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## Ferrocene modified g-C<sub>3</sub>N<sub>4</sub> as a heterogeneous catalyst for photo-assisted activation of persulfate for the degradation of tetracycline

Zixuan Wang<sup>a,b,1</sup>, Han Wang<sup>a,b,1</sup>, Ziwei Wang<sup>a,b,1</sup>, Danlian Huang<sup>a,b</sup>, Hong Qin<sup>a,b</sup>, Yangzhuo He<sup>a,b</sup>, Ming Chen<sup>c,\*</sup>, Guangming Zeng<sup>a,b,\*\*</sup>, Piao Xu<sup>a,b,\*\*</sup>

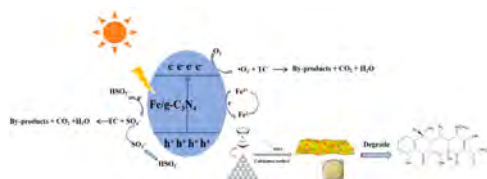
<sup>a</sup> College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China

<sup>b</sup> Key Laboratory of Environmental Biology and Pollution Control, Ministry of Education, Hunan University, Changsha 410082, PR China

<sup>c</sup> Key Laboratory of Reservoir Aquatic Environment, Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, PR China

### GRAPHICAL ABSTRACT

In this paper, the synthesis of ferrocene doped graphite phase carbon nitride and the removal of tetracycline in water by activated persulfate are mainly introduced.



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### ABSTRACT

In this study, the oxidative degradation of tetracycline (TC) by ferrocene-modified graphite phase carbon nitride (Fe/g-C<sub>3</sub>N<sub>4</sub>) activated persulfate (PS) under light-assisted conditions is examined. The materials are characterized by a series of methods such as SEM, TEM, XRD, FTIR, XPS, etc. This article explores the influence of the amount of sulfate, the initial concentration of pollutants, the amount of catalyst, and the pH value on the reaction system. When the amount of PS added reaches 2.5 mM and the catalyst dosage is 1 g L<sup>-1</sup>, the Fe/g-C<sub>3</sub>N<sub>4</sub>/PS/Vis exhibit the best performance for tetracycline removal. In 60 min, the removal of tetracycline reaches 93% under its natural pH. In the reaction system acidic neutral conditions are more conducive to degrade TC. The results show that the doping of ferrocene inhibits the recombination of electron-hole pairs in the g-C<sub>3</sub>N<sub>4</sub>, expands the light response range to speed up the removal rate of tetracycline. At the same time, iron cycle generated by ferrocene modification helps to activate persulfate to produce sulfate radicals with strong oxidizing properties. Sulfate radicals, hydroxyl radicals, superoxide radicals and holes are the main active species proved by ESR test and the quenching experiments. The synergy between photocatalysis and PS activation promotes the production of active species and the tetracycline removal. The results show that the Fe/g-C<sub>3</sub>N<sub>4</sub> composite material activated persulfate under visible light is an effective method to remove tetracycline from water.

\* Corresponding author.

\*\* Corresponding authors at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China.

E-mail addresses: [mchensn@hnu.edu.cn](mailto:mchensn@hnu.edu.cn) (M. Chen), [zgming@hnu.edu.cn](mailto:zgming@hnu.edu.cn) (G. Zeng), [piaoxu@hnu.edu.cn](mailto:piaoxu@hnu.edu.cn) (P. Xu).

<sup>1</sup> These authors contribute equally to this article.

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## 1. Introduction

In recent years, urbanization process is speeding up, along with the rapid economic development, but also accompanied by a series of environmental problems [1]. Antibiotic is an important drug to kill or inactivate pathogenic bacteria in animal and humans [2]. Furthermore, antibiotic has been widely used in aquaculture and livestock and poultry industries as growth promoters and veterinary drugs [3]. Statistics show that the European Union consumes about 5000 tons of antibiotics each year, of which tetracycline antibiotics are as high as 2300 tons; in the United States, tetracycline antibiotics account for 15.8% of the entire antibiotic market share; China is a large country in the production, sales and use of antibiotics, with annual export volume up to  $1.34 \times 10^7$  kg [4, 5]. Nowadays, antibiotic pollution of wastewater has become a current prominent environmental risk problem, which has attracted the attention of some researchers [6–9]. Tetracycline (TC) as one of the most common antibiotics has been widely used in animal husbandry, agriculture and medicine [10]. Compared with other antibiotics, TC has strong persistence in the environment and is difficult to degrade, so its residual time in the environment is long and is more likely to affect human health [11]. However, it is difficult to completely remove the antibiotics in the wastewater with conventional water treatment technology.

Nowadays, advanced oxidation processes (AOPs) has received extensive attention in the removal of organic pollutants due to its low cost, environmental friendliness and simple reaction conditions [12]. Advanced oxidation processes (AOPs) based on sulfate radicals are receiving more and more attention due to their high purification efficiency [13]. Many methods are used to activate PMS to remove pollutants, including transition metal doping, metal oxide modification, and photocatalysis [14]. Photocatalysis is the optical-driven chemical process on the surface of the catalyst, which can convert solar energy into chemical energy, generate holes and electrons, degrade various organic pollutants to remediate the environment [15]. However, photocatalysis technology suffers from insufficient absorption of solar light, high recombination rate of electron-holes pairs and weak mineralization efficiency [16]. Persulfate activation which generate sulfate radicals ( $\text{SO}_4^{\bullet-}$ ) possessing stronger oxidation capacity compared with  $\bullet\text{OH}$  radicals [17]. Activate peroxydisulfate (PMS) or peroxydisulfate ( $\text{S}_2\text{O}_8^{2-}$ ) by ultraviolet light, alkali or transition metal to generate sulfate radicals [18]. However, its practical application is still limited by intensive energy input, secondary pollution and low cycle ability [19]. Therefore, many studies combined photocatalysis and persulfate oxidation technologies to synergistically degrade antibiotics [20,21]. Undoubtedly, the key issue for great persulfate activation under visible light irradiation is the reasonable design of catalysts [22].

Some classic semiconductor photocatalysts, such as  $\text{TiO}_2$ ,  $\text{ZnO}$ , and  $\text{SnO}_2$ , have become research hotspots due to their stable chemical properties, photocorrosion resistance, and environment friendly [23]. However, the electron-hole recombination rate is high, wide band-gap and low solar energy utilization limit the application [24]. Metal-free semiconductor graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) with good chemical stability and thermal stability has been widely used in photocatalytic degradation of organic pollution [25].  $\text{g-C}_3\text{N}_4$  is also a newly emerging photocatalyst for advanced oxidation of sulfate radicals [26]. The photogenerated electrons in  $\text{g-C}_3\text{N}_4$  are excited to break the peroxy (O-O) bond in the persulfate and the oxidant, and generate active free radicals, that is, sulfate free radicals and hydroxyl free radicals except superoxide free radicals [27]. The  $\text{g-C}_3\text{N}_4$ -mediated persulfate photocatalytic activation synergistic mechanism can ensure the generation of hydroxyl radicals, overcome the low reduction potential of  $\text{g-C}_3\text{N}_4$ , and increase the degradation reaction rate [28]. However,  $\text{g-C}_3\text{N}_4$  with rapid electron and hole recombination, small specific surface area, low quantum yield and other shortcomings usually shows limited the application of photocatalysis-persulfate activation [29]. In this regard, many researchers have devoted to modifying graphite-phase carbon nitride

through metal doping, semiconductor connection, heterostructure fabrication, or modified carbon material to improve its photocatalytic performance [30]. Activation of persulfate with transition metals such as copper, iron, and nickel has proven to be an effective way to produce sulfate [31]. Guan et al. have investigated that chemical modification of  $\text{g-C}_3\text{N}_4$  by iron doping is an effective way to solve this problem [32]. Li et al. modified  $\text{g-C}_3\text{N}_4$  through  $\text{Fe}_3\text{O}_4$  to construct a heterojunction, which improved its ability to activate persulfate to degrade pollutants [33]. From an environmental protection perspective, iron is a relatively green metal, which is conducive to sustainable environmental restoration [34]. The discovery of ferrocene has brought metal organic chemistry into a new field [35]. Each ring of ferrocene is aromatic and prone to electrophilic substitution reactions. And it has good stability and low toxicity, and has a variety of physiological activities [27]. At the same time, ferrocene has excellent reversible oxidation-reduction performance and electrochemical activity [36]. In addition, the study on the removal of tetracycline by using ferrocene as the iron source to synthesize iron-modified graphite phase carbon nitride has not been reported.

In this study, TC was used as the target pollutant to study the effect of ferrocene modified carbon nitride on antibiotics removal and the mechanism. Composite materials were synthesized by thermal polymerization and characterized by various methods. This paper focuses on the role of Fe and carbon nitride in the optimized  $\text{Fe/g-C}_3\text{N}_4$  skeleton and the possible mechanism of tetracycline removal. The degradation efficiency based on different PS concentration, initial TC concentration, catalyst dosage and solution pH were all studied. And the catalytic activity, stability and repeatability of the catalyst were investigated at the same time.

## 2. Material and methods

### 2.1. Chemical materials

The reagents used in this study were all analytical grade without further purification. Melamine and ethyl alcohol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), ferrocene were obtained from Spectrochem, sodium peroxydisulfate (PS;  $\geq 98\%$ ), Tetracycline (TC) were obtained from Aladdin Biochemical co., Ltd. (Shanghai, China). The deionized water (DI water, resistivity of  $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ) was used as solvent in the all experiments.

### 2.2. Preparation of materials

#### 2.2.1. Synthesis of graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ )

$\text{g-C}_3\text{N}_4$  was synthesized by a traditional polymerization method [37]. Briefly, 2 g of melamine was put in a ceramic covered crucible; calcined in a muffle furnace at  $550^\circ\text{C}$  with a heating rate of  $2.3^\circ\text{C min}^{-1}$ , and maintained for 4 h in air; cooled down to room temperature; collect and grind to obtain  $\text{g-C}_3\text{N}_4$  powder.

