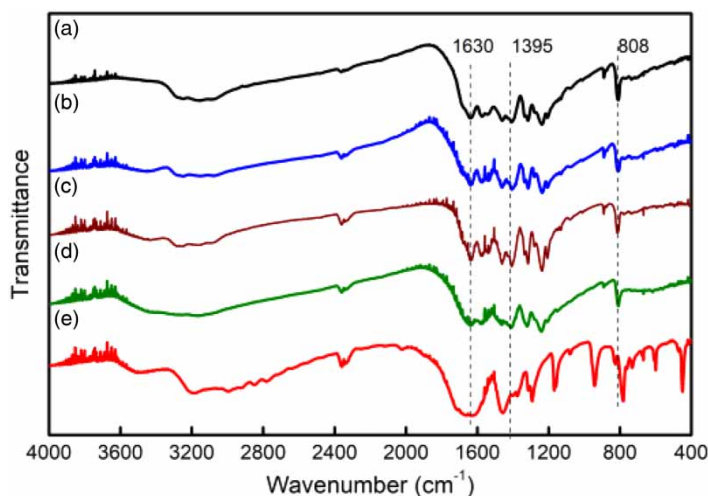


**Figure 1** | XRD patterns of (a) bulk  $g\text{-C}_3\text{N}_4$  and  $g\text{-C}_3\text{N}_4$  nanosheets prepared via (b) ultrasonic, (c) thermal, (d) acid, and (e) alkali exfoliation.

larger size after the ultrasound treatment. For the sample prepared by thermal exfoliation, the sharp peak slightly shifted from  $27.5^\circ$  to  $27.7^\circ$ , 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  $g\text{-C}_3\text{N}_4$  (Niu *et al.* 2012). After acid exfoliation, the XRD peak at  $27.5^\circ$  obviously decreased and widened, and the peak at  $12.8^\circ$  almost disappeared, showing the formation of nano-sized ultrathin nanosheets (Xu *et al.* 2013).

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

The structures of the prepared bulk  $g\text{-C}_3\text{N}_4$  and  $g\text{-C}_3\text{N}_4$  nanosheets were further characterized by FTIR (Figure 2). The results indicated that all the prepared exfoliated samples preserved the main structure of the bulk  $g\text{-C}_3\text{N}_4$  (Liu *et al.* 2011; Sudhaik *et al.* 2018). The wide band between  $3,000$  and  $3,500\text{ cm}^{-1}$  was attributed to an uncondensed amino N-H stretching vibration. The strong bands at  $1,630$ ,  $1,569$ ,  $1,454$ , and  $1,395\text{ cm}^{-1}$  were assigned to the stretching vibration of