#### 2.2.2. Preparation of the composite

Composite of  $\text{Fe/g-C}_3\text{N}_4$  was synthesized by mixing melamine and

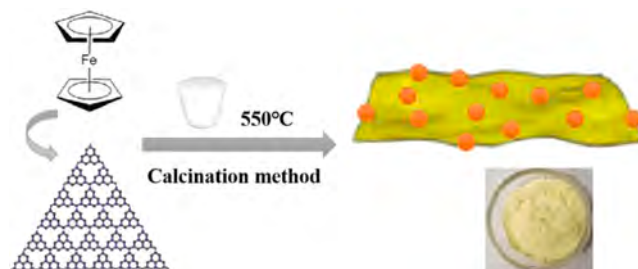


Fig. 1. Construction of  $\text{Fe/g-C}_3\text{N}_4$  heterojunction.

ferrocene (Fig. 1). For a typical process, a known amount of ferrocene was mixed with 2 g of melamine in a crucible at 550 °C for 4 h with a heating rate of 2.3 °C min<sup>-1</sup>. Different percentages of ferrocene in the Fe/g-C<sub>3</sub>N<sub>4</sub> composites were tuned to be 1.0%, 2.5%, 5.0%, 7.5%, 10.0% and 15.0% by adding suitable amount of ferrocene. After cooling to 25 °C, they were dried and grinded to obtain Fe/g-C<sub>3</sub>N<sub>4</sub> powder.

### 2.3. Characterization

The samples morphologies were recorded with a scanning electron microscopy (SEM, Hitachi S-4800, Japan). The surface morphology of the samples was measured by transmission electron microscope (TEM). The crystal structures of ferrocene/g-C<sub>3</sub>N<sub>4</sub> were determined by X-ray power diffractometer (XRD, Shimadzu XRD-6000, Japan), equipped with Cu K $\alpha$  radiation in the region of 2 $\theta$  from 5° to 80°. The infrared spectra were recorded by a fourier transform infrared spectrophotometer (FT-IR). The elemental mappings of the samples were identified by X-ray photoelectron spectroscopy (XPS) on an Escalab 250Xi spectrometer with an Al-K $\alpha$  X-ray source. The UV-vis diffuse reflectance spectroscopy (UV-DRS) was carried out on a Cary 300 UV-vis spectrophotometer in the wavelength range from 300 to 800 nm. The electron spin resonance (EPR) signals of the free radicals were recorded by a JEOL JES-FA200 Spectrometer.

### 2.4. Experimental procedures

Under visible light irradiation, TC was degraded by synthetic materials and its photocatalytic oxidation activity was studied. The visible light source was provided by a PLS-SXE 300 W Xenon lamp, and its light density parameter was 0.33 W cm<sup>-2</sup>. In detail, 0.05 g of the catalyst was dispersed in the 50 mL pollutant reaction solution and irradiated it with light. In order to establish the adsorption-desorption equilibrium, the mixture was stirred for 30 min in the dark firstly. Then, a certain concentration of PS was added dropwise to the sample and stirred for 60 min under light conditions. In order to study the effect of pH, the reaction solution was adjusted by using 0.1 M NaOH and 0.1 M HCl. Then the reaction suspension was taken out by 5 mL syringe at a given interval time and filtered using a 0.45  $\mu$ m membrane filter, and then

analyzed by a Shimadzu UV-2700 spectrophotometer to record the concentration of TC (357 nm). By changing the reaction conditions, such as the catalytic dose, initial TC concentration, proportion of iron doping in the composite material and the pH on the reaction system were studied. Collect the finished catalyst and clean it several times with deionized water and anhydrous ethanol to remove surface contaminants and impurities for next use. Four consecutive cycles of TC removal were performed.

## 3. Results and discussion

### 3.1. Characterization of the catalysts

The morphologies and microstructures of the as-prepared materials were characterized by SEM and TEM. Fig. 2 presented that the prepared g-C<sub>3</sub>N<sub>4</sub> were mainly stacked by lamellar structures with micron dimensions. During the calcination process, some ferrocene adhered to the surface of graphite phase carbon nitride, and some was embedded in its structure. The majority of g-C<sub>3</sub>N<sub>4</sub> exhibited irregular and thick features, while the iron-doped g-C<sub>3</sub>N<sub>4</sub> had a significantly smaller particle size and was composed of smooth paper folded sheets, similar to the morphology of graphene nanosheets. Previous literature reports showed that iron atoms played a very important role in the condensation of g-C<sub>3</sub>N<sub>4</sub> and the formation of nanostructures. Further, from TEM images (Fig. 3), attached nanoparticles could be clearly seen on the surface of the g-C<sub>3</sub>N<sub>4</sub> sheet and inside its structure, which were converted from the ferrocene during the calcination process. Meanwhile, the TEM-EDS mapping results in Fig. 4 showed that carbon, nitrogen, oxygen and iron were almost uniformly distributed on the surface of the catalyst, which proved that Fe was successfully introduced into Fe/g-C<sub>3</sub>N<sub>4</sub> composite material once again. The above results indicated that Fe/g-C<sub>3</sub>N<sub>4</sub> composite had been synthesized by calcination. Moreover, the ferrocene-modified g-C<sub>3</sub>N<sub>4</sub> had a high specific surface area (Fig. 5), which provided more adsorption sites and active centers for the photocatalytic reaction. The chance of pollutants coming into contact with the composite catalyst was increased, and the active species produced in the reaction process had more room for action.

Fig. 5 exhibited the N<sub>2</sub> adsorption and desorption curves of g-C<sub>3</sub>N<sub>4</sub>

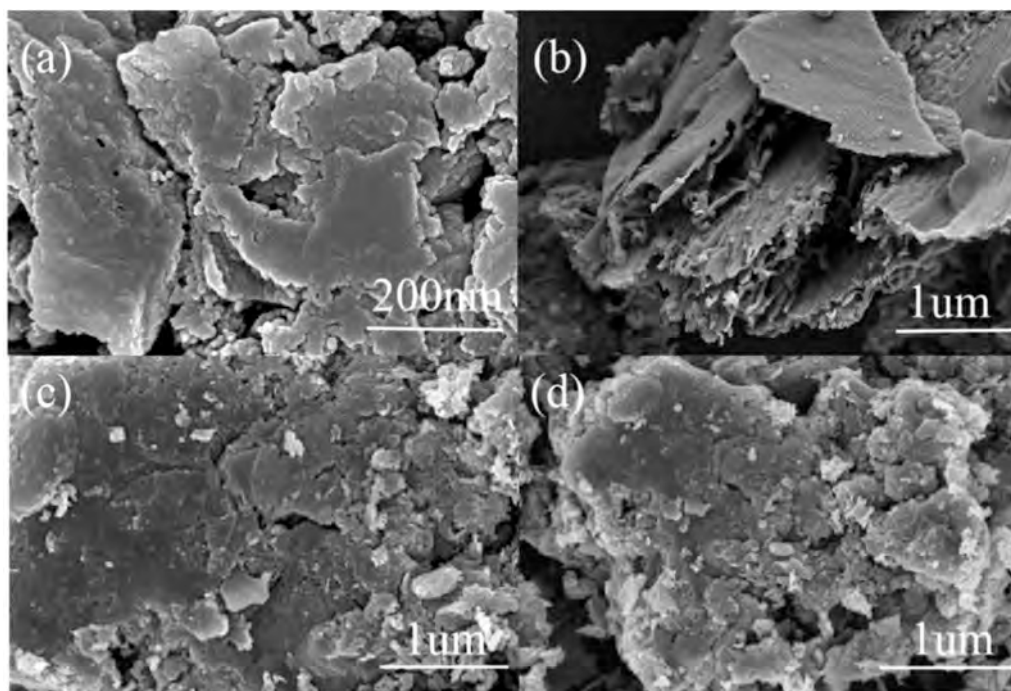


Fig. 2. SEM images of g-C<sub>3</sub>N<sub>4</sub> (a-b) and Fe/g-C<sub>3</sub>N<sub>4</sub> (10%) (c-d) samples.



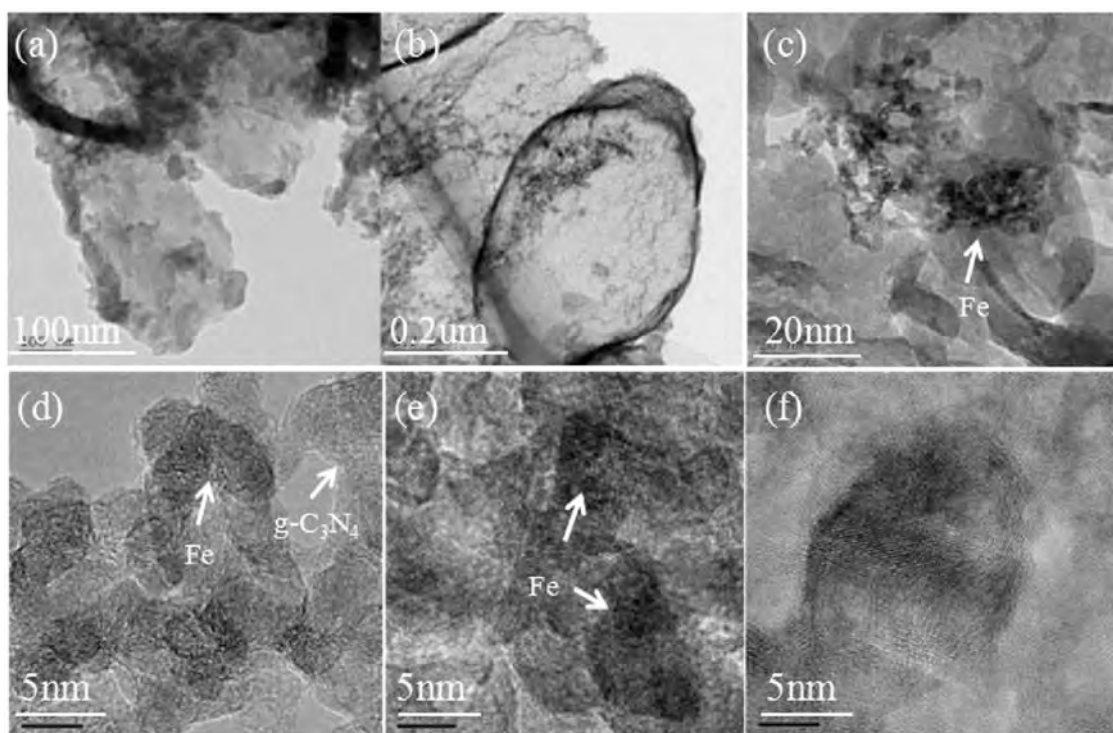


Fig. 3. TEM micrograph images of g-C<sub>3</sub>N<sub>4</sub> (a), Fe/g-C<sub>3</sub>N<sub>4</sub> (10%) (b-c), and crystal structure of the Fe/g-C<sub>3</sub>N<sub>4</sub> (10%) (d-f).

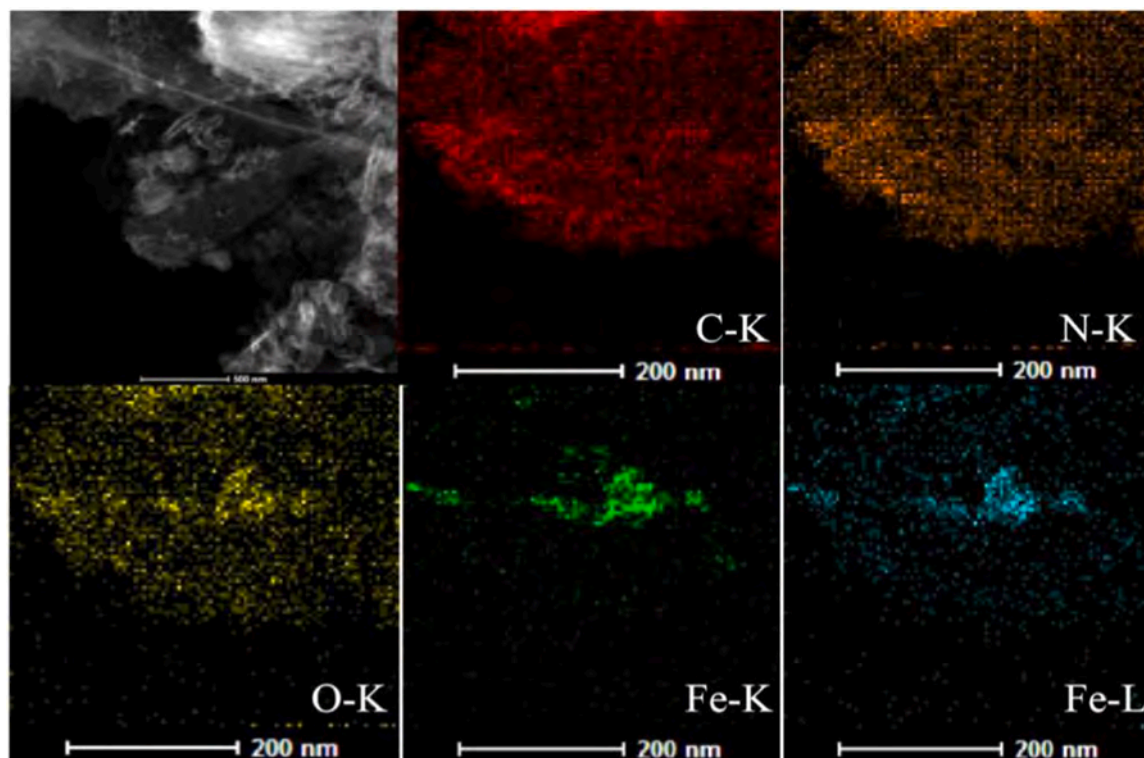


Fig. 4. TEM-EDS elemental mapping images of Fe/g-C<sub>3</sub>N<sub>4</sub> (10%).

and Fe/g-C<sub>3</sub>N<sub>4</sub> composites. It could be seen in the figure that the N<sub>2</sub> adsorption and desorption curves of the two samples conform to the typical type II isotherm [38]. When the relative pressure was in the range of 0.4–1.0, the catalyst had a H3 hysteresis loop, which indicated that there were macropores in the g-C<sub>3</sub>N<sub>4</sub> and Fe/g-C<sub>3</sub>N<sub>4</sub> composites

[39]. This might be due to the accumulation of large particles to form random interstitial pores. The specific surface areas of g-C<sub>3</sub>N<sub>4</sub> and Fe/g-C<sub>3</sub>N<sub>4</sub> composites were 10.4395 m<sup>2</sup> g<sup>−1</sup> and 18.076 m<sup>2</sup> g<sup>−1</sup> respectively (Table 1). Compared with the specific surface area of g-C<sub>3</sub>N<sub>4</sub> monomer in the literature, the carbon nitride obtained by

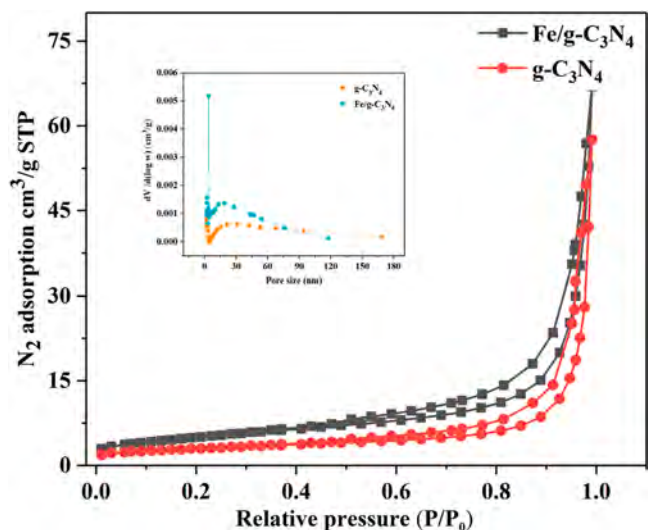


Fig. 5.  $N_2$  adsorption-desorption isotherm of  $g-C_3N_4$  and  $Fe/g-C_3N_4$  (10%) samples.

Table 1

Physicochemical properties of the synthesized pristine  $g-C_3N_4$  and  $Fe/g-C_3N_4$  (10%).

Activators	BET specific surface area ( $m^2 g^{-1}$ )	Pore volume ( $m^3 g^{-1}$ )	Average pore radius (nm)
$g-C_3N_4$	10.4395	0.088987	21.5
$Fe/g-C_3N_4$ (10%)	18.0076	0.103616	21.6

calcination of melamine at 550 °C had a larger specific surface area. It might be because melamine produces  $CO_2$ ,  $CO$ ,  $H_2O$  and other gases under high conditions, resulting in a loose structure on the surface of the material [40]. The ferrocene modified  $g-C_3N_4$  composite material had an increased specific surface area, which provided a larger space for the catalytic reaction, and further explains the reason for the high-quality photocatalytic effect of the composite material.

The XRD patterns (Fig. 6a) presented the crystal structure information of  $g-C_3N_4$  and  $Fe/g-C_3N_4$  composites. Same as the previous research reports, all samples had an enhanced diffraction peak at 27.4° and 13.1°

[41]. The characteristic peaks at 13.1° and 27.4° corresponded to the (100) crystal plane and (002) diffraction surface of  $g-C_3N_4$ , which was caused by the periodic arrangement of crystal planes in the layers and the stacking of conjugated aromatic rings between the layers [42]. There were three obvious diffraction peaks at  $2\theta = 18.1^\circ$ ,  $41.3^\circ$  and  $57.0^\circ$ , corresponding to the (111), (400) and (511) diffraction planes respectively, which were similar to the structure of  $Fe_3O_4$  reported in the previous literature [43]. It showed that ferrocene transforms into iron oxide during the calcination process, mainly in the form of  $Fe_3O_4$  [44]. The XRD pattern of  $Fe/g-C_3N_4$  was similar to the original  $g-C_3N_4$ . With the increase of iron doping, the (001) peak of  $g-C_3N_4$  increases, indicating that iron causes slight changed in the graphite layer of  $g-C_3N_4$  structure, resulting in enhanced crystallinity of  $g-C_3N_4$  [45]. In the composite catalyst, the peak position of the characteristic peak of  $g-C_3N_4$  did not change significantly, indicating that the ferrocene modification did not significantly change the crystal structure of  $g-C_3N_4$ , which was beneficial to the photocatalysis of the composite catalyst. We could see that there are no other impurity peaks in all samples, which proved that the composite catalyst was composed of an iron-containing compound phase and a  $g-C_3N_4$  phase. The sample had high purity and had been successfully prepared.