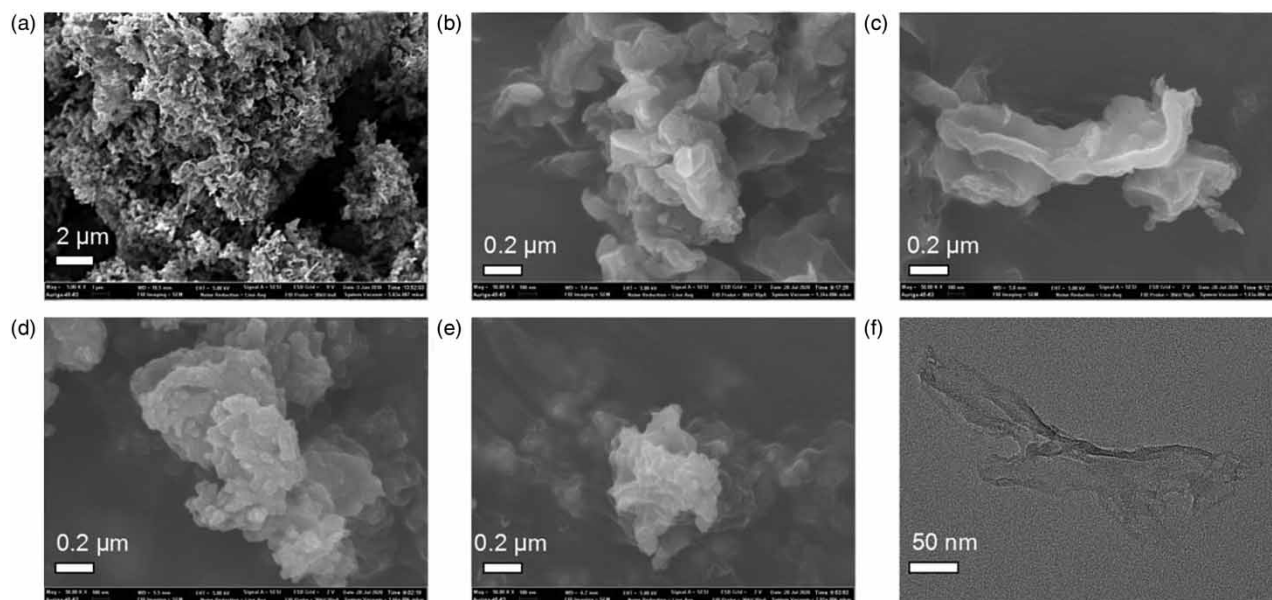


**Figure 2** | FTIR spectra of (a) bulk  $g\text{-C}_3\text{N}_4$  and  $g\text{-C}_3\text{N}_4$  nanosheets prepared via (b) ultrasonic, (c) thermal, (d) acid, and (e) alkali exfoliation.

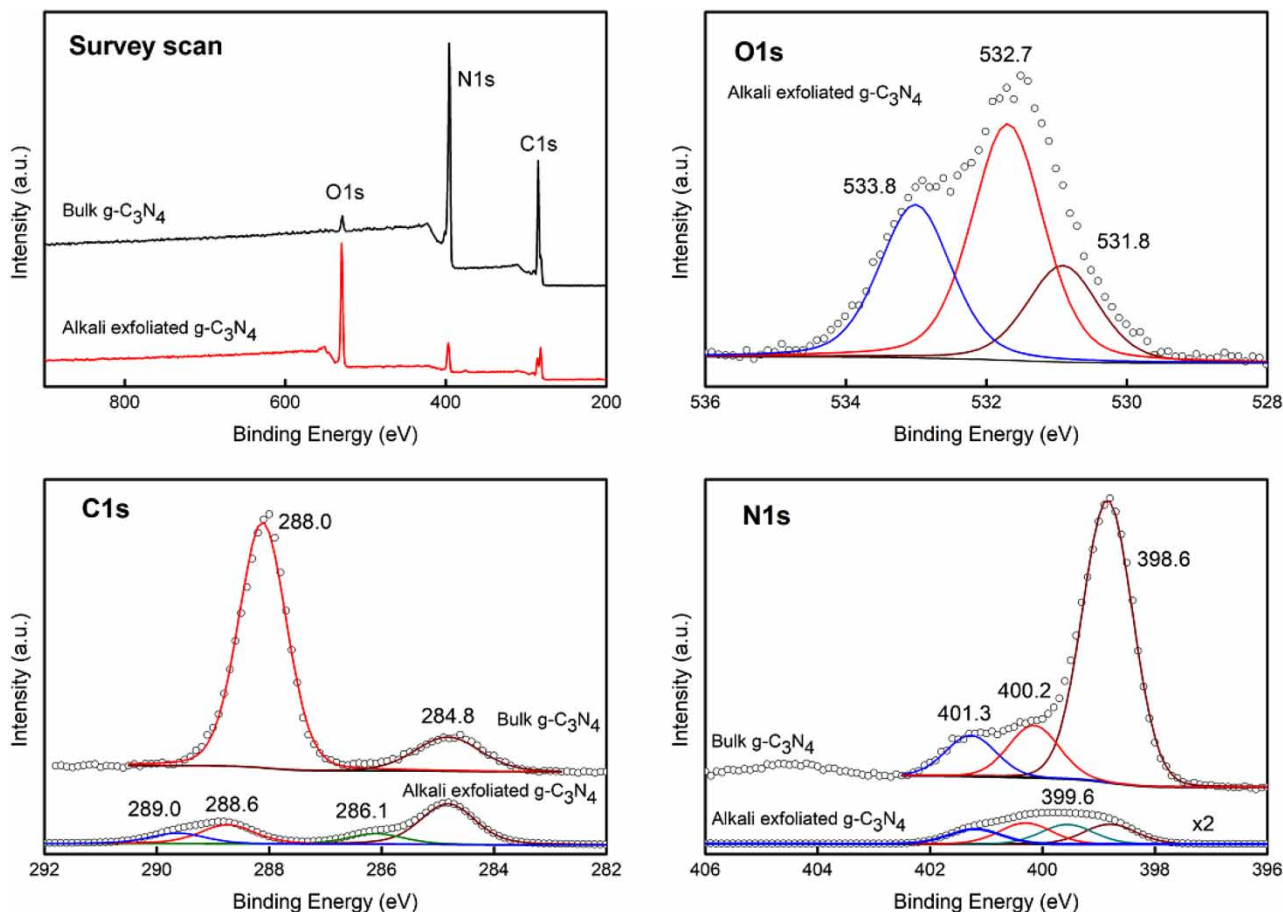
heptazine-derived repeating units. The bands at 1,313 and 1,229  $\text{cm}^{-1}$  corresponded to the stretching vibration of connected units of N-(C)<sub>5</sub> or C-NH-C. The sharp band at 808  $\text{cm}^{-1}$  represented the out-of-plane bending vibration of heptazine rings. However, there were 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<sub>3</sub>N<sub>4</sub>. The band at about 3,400  $\text{cm}^{-1}$  could be assigned to the absorbed or substituted OH groups. The shoulder band at about 1,700  $\text{cm}^{-1}$  indicated the formation of the C = O group. The bands at 451, 600, 732, 782, 829, 944, and 1,163  $\text{cm}^{-1}$  may be related to the bending vibration of oxygen-containing groups. In addition, the band at 808  $\text{cm}^{-1}$ , which represented the out-of-plane bending vibration of heptazine rings, shifted slightly to 782  $\text{cm}^{-1}$ .

The morphology of the g-C<sub>3</sub>N<sub>4</sub> samples is shown in Figure 3. The as-prepared bulk g-C<sub>3</sub>N<sub>4</sub> showed loose aggregation of thin sheets. Its specific surface area was measured as about 77  $\text{m}^2 \text{g}^{-1}$ , near the values for g-C<sub>3</sub>N<sub>4</sub> prepared by using similar methods (Liu *et al.* 2011; Sudhaik *et al.* 2018). All of the four exfoliated g-C<sub>3</sub>N<sub>4</sub> samples generally showed the stacking structure of nanosheets, although their morphologies were different. In addition, the thin chiffon-like nanosheets could be observed from the TEM image of the re-stacked sample of the alkali exfoliated g-C<sub>3</sub>N<sub>4</sub>.

In view of the fact that the alkali exfoliated g-C<sub>3</sub>N<sub>4</sub> exhibited the best catalytic performance among the prepared g-C<sub>3</sub>N<sub>4</sub> samples (see below), the XPS technique was employed to further detect any changes in the surface groups. As shown in Figure 4, the survey scan showed that the bulk g-C<sub>3</sub>N<sub>4</sub> was composed primarily of carbon and nitrogen. The very weak O1s peak commonly observed in XPS spectra of g-C<sub>3</sub>N<sub>4</sub> may come from adsorbed oxygen. However, in the survey scan of the alkali exfoliated g-C<sub>3</sub>N<sub>4</sub>, the C1s and N1s peaks decreased significantly, meanwhile, an obvious enhanced O1s peak could be observed, indicating that the treatment of alkali exfoliation resulted in partial destruction of the g-C<sub>3</sub>N<sub>4</sub> structure and formation of oxygen-containing groups. The high-resolution spectrum of O1s showed that the deconvoluted three peaks at 531.8, 532.7, and 533.8 eV, were 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<sub>3</sub>N<sub>4</sub> (Pisanu *et al.* 2018). In addition, the deconvoluted peak corresponded to sp<sup>2</sup>-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<sub>3</sub>N<sub>4</sub>, also decreased. The high-resolution spectrum of N1s showed that the deconvoluted three peaks at 398.6, 400.2, and 401.3 eV, which could be attributed to sp<sup>2</sup> hybrid nitrogen (C - N = C), tertiary nitrogen (N - (C)<sub>3</sub>), and amino groups with a hydrogen atom (C - N - H), respectively, still existed after treatment with alkali exfoliation. The peak deconvoluted at 399.6 eV was attributed to the new N-containing group resulting from the alkali treatment.



**Figure 3** | SEM images of (a) bulk g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> nanosheets prepared via (b) ultrasonic, (c) thermal, (d) acid, and (e) alkali exfoliation. (f) TEM image of alkali exfoliated g-C<sub>3</sub>N<sub>4</sub>.



**Figure 4** | Comparison of XPS survey spectra, O1s, C1s, and N1s of bulk  $g\text{-C}_3\text{N}_4$  and alkali exfoliated  $g\text{-C}_3\text{N}_4$ .