The FTIR diagram of  $Fe/g-C_3N_4$  composites was shown in Fig. 6(b). For  $g-C_3N_4$ , a series of diffraction peaks occur at  $1200-1600 cm^{-1}$ , which was a very classical stretching pattern for CN heterocyclic compounds [46]. The strong vibration peak at  $810 cm^{-1}$  was caused by the bending vibration of the Heptazine ring, indicating that the synthesized  $g-C_3N_4$  was mainly composed of triazine ring structure [47]. The diffraction peak of  $Fe/g-C_3N_4$  composite was slightly shifted. The extensive absorption peak band in  $3200 cm^{-1}$  was derived from the stretching vibration of N-H bond in  $g-C_3N_4$ , indicating the presence of incomplete polymerization of amino in the synthesized  $g-C_3N_4$  [48]. The diffraction peak of  $Fe/g-C_3N_4$  (10%) composite was shifted to  $3162 cm^{-1}$ , indicating that ferrocene and  $g-C_3N_4$  interact during calcination. The FTIR diagram of  $Fe/g-C_3N_4$  composite material did not deviate significantly, surface iron doping did not change the structure of carbon nitride, and there was no obvious iron compound diffraction peak, which was also due to the low doping amount of Fe in the composite material.

In order to explore the element composition, internal structure and chemical bonds of the synthetic material, the material was analyzed by XPS spectrum. Fig. 7(a) showed the full spectrum of  $g-C_3N_4$  and  $Fe/g-C_3N_4$ , in which the obvious peaks of C, N, O, and Fe could be detected. C

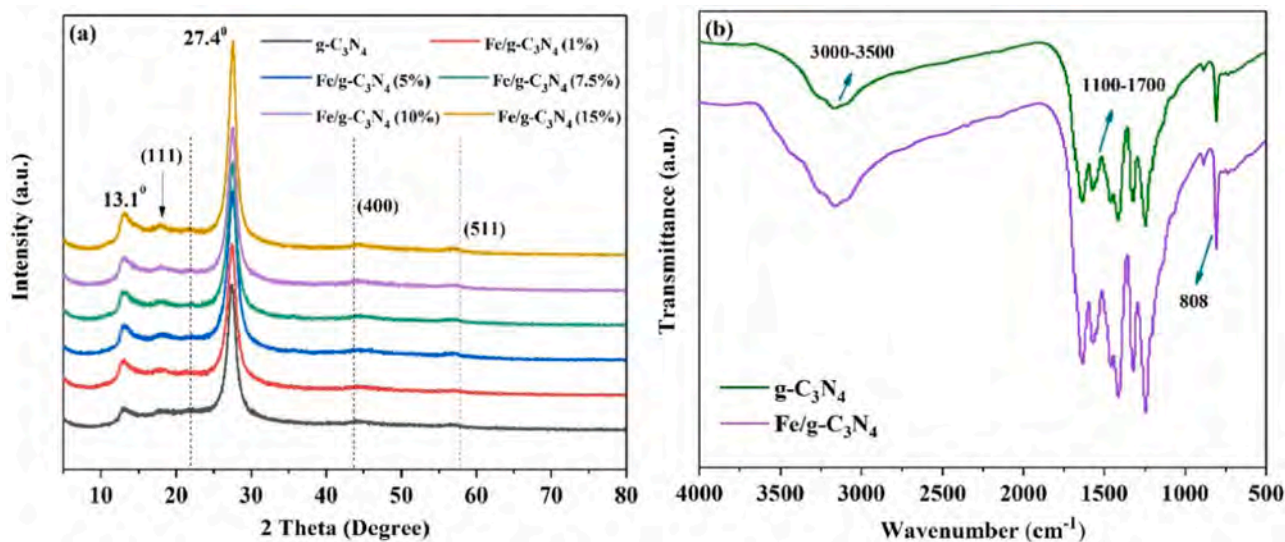


Fig. 6. (a) XRD patterns of  $g-C_3N_4$ ,  $Fe/g-C_3N_4$  (1%),  $Fe/g-C_3N_4$  (5%),  $Fe/g-C_3N_4$  (7.5%),  $Fe/g-C_3N_4$  (10%), and  $Fe/g-C_3N_4$  (15%), and (b) The FTIR spectra of  $g-C_3N_4$  and  $Fe/g-C_3N_4$  (10%).



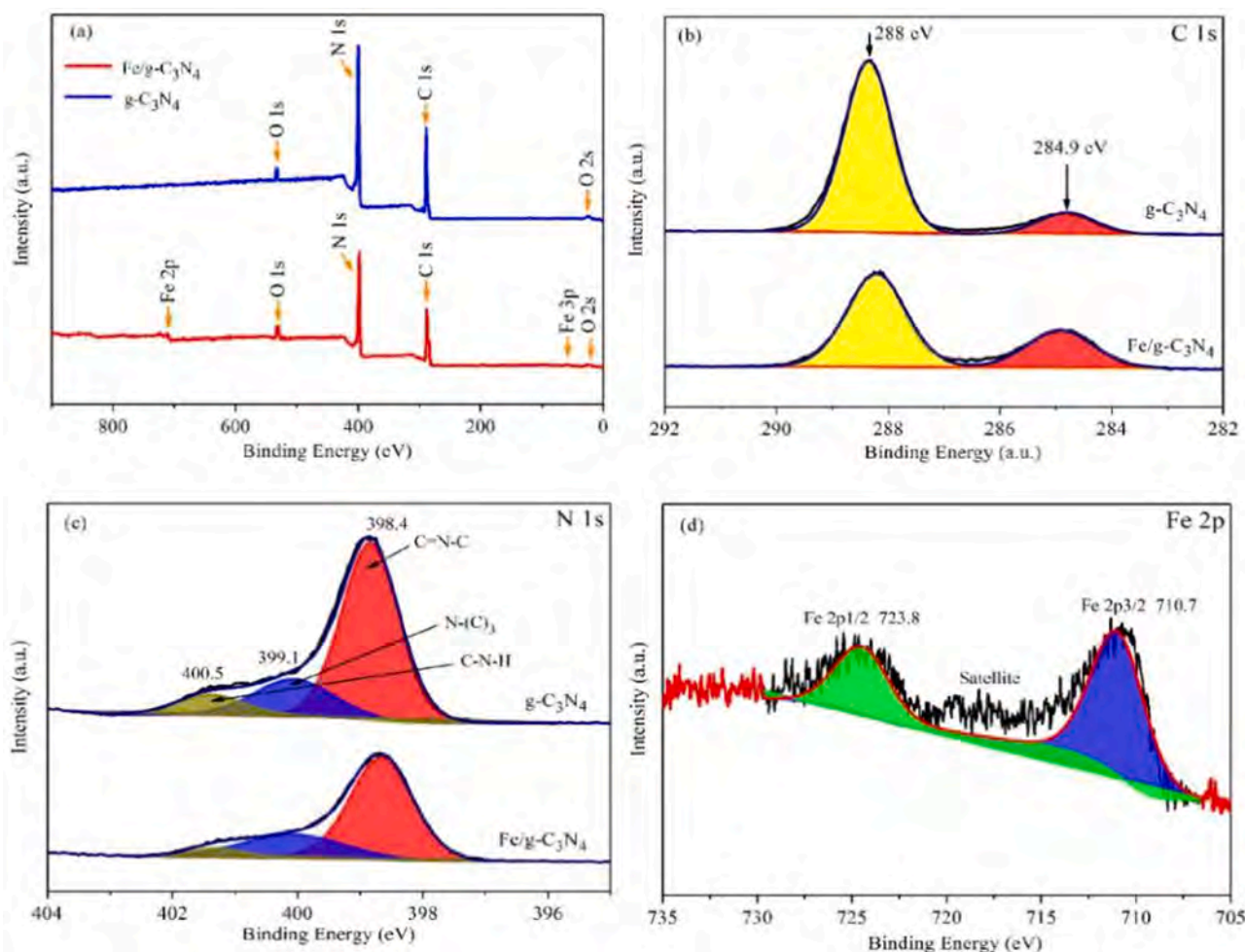


Fig. 7. XPS analyses of  $g\text{-C}_3\text{N}_4$  and  $\text{Fe/g-C}_3\text{N}_4$  (10%) samples: (a) full-survey, (b) C1s core-level, (c) N1s core-level and (d) Fe2p core-level spectrum.

and N elements are mainly derived from  $g\text{-C}_3\text{N}_4$ , and the presence of Fe is caused by ferrocene doping. Although  $g\text{-C}_3\text{N}_4$  and ferrocene did not contain oxygen, the detection of oxygen in graphite phase carbon nitride had been reported by many studies [49]. It was attributed to physical oxygen absorption, and the material was also doped in calcination at high temperature. The C1s core-level spectrum was shown in Fig. 7(b), and two characteristic peaks appear at 288 and 284.9 eV, which correspond to  $\text{C}=\text{N}$  and  $\text{C}=\text{C}$  respectively [50]. Three characteristic peaks of N element in different chemical forms at 398.4, 399.1 and 400.5 eV (Fig. 7c), which were attributed to the  $\text{SP}^2$  hybridization of the connected C atoms in the  $\text{C}=\text{N}-\text{C}$  structure, the connected N atoms in the  $\text{N}-(\text{C})_3$  structure, and the N atoms in the partially polymerized  $\text{C}-\text{N}-\text{H}$  structure respectively, and the action of the N-H side group [51]. The C1s and N1s spectra of  $\text{Fe/g-C}_3\text{N}_4$  also had similar laws. Compared with  $g\text{-C}_3\text{N}_4$ , the binding energy of  $\text{Fe/g-C}_3\text{N}_4$  obviously shifted to the lower energy level [52]. This was because the chemical environment of carbon nitride has changed after ferrocene doping. The electrons in the lone electron pair of the nitrogen atom in  $g\text{-C}_3\text{N}_4$  were transferred to the iron atom, which causes the electron density of the nitrogen atom to decrease, which caused the electrons in  $\text{C}-\text{N}$  to move toward the N atom, resulting in the decrease of the C atom density [53]. The composite state analysis of the Fe element doped on the surface of the composite material, as shown in Fig. 7(d), shown two obvious diffraction peaks at 723.8 and 710.7 eV, corresponding to the hybridization of Fe elements  $2\text{P}^{1/2}$  and  $2\text{P}^{3/2}$ , respectively [54]. This indicates that iron was successfully doped into carbon nitride, which further verified the existence of iron and retained the divalent state of iron in ferrocene.