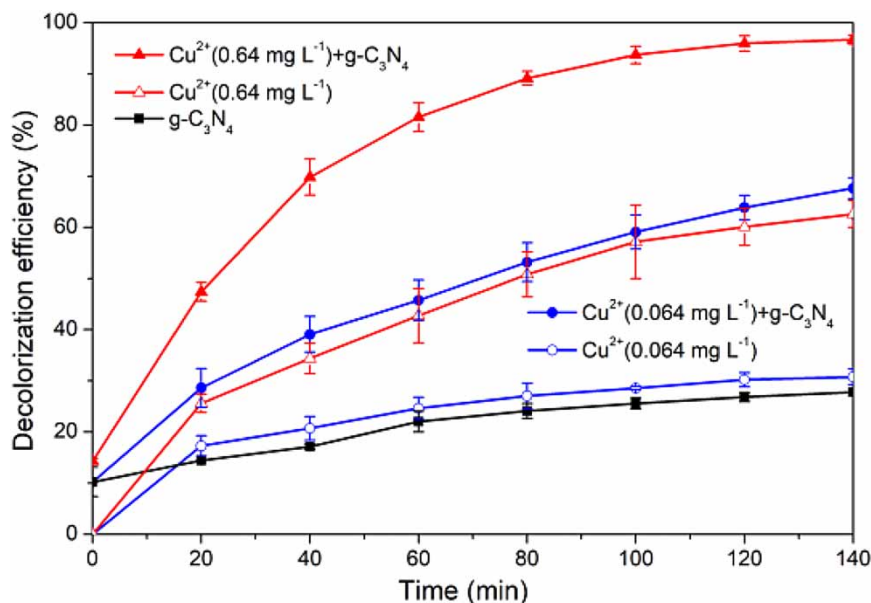
### Synergistic catalysis between $\text{Cu}^{2+}$ and bulk $g\text{-C}_3\text{N}_4$

The existence of synergistic catalysis between  $\text{Cu}^{2+}$  and  $g\text{-C}_3\text{N}_4$  was firstly proved by using the bulk  $g\text{-C}_3\text{N}_4$  (Figure 5). At pH 5 and  $50^\circ\text{C}$ , the bulk  $g\text{-C}_3\text{N}_4$  alone showed only weak catalytic activity, and the decolorization efficiency was only about 20% in 140 min, and the catalytic activity of  $\text{Cu}^{2+}$  with the concentration as low at  $0.064\text{ mg L}^{-1}$  was nearly same as that of the bulk  $g\text{-C}_3\text{N}_4$ . 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.

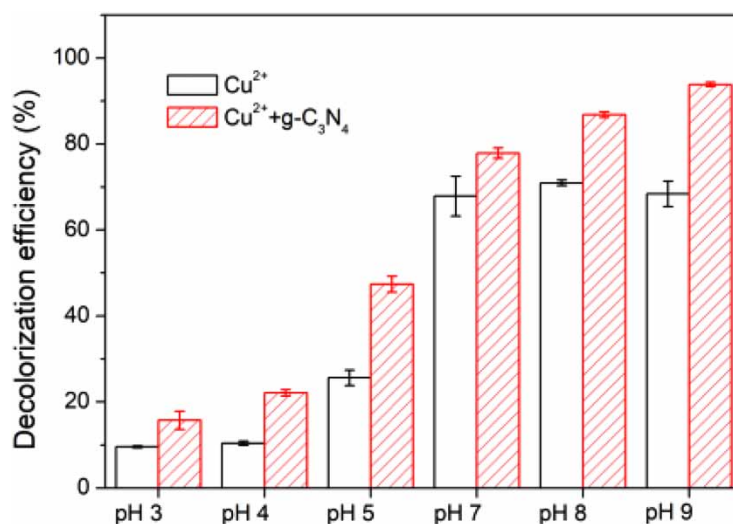
Further increasing the concentration of  $\text{Cu}^{2+}$  to  $0.64\text{ mg L}^{-1}$ , the catalytic activity of  $\text{Cu}^{2+}$  was obviously improved, and the dye degradation efficiency reached about 60% in 140 minutes. However, when this  $\text{Cu}^{2+}$  coexisted with the bulk  $g\text{-C}_3\text{N}_4$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

The synergistic catalysis at different pH was investigated by using the bulk  $g\text{-C}_3\text{N}_4$  (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. Under alkaline conditions, the catalytic activity of single  $\text{Cu}^{2+}$  was higher than that of the bulk  $g\text{-C}_3\text{N}_4$ , partially concealing the synergistic effect.

It should be pointed out that, although the above investigation doubtlessly proved that there was a synergistic effect between  $\text{Cu}^{2+}$  and the bulk  $g\text{-C}_3\text{N}_4$ , higher catalytic activity emerged only at higher temperatures. At room temperature the catalytic activity was relatively low. For example, at  $50^\circ\text{C}$ , the degradation efficiency reached more than 90% in 140 min, while at



**Figure 5** | Effect of copper ion concentration on synergetic catalysis. The slight decolorization at Time = 0 was caused by the adsorption of the bulk g-C<sub>3</sub>N<sub>4</sub>.



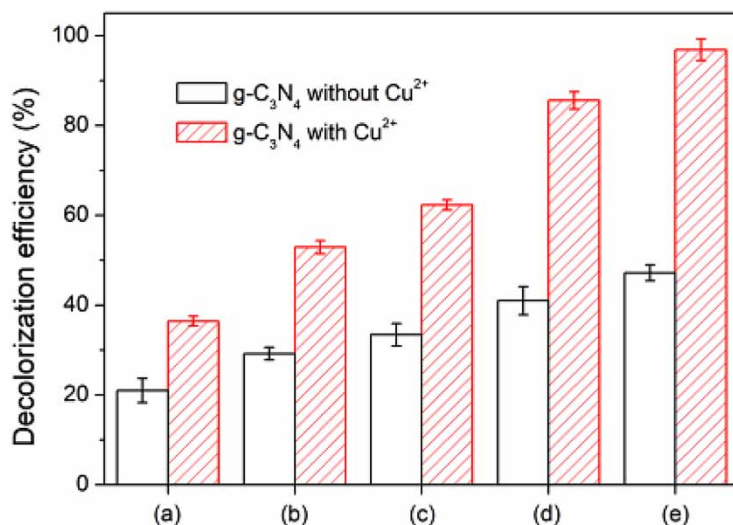
**Figure 6** | Effect of pH on synergetic catalysis (20 min).

30 °C, it was only about 40% (Figure S2). This may be due to the lack of active sites provided by the bulk g-C<sub>3</sub>N<sub>4</sub>. Therefore, we prepared four g-C<sub>3</sub>N<sub>4</sub> nanosheets via various exfoliations and studied their synergistic catalysis with Cu<sup>2+</sup> to expectantly obtain high catalytic activity at room temperature.

### Synergistic catalysis between Cu<sup>2+</sup> and g-C<sub>3</sub>N<sub>4</sub> nanosheets

Figure 7 and Figure S3 show the catalytic activities of the g-C<sub>3</sub>N<sub>4</sub> samples with and without Cu<sup>2+</sup> at pH 9 and 25 °C. In the absence of Cu<sup>2+</sup>, the Fenton catalytic activity of the g-C<sub>3</sub>N<sub>4</sub> nanosheets prepared by different methods was obviously higher than that of the bulk g-C<sub>3</sub>N<sub>4</sub>. When each nanosheet separately coexisted with Cu<sup>2+</sup>, the synergistic catalysis was more significant than that of the Cu<sup>2+</sup> and bulk g-C<sub>3</sub>N<sub>4</sub> system. In particular, the alkali applied g-C<sub>3</sub>N<sub>4</sub> and Cu<sup>2+</sup> system exhibited the best catalytic performance. The dye degradation efficiency reached about 97% in 10 min at room temperature, which was much



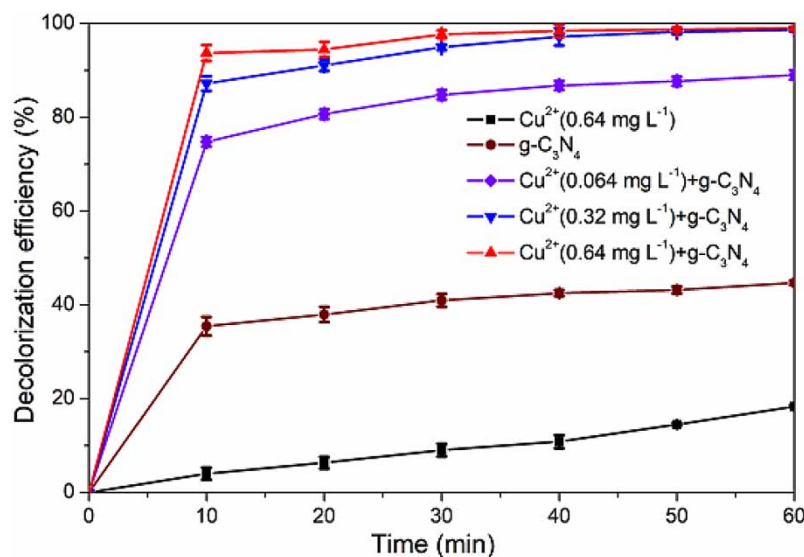


**Figure 7** | Effect of (a) bulk g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> nanosheet prepared via (b) ultrasonic, (c) thermal, (d) acid, and (e) alkali exfoliation on synergetic catalysis (10 min).