### 3.2. Optical property

The optical properties of the previously prepared  $g\text{-C}_3\text{N}_4$  and  $\text{Fe/g-C}_3\text{N}_4$  materials were studied by UV-vis diffuse adsorption spectrum. As shown in Fig. 8(a), electrons transition from the valence band formed by the  $\text{N}2\text{p}$  orbital of  $g\text{-C}_3\text{N}_4$  to the conduction band formed by the  $\text{C}2\text{p}$  orbital [55].  $g\text{-C}_3\text{N}_4$  exhibits a typical semiconductor light absorption capacity, and its absorption band edge was located at about 450 nm, showing a capability of utilizing solar spectrum energy with a wavelength less than 450 nm [35]. After ferrocene modification, the absorption band of  $\text{Fe/g-C}_3\text{N}_4$  was around 550 nm, with a significant red shift. This was the doping of iron ions into the  $g\text{-C}_3\text{N}_4$  lattice, which affects the electronic structure of graphite phase carbon nitride and changes its optical properties. It could be clearly seen in the figure that the ferrocene doped composite material could greatly broaden the light absorption range of  $g\text{-C}_3\text{N}_4$ , which was beneficial to its use of sunlight and improves the photocatalytic performance.

The combination of photogenerated carriers greatly affects the performance of photocatalytic activation system. Fig. 8(b) illustrated the photoluminescence (PL) spectra of different photocatalysts. The figure shown the PL spectra of  $g\text{-C}_3\text{N}_4$  and  $\text{Fe/g-C}_3\text{N}_4$  composites with different proportions at about 450 nm when excited at 320 nm [56]. It could be seen that the PL peak of the original  $g\text{-C}_3\text{N}_4$  material was the strongest, indicating that the photogenerated electron and hole pair recombination rate is high. With the doping of Fe, the PL peak of  $\text{Fe/g-C}_3\text{N}_4$  composite material gradually weakens, which was because the introduction of iron could effectively inhibit the photocarrier recombination and accelerate

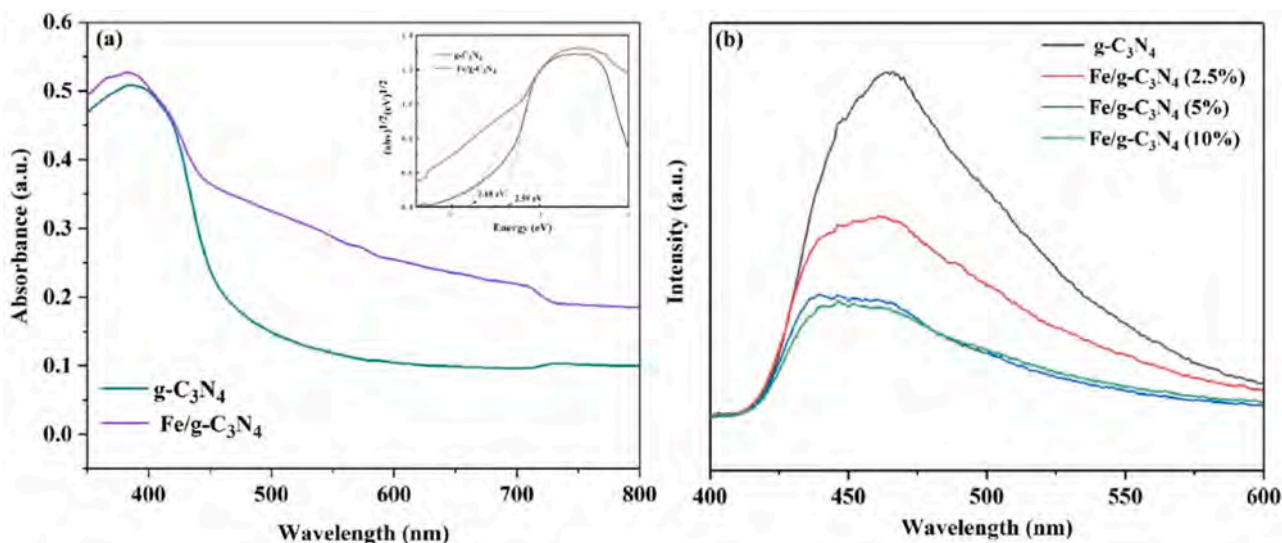


Fig. 8. (a) UV-vis diffuse reflectance spectra of the as-prepared  $g\text{-C}_3\text{N}_4$  and  $\text{Fe/g-C}_3\text{N}_4$  (10%) samples and (b) Photoluminescence spectra of the as-prepared samples.

the electron migration, so as to promote the photocatalysis and facilitate the effective removal of TC. Among them, the PL peak value of  $\text{Fe/g-C}_3\text{N}_4$  (10%) composite material was the weakest, indicating that  $\text{Fe/g-C}_3\text{N}_4$  (10%) photogenic carrier composite rate was the lowest, which further proves that  $\text{Fe/g-C}_3\text{N}_4$  (10%) composite material was the best composite ratio for effectively removing TC in water.

The band gap ( $E_g$ ) of  $g\text{-C}_3\text{N}_4$  and  $\text{Fe/g-C}_3\text{N}_4$  (10%) were 2.59 eV and 2.18 eV, respectively, by analyzing the UV-visible diffuse reflectance spectra (Fig. 9a).  $\text{Fe/g-C}_3\text{N}_4$  (10%) photocatalyst had a narrower band gap than  $g\text{-C}_3\text{N}_4$ , and could generate more photogenerated electrons under visible light irradiation. Using the Mott Schottky spectrum (Fig. 9b), the conduction band values of  $g\text{-C}_3\text{N}_4$  and  $\text{Fe/g-C}_3\text{N}_4$  (10%) had CB potentials of  $-0.80$  eV and  $-0.43$  eV, respectively. According to the formula  $E_{CB} = E_{VB} - E_g$ , the valence band (VB) values of  $g\text{-C}_3\text{N}_4$  and  $\text{Fe/g-C}_3\text{N}_4$  (10%) were 1.79 eV and 1.75 eV, respectively [57]. Where  $E_{VB}$ ,  $E_g$ ,  $E_{CB}$  were the band gap energy, VB potential and the band gap potential CB potential, respectively. The detailed positions of the VB and CB bands of  $\text{Fe/g-C}_3\text{N}_4$  (10%) were shown in Fig. 9(c).

### 3.3. Catalytic performance

#### 3.3.1. TC removal in different systems

As a typical antibiotic, TC has been widely used in agriculture, animal husbandry, and pharmaceutical industries [58]. From Fig. 10(a), PS could not directly degrade TC, nor could it be stimulated directly under visible light. From this we concluded that PS alone had little effect on the

removal of TC, indicating that PS was difficult to oxidize TC and the photolysis effect of TC was weak under visible light conditions for its high stability. The removal rate of TC was negligible in the PS/Vis system without catalyst. In the  $\text{Fe/g-C}_3\text{N}_4$ /PS system, the removal rate of TC within 60 min was higher than that without catalyst, indicating that the presence of catalyst could promote the removal of TC, it was also possible that the presence of the catalyst could activate PS to remove TC. When  $\text{Fe/g-C}_3\text{N}_4$  (10%) reacted alone in the catalytic system, the removal rate of TC was relatively low. The degradation rate of TC in  $\text{Fe/g-C}_3\text{N}_4$ /PS system and  $\text{Fe/g-C}_3\text{N}_4$ /Vis system was improved compared with the system with only catalyst, because the catalyst could activate PS to produce hydroxyl radicals and sulfate radicals, etc. Light could promote the degradation of pollutants, but its enhancement effect was not great. In the  $\text{Fe/g-C}_3\text{N}_4$ /PS/Vis system, the TC could be removed quickly, and after 30 min of visible light irradiation the removal of TC reached 80%, indicating that light could promote the activation of PS. In the  $\text{Fe/g-C}_3\text{N}_4$ /PS/Vis system, the pollutant could be almost completely degraded. When  $\text{Fe/g-C}_3\text{N}_4$  activated PS, light accelerated the activation of PS.

#### 3.3.2. Effect of different amounts of iron doping

As depicted in Fig. 10(b), the degradation effect became better when the iron doping increased, and  $\text{Fe/g-C}_3\text{N}_4$  (10%) had the best degradation effect. Previous studies have demonstrated that metal doping could adjust the morphology and crystal phase of  $g\text{-C}_3\text{N}_4$ , create oxygen vacancies or construct heterogeneous structures to enhance the

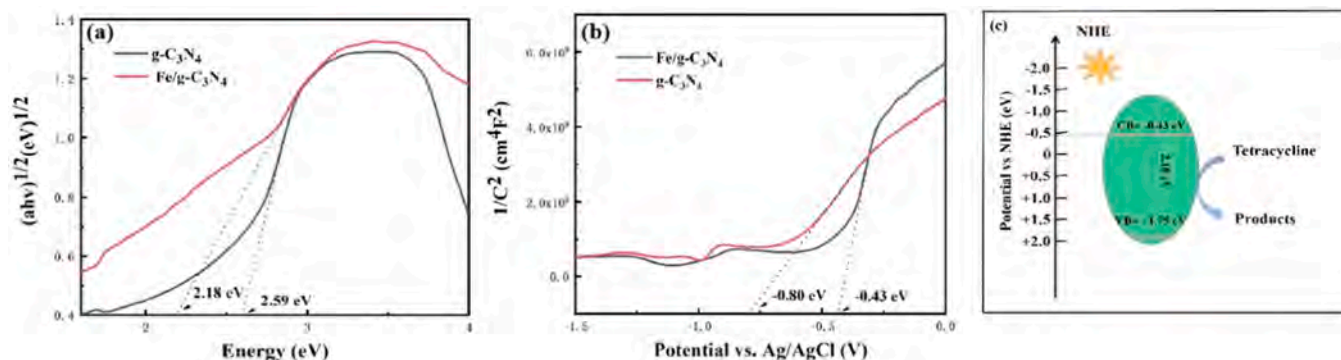


Fig. 9. Band gap of  $g\text{-C}_3\text{N}_4$  and  $\text{Fe/g-C}_3\text{N}_4$  (10%), (b) Mott Schottky spectrum of  $g\text{-C}_3\text{N}_4$  and  $\text{Fe/g-C}_3\text{N}_4$  (10%), (c) Possible mechanism of  $\text{Fe/g-C}_3\text{N}_4$  (10%) for TC degradation.

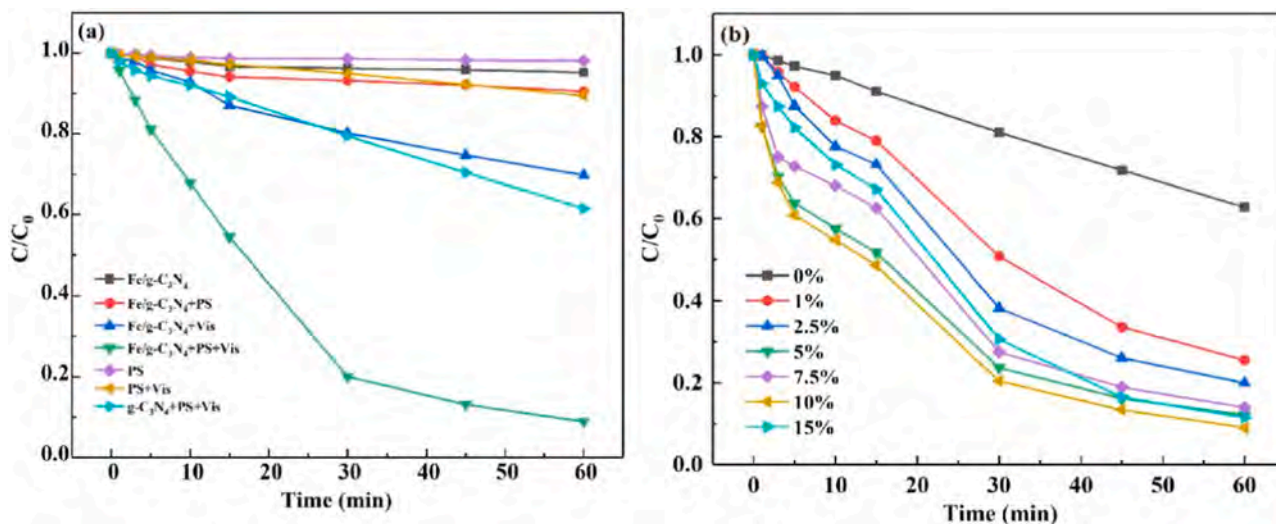


Fig. 10. (a) Degradation performance of catalysts in different systems. (b) Degradation performance of catalysts with different amounts of iron doping. Experimental conditions:  $[\text{Fe/g-C}_3\text{N}_4]_0 = 1.0 \text{ g L}^{-1}$ ,  $[\text{TC}]_0 = 40 \text{ mg L}^{-1}$ ,  $[\text{PS}]_0 = 2.5 \text{ mM}$ , and  $T = 25^\circ \text{C}$ .

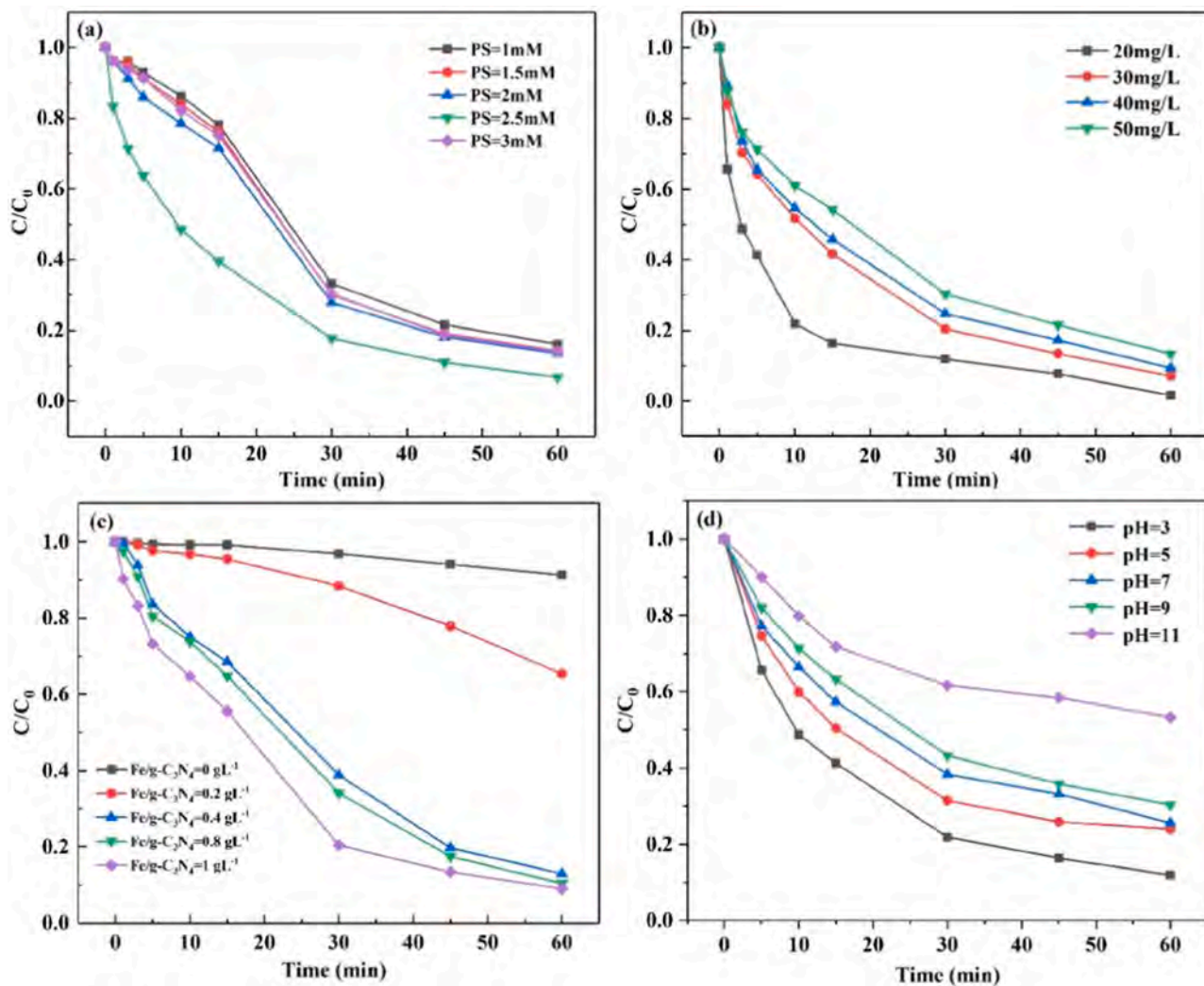


Fig. 11. Effects of (a) PS dosage, (b) initial pollutant concentration, (c) catalysts dosage, and (d) pH on TC degradation by the  $\text{Fe/g-C}_3\text{N}_4/\text{PS}$  system. Experimental conditions: (a)  $[\text{TC}]_0 = 40 \text{ mg L}^{-1}$ ,  $[\text{Fe/g-C}_3\text{N}_4]_0 = 1.0 \text{ g L}^{-1}$ , and  $T = 25^\circ \text{C}$ . (b)  $[\text{Fe/g-C}_3\text{N}_4]_0 = 1.0 \text{ g L}^{-1}$ ,  $[\text{PS}]_0 = 2.5 \text{ mM}$ , and  $T = 25^\circ \text{C}$ . (c)  $[\text{PS}]_0 = 2.5 \text{ mM}$ ,  $[\text{TC}]_0 = 40 \text{ mg L}^{-1}$ , and  $T = 25^\circ \text{C}$ . (d)  $[\text{Fe/g-C}_3\text{N}_4]_0 = 1.0 \text{ g L}^{-1}$ ,  $[\text{TC}]_0 = 40 \text{ mg L}^{-1}$ ,  $[\text{PS}]_0 = 2.5 \text{ mM}$ , and  $T = 25^\circ \text{C}$ .



photocatalytic activity of the catalyst [59]. Pure g-C<sub>3</sub>N<sub>4</sub> were restricted by its high recombination rate of light induced  $e^-/h^+$ , while carbon nitride modified by ferrocene could effectively separate photogenic electrons from holes, improve photoquantum yield, and greatly enhance its removal effect [60]. When the iron proportion was increased again, the TC removal decreases. This was because Fe ions adsorbed on the surface of the catalyst compete for photo-generated electrons. Excess Fe ions would capture more  $e^-$  and carry out iron ion valence conversion, which affected the activation of PS by the catalyst, thereby reducing the number of active free radicals and effecting the removal of TC.