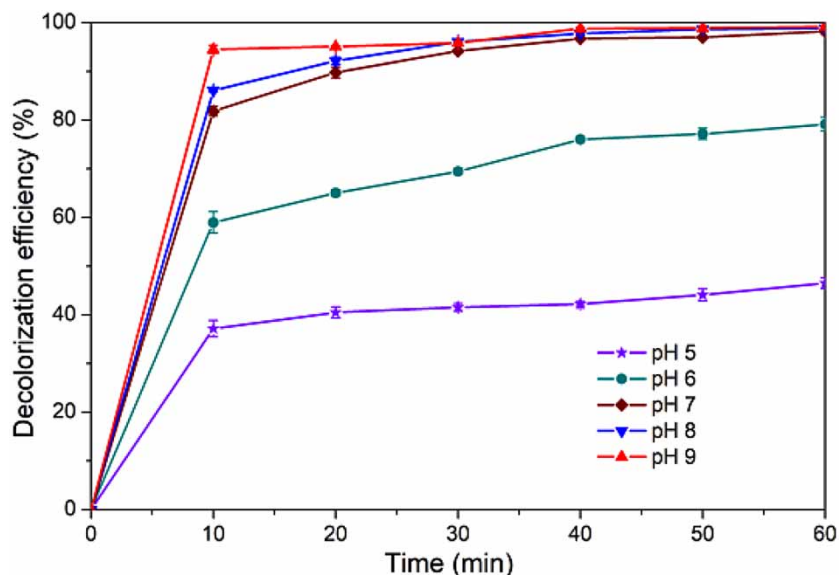
better than that of the Cu<sup>2+</sup> and bulk g-C<sub>3</sub>N<sub>4</sub> system. Even if the concentration of Cu<sup>2+</sup> was reduced to 0.064 mg L<sup>-1</sup>, the mixed system still showed fairly good catalytic activity. The degradation efficiency of the dye reached 75% in 10 min and 90% in 60 min (Figure 8).

The effect of pH value on the catalytic performance of the alkali exfoliated g-C<sub>3</sub>N<sub>4</sub> and Cu<sup>2+</sup> system was also investigated (Figure 9). It was found that the catalytic activity was excellent in the range pH 7–9. The activity decreased when the pH dropped below 6. In fact, the re-stacked product of the alkali exfoliated g-C<sub>3</sub>N<sub>4</sub> could dissolve in water under 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<sub>3</sub>N<sub>4</sub> via restacking.

The alkali exfoliated g-C<sub>3</sub>N<sub>4</sub> and trace Cu<sup>2+</sup> constituted an excellent synergistic catalytic system. This system still showed high degradation efficiency for RhB under the condition of low g-C<sub>3</sub>N<sub>4</sub> dosage (0.05 g L<sup>-1</sup>), low concentration of H<sub>2</sub>O<sub>2</sub> (5 mmol L<sup>-1</sup>), and higher dye concentration (100 mg L<sup>-1</sup>). 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 (Supporting information).



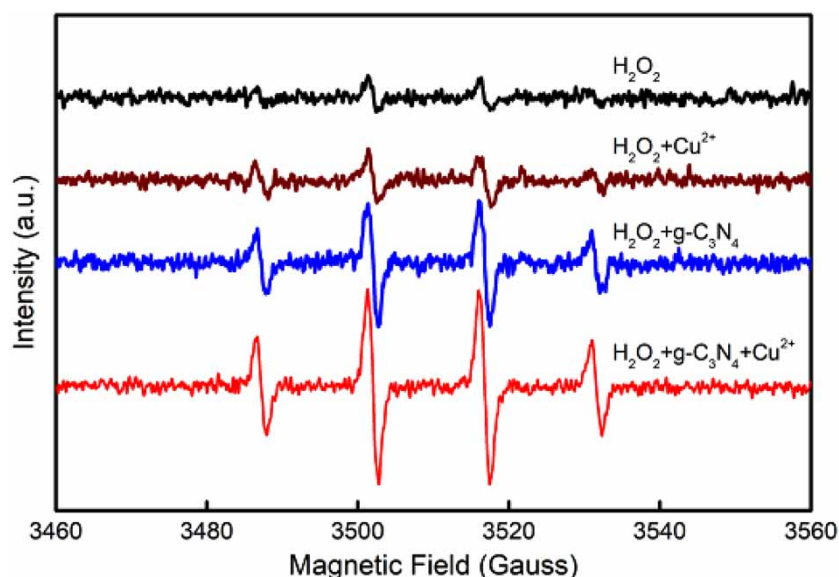
**Figure 8** | Effect of copper ion concentration on synergetic catalysis.