### 3.3.3. Effect of PS concentration

This experiment was conducted to study the removal effect of tetracycline at different PS concentrations (1.0–3.0 mM). When the concentration of PS increased from 1.0 mM to 2.5 mM, the removal rate of TC increased to 93.0%. When PS concentration was higher than 2.5 mM, the removal rate of TC was reduced to 79.0% (Fig. 11a). The results could be explained by the following factors: when the concentration of PS increased, the catalyst could activate more PS and produce more sulfate radical for the oxidation and removal of tetracycline. Many studies had shown that excessive  $SO_4^{\bullet-}$  free radicals would undergo self-quenching reactions or react with  $HSO_5^-$  to generate  $SO_5^{\bullet-}$  free radicals with weaker oxidizing ability, which leads to the  $SO_4^{\bullet-}$  involved in the reaction reduced and caused the reactivity was weakened, thereby the TC removal rate decreased [61]. Therefore, 2.5 mM PS was used in the subsequent experiments.

### 3.3.4. Effect of TC concentration

As revealed in Fig. 11(b), show the removal rate curve of TC at concentration of 20, 30, 40, 50 mg L<sup>-1</sup>. We could see that the removal rate of TC decreases with the increase of the initial concentration of pollutant. When the initial TC concentration was 20 mg L<sup>-1</sup>, TC could be almost completely removed within 60 min (97.9%). However, the removal rate of pollutants could still high within 60 min when the concentration of TC increased to 50 mg L<sup>-1</sup>. It was because the same concentration of catalyst and PS will produce the same number of reactive species, while the high concentration of TC solution needs a longer reaction time to achieve the same removal efficiency. When the reaction time was prolonged, 50 mg L<sup>-1</sup> TC could be completely degraded based on pre-experimental data, which indicates that Fe/g-C<sub>3</sub>N<sub>4</sub> could be used as a catalyst to photocatalyze the high efficiency of PS activation and could be used in the treatment of high-concentration antibiotic wastewater.

### 3.3.5. Effect of catalyst dosage

For investigating the effect of the amount of catalyst in the process of TC removal by persulfate activation, a set of experiments were carried out with an Fe/g-C<sub>3</sub>N<sub>4</sub> dose of 0.2–1.0 g L<sup>-1</sup>. As depicted in Fig. 11(c), when the catalyst dose increased, the TC removal improved. This was because the increase of Fe/g-C<sub>3</sub>N<sub>4</sub> concentration would have more reactive sites, thereby generating more strong oxidizing free radicals, which would help the degradation of pollutants. However, when the catalyst concentration continued to increase, the catalytic effect was not obvious, or even slightly decreased. It was attributed to the fact that the high concentration of catalyst leads to the turbidity of the reaction solution and reduces the light transmittance, thus reducing the surface area exposed to light and affecting the photocatalytic effect. Therefore, considering the actual application cost of the catalyst, 1 g L<sup>-1</sup> was adopted for next experiments.

### 3.3.6. Effect of pH

In this experiment, the effect of pH on the reaction system was studied. NaOH and HCl at certain concentrations were used to adjust the initial pH of the reaction solution. In Fig. 11(d), we could see that with the increase of pH, the removal rate of the TC decreased. But, in the range of pH 3–9, the removal rate of TC was still very high. When pH

= 11, the removal rate of TC decreased significantly. The results showed that under acidic and neutral conditions, the material could activate persulfate to remove organic pollutants under the light. In alkaline environment, the removal rate was not high, because strong oxidizing  $SO_4^{\bullet-}$  reacts with  $OH^-$  to produce weak oxidizing  $\bullet OH$ , thus weakening the degradation activity of catalytic system.

### 3.4. Recyclability and stability

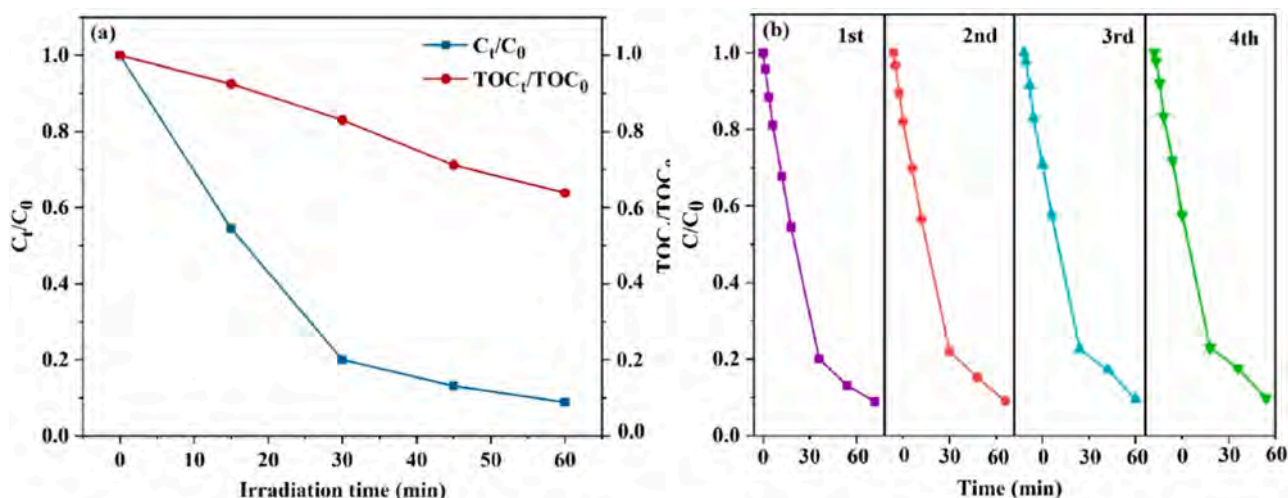
The reusability is an important parameter to determine whether photocatalyst can be used in water remediation. In order to evaluate the recyclability of Fe/g-C<sub>3</sub>N<sub>4</sub> composite, five consecutive tests of degradation of tetracycline were conducted under the same reaction conditions. As exhibited in Fig. 12(b), the bar chart visually shown the removal efficiency of tetracycline in each cycle, and the difference between each cycle could be clearly seen. After three cycles, the removal efficiency of Fe/g-C<sub>3</sub>N<sub>4</sub> was 87.50%, not much different from that of the first experiment. After the fifth cycle, the removal efficiency of the composite was still high. It showed that the stability and recyclability of the material was good, recycling could also be used. Compared with the first cycle, the reduction effect of the fifth cycle might be attributed to the loss caused by the inevitable leaching of the catalyst during the recovery and washing process, and the blockage of the active site covering the surface with tetracycline and its degradation intermediates. As displayed in Fig. 12(a), the mineralization efficiency of TC reached 41% within the stimulation range of 60 min of visible light.

In order to further observe the stability of Fe/g-C<sub>3</sub>N<sub>4</sub> (10%), the composite catalysts which were cycled four times were analyzed by XRD and FTIR. As presented on Fig. 13, the structure of the catalyst after the cycle did not change much compared with that of the initial cycle. The stability of the composite structure was pretty good, which further explained its excellent catalytic effect.

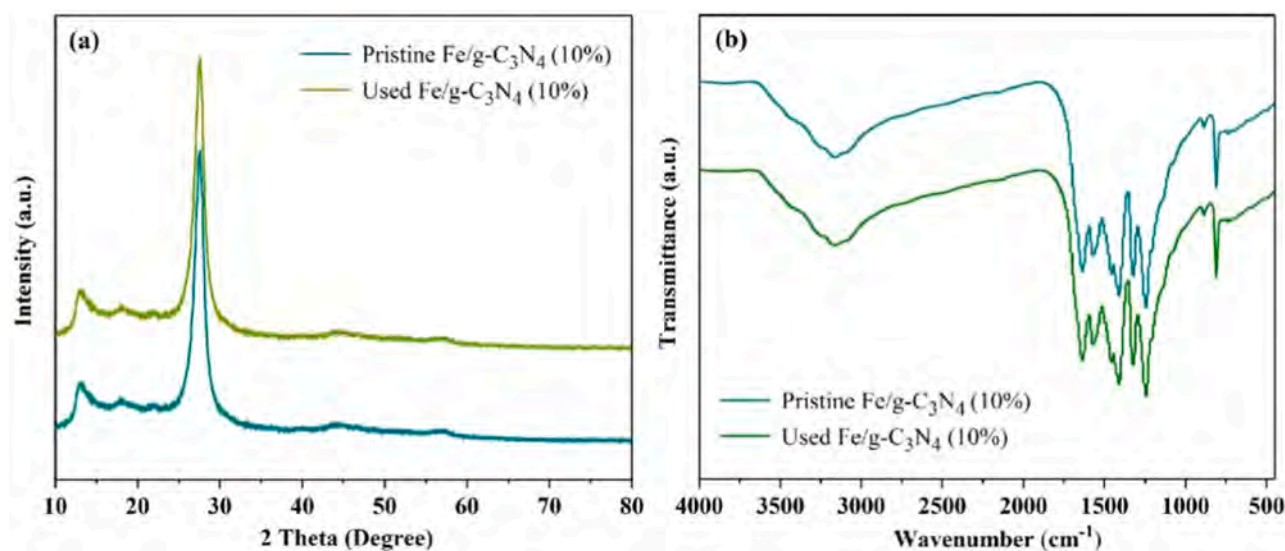
### 3.5. TC removal mechanisms by Fe/g-C<sub>3</sub>N<sub>4</sub>

High temperature, ultraviolet light, and addition of catalyst can activate PS to generate sulfate radicals and hydroxyl radicals, and g-C<sub>3</sub>N<sub>4</sub> materials can generate superoxide radicals and holes under visible light irradiation. In order to further study the contribution of active species in the Fe/g-C<sub>3</sub>N<sub>4</sub>/PS/Vis system, we carried out free radical capture experiments. Tert-butanol (TBA) reacts with hydroxyl radicals faster than sulfate radicals and can selectively quench hydroxyl radicals in the reaction system [62]. Ethanol (EtOH) can react with sulfate radicals ( $SO_4^{\bullet-}$ ) and hydroxyl radicals ( $\bullet OH$ ) [63]. Therefore, TBA and ethanol were used as trapping agents for hydroxyl radical and sulfate radical. In addition, EDTA-2Na and 1,4-benzene quinone (BQ) were added as hole ( $h^+$ ) and superoxide radical ( $\bullet O_2^-$ ) quenchers in the control experiment [64]. 1 mol L<sup>-1</sup> quencher was added to the reaction system. In Fig. 14(a), the removal effect of the catalyst dropped to about 30% after adding EDTA-2Na, indicating that the holes had a great influence on the reaction. After adding TBA and EtOH, the removal of TC was obviously inhibited. This was because Fe/g-C<sub>3</sub>N<sub>4</sub> activated PMS to produce a large amount of strong oxidizing  $SO_4^{\bullet-}$ , which promoted the oxidative removal of TC. On the other hand, with the addition of BQ, the removal rate decreased but it was not obvious, indicating that superoxide radicals did not contribute much to the TC oxidation decomposition reaction. In conclusion, in the free radical capture experiment, hydroxyl radicals, sulfate radicals and holes were the main active species in the Fe/g-C<sub>3</sub>N<sub>4</sub>/PMS/Vis system.