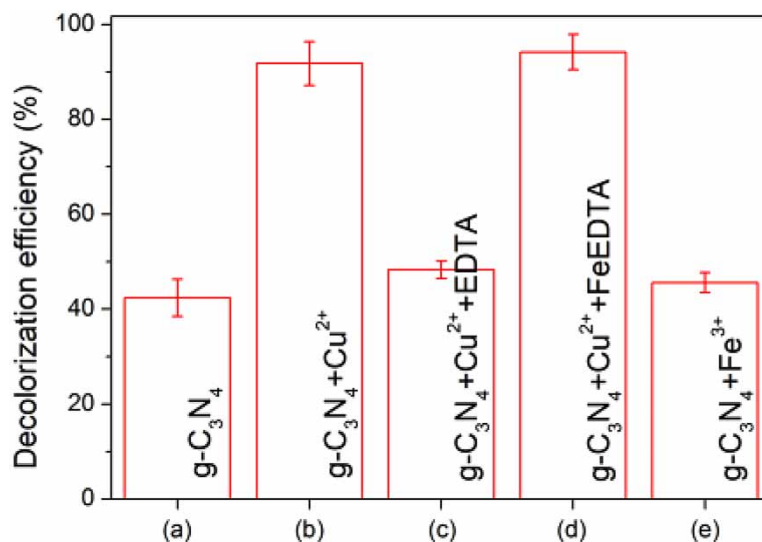
**Figure 9** | Effect of pH on synergetic catalysis.

### Possible mechanism

Hydroxyl radicals ( $\text{HO}\cdot$ ) generated by activating  $\text{H}_2\text{O}_2$  as oxidizing species were confirmed in the  $\text{Cu}^{2+}/\text{g-C}_3\text{N}_4$  system by the characteristic electron spin resonance (ESR) spectrum of DMPO-OH spin adduct (Figure 10). As controlled experiments, a very weak signal can be observed in the presence of  $\text{H}_2\text{O}_2$  alone without  $\text{Cu}^{2+}$  and  $\text{g-C}_3\text{N}_4$ , it may be due to the decomposition of  $\text{H}_2\text{O}_2$  caused by impurities. In the presence of  $\text{Cu}^{2+}$ , the signal was slightly enhanced, indicating that the low concentration  $\text{Cu}^{2+}$  had only a weak ability to activate  $\text{H}_2\text{O}_2$ . In the presence of the alkali exfoliated  $\text{g-C}_3\text{N}_4$ , the signal became stronger, indicating that the alkali exfoliated  $\text{g-C}_3\text{N}_4$  had obvious Fenton catalytic activity. However, in the presence of  $\text{Cu}^{2+}$  and the alkali exfoliated  $\text{g-C}_3\text{N}_4$ , the signal significantly enhanced, clearly indicating that the  $\text{Cu}^{2+}$  and the alkali exfoliated  $\text{g-C}_3\text{N}_4$  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 xanthen-conjugated chromophore (554 nm) of the RhB molecule was destroyed quickly by hydroxyl radicals.



**Figure 10** | EPR spectra of DMPO-OH in various systems.



**Figure 11** | Effect of adding EDTA on synergetic catalysis.

That  $HO\cdot$  was the major reactive oxidizing species was further supported by a scavenging experiment of free radicals. The addition of isopropanol, a  $HO\cdot$  scavenger, in the  $Cu^{2+}$  and the alkali exfoliated  $g-C_3N_4$  system significantly decreased the degradation of RhB (Figure S6).

As mentioned above, homogeneous  $Cu^{2+}$  as a Fenton catalyst has been extensively studied. It is generally believed that the activation of  $H_2O_2$  to generate  $HO\cdot$  is through a  $Cu^{2+}/Cu^+$  redox cycle mechanism, similar to the  $Fe^{3+}/Fe^{2+}$  cycle. However, if the  $Cu^{2+}$  concentration is as low as less than  $1\text{ mg L}^{-1}$ , its catalytic activity is difficult to detect. For the  $Cu^{2+}$  and  $g-C_3N_4$  system we can reasonably speculate that  $Cu^{2+}$ , which is adsorbed on the  $g-C_3N_4$ , was the active sites of the Fenton catalysis. Mainly in these sites  $H_2O_2$  was activated to generate  $HO\cdot$ . The catalysis of the unabsorbed homogeneous  $Cu^{2+}$  in the aqueous phase can be ignored due to its very low concentration. The catalysis of the  $g-C_3N_4$  itself may only contribute slightly to the dye degradation. For other ions with the same concentration, such as  $Ni^{2+}$ ,  $Zn^{2+}$ , even  $Fe^{2+}$ , the classical Fenton catalyst, did not enhance the catalytic activity of the bulk  $g-C_3N_4$ . Adding these ions to the  $Cu^{2+}$  and bulk  $g-C_3N_4$  system also did not influence the catalytic activity (Figure S7).

It should be pointed out that the adsorbed  $Cu^{2+}$  is different from the supported  $Cu^{2+}$ . The existence of adsorbed  $Cu^{2+}$  depends on the dissolved  $Cu^{2+}$  in the solution. To examine this idea, we carried out several preliminary experiments. We measured the aqueous equilibrium concentration of  $Cu^{2+}$  in the  $Cu^{2+}$  and bulk  $g-C_3N_4$  system and found that it was obviously lower than its initial concentration. The bulk  $g-C_3N_4$  was separated from the equilibrium system, washed with water, and dried, then used to catalytically degrade the dye without adding additional  $Cu^{2+}$ . It was found that this  $g-C_3N_4$  performed obviously higher activity than the original  $g-C_3N_4$ , but lower activity than the  $Cu^{2+}$  and bulk  $g-C_3N_4$  systems (Figure S8). This implied that there existed adsorbed  $Cu^{2+}$  on the separated  $g-C_3N_4$ . We also added EDTA into the  $Cu^{2+}$  and alkali exfoliated  $g-C_3N_4$  system and found that the synergistical effect of  $Cu^{2+}$  completely disappeared due to the formation of stable  $Cu-EDTA$  complexes. However, when adding more stable  $Fe-EDTA$  complexes in the system, the catalytic activity was not influenced as in this case EDTA did not react with  $Cu^{2+}$ . As a control, the replacement of  $Cu^{2+}$  by  $Fe^{3+}$  with the same concentration did not accelerate the Fenton catalytic activity of the  $g-C_3N_4$  (Figure 11).

Previous results have shown that the properties of  $g-C_3N_4$  strongly affected the catalytic activity of the  $Cu^{2+}/g-C_3N_4$  system. The role of  $g-C_3N_4$  may not only be used as adsorbent to enrich  $Cu^{2+}$ . Its conductivity and surface groups may contribute to the reduction of  $Cu^{2+}$ , which is the rate controlling step of the Fenton reaction. These problems need to be further studied.

## CONCLUSIONS

There may exist synergistic catalysis between the metal ions leached from heterogeneous Fenton catalysts and the supports. This problem seems to have been ignored in previous relevant research. This study, may be for the first time, confirmed that a significant synergistical Fenton catalysis between trace  $Cu^{2+}$  and  $g-C_3N_4$  exists. The properties of  $g-C_3N_4$  strongly influenced

the catalytic activity of the  $\text{Cu}^{2+}/\text{g-C}_3\text{N}_4$  system. The coexistence of  $\text{Cu}^{2+}$  and the alkali exfoliated  $\text{g-C}_3\text{N}_4$  showed the best catalytic activity. Synergistic catalysis may be attributed to the easier reduction of  $\text{Cu}^{2+}$  adsorbed onto  $\text{g-C}_3\text{N}_4$ . The discharge of  $\text{Cu}^{2+}$  with concentrations below  $1 \text{ mg L}^{-1}$  would not threaten the safety of the water environment. This study partly solved the rapid deactivation of heterogeneous Fenton catalysts caused by leaching of metal ions, and also reminds researchers to pay attention to the possible synergistic catalysis between leached  $\text{Cu}^{2+}$  and carbon supports when using copper supported on carbon materials as heterogeneous Fenton catalysts. The recovery of  $\text{g-C}_3\text{N}_4$  nanosheets is still a problem. An obvious strategy is to combine  $\text{g-C}_3\text{N}_4$  with magnetic materials, thus the catalyst could be recovered by magnetic separation. In addition, as the discussion of the mechanism in this study is still at an early stage, 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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