The thermogravimetric curve was shown in Fig. 14(b). The ferrocene and g-C<sub>3</sub>N<sub>4</sub> interacted during the calcination process to form a graphite phase carbon nitride-based composite material doped with iron oxide. The substance began to decompose when the temperature was around 400 °C, and the end temperature when the mass change reached the maximum was 550 °C. It was reported in the literature that melamine begins to decompose at 354 °C, and ferrocene decomposes at 400 °C



**Fig. 12.** (a) The photodegradation and TOC removal curves of TC on Fe/g-C<sub>3</sub>N<sub>4</sub> (10%) composites. (b) The column chart of degradation efficiency of TC leaching concentration in the photo-assisted PMS activation catalytic processes over Fe/g-C<sub>3</sub>N<sub>4</sub> (10%) for five cycles.



**Fig. 13.** (a) XRD pattern of Fe/g-C<sub>3</sub>N<sub>4</sub> (10%) before and after usage. (b) The FTIR spectra of Fe/g-C<sub>3</sub>N<sub>4</sub> (10%) before and after usage.

[65]. Since the two were mixed and calcined, the mixed material started to decompose at about 400 °C. The first plateau in the thermogravimetric curve was a mixture of ferrocene and melamine before 400 °C. Weight loss occurred between 400 and 550 °C, and the solid component of the second platform was a mixture of Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>. Combining XPS, TEM-EDS elemental mapping images and XRD characterization, we analyzed that ferrocene was converted to iron oxide during the calcination process, and the main form was Fe<sub>3</sub>O<sub>4</sub>. And it could be seen from the figure that the composite material maintained the good thermal stability of the ferrocene monomer.

To further prove that hydroxyl radicals, superoxide radicals and sulfate radicals were produced during the reaction, we carried out EPR experiments. The EPR experiment is the most effective method to determine the types of free radicals produced during the removal of tetracycline [66]. As we can see in Fig. 16, under dark conditions, no obvious ESR signals of hydroxyl radicals, superoxide radicals and sulfate radicals were observed, which proved the importance of light to the production of active species in the reaction system [67]. Meanwhile, the characteristic peaks of hydroxyl radicals, sulfate radicals and superoxide radicals fluctuate significantly after light was provided, indicating that these active free radicals could be generated under the excitation of

visible light.

In order to study the effect of ferrocene modification on the separation efficiency of photogenerated carriers in g-C<sub>3</sub>N<sub>4</sub>, a photocurrent experiment was carried out to study the photocurrent response properties of Fe/g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>. The photocurrent test results (Fig. 15) showed that both Fe/g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> catalysts had photoresponse properties under visible light, but their intensities were different. From the figure, we could see that the photocurrent response intensity of ferrocene-modified g-C<sub>3</sub>N<sub>4</sub> was more than twice that of g-C<sub>3</sub>N<sub>4</sub> alone, indicating that the iron introduction can help the separation of photogenerated electrons and holes in g-C<sub>3</sub>N<sub>4</sub> materials[68]. The efficiency allowed more holes and electrons to participate in the reaction, which was conducive to the conversion between divalent iron and trivalent iron, accelerated the activation efficiency of PS, enhanced the photocatalytic activity, and promoted the removal of tetracycline.

Based on the above results, we proposed the reaction mechanism of Fe/g-C<sub>3</sub>N<sub>4</sub> composite material activated PS to remove tetracycline under visible light irradiation (Scheme 1) and summarized as follows:



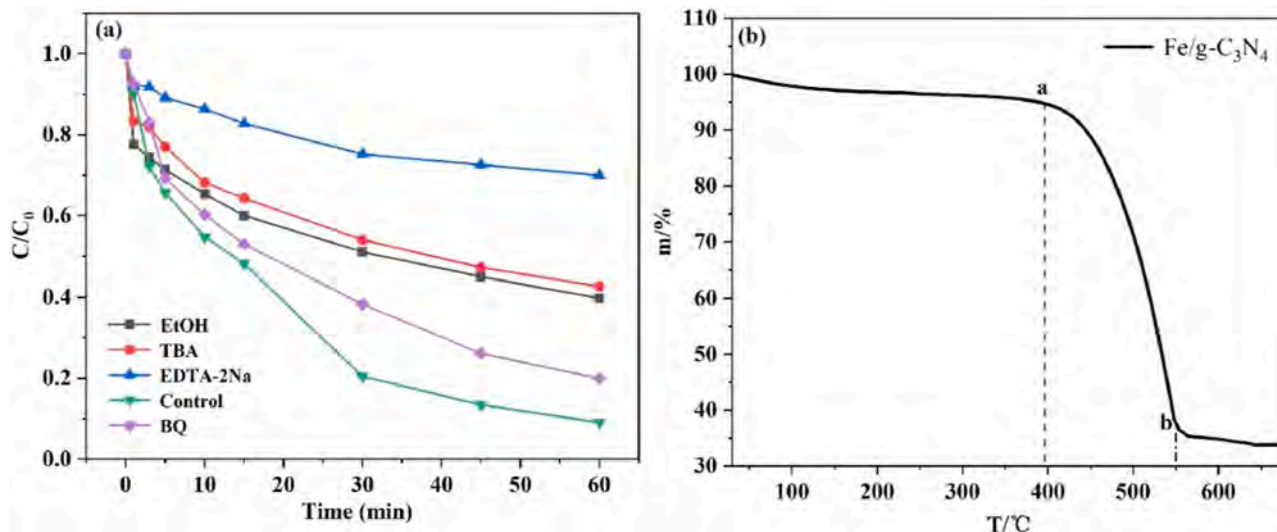


Fig. 14. (a) Effect of EtOH, TBA, EDTA-2Na and BQ as radical scavengers on removal of TC, (b) Thermogravimetric analysis (TGA).

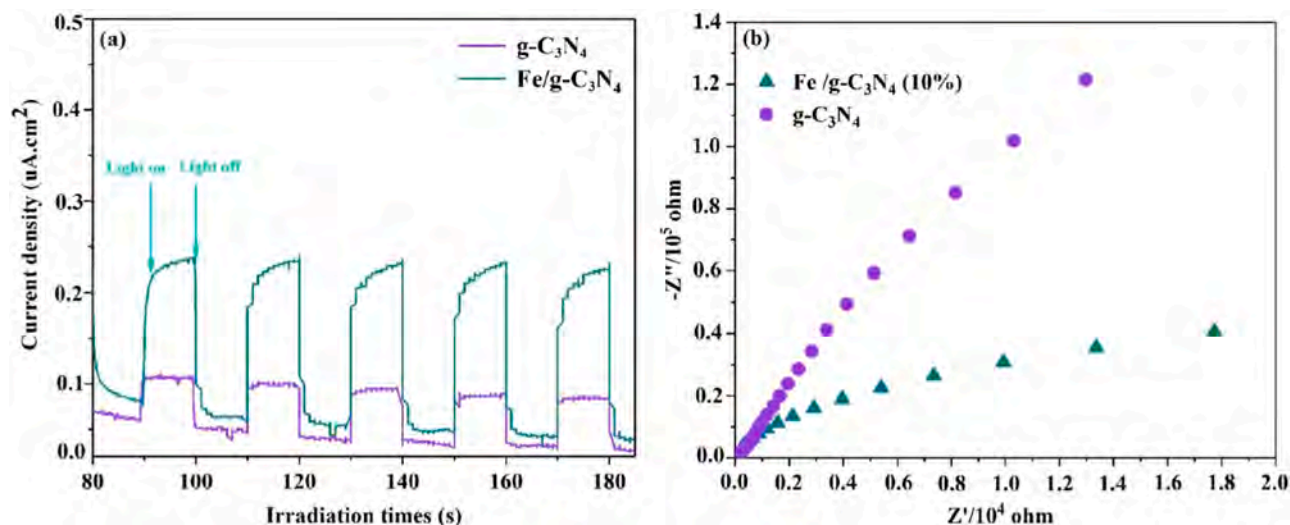
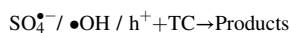
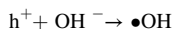
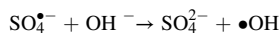
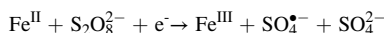
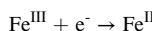
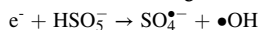


Fig. 15. (a) Photocurrent responses under visible light, (b) EIS Nyquist plots for bulk g-C<sub>3</sub>N<sub>4</sub> and Fe/g-C<sub>3</sub>N<sub>4</sub> (10%) samples.



Briefly, the conduction band (CB) and valence band (VB) of the Fe/g-C<sub>3</sub>N<sub>4</sub> catalyst generated photo-generated electrons (e<sup>-</sup>) and photo-generated holes (h<sup>+</sup>), respectively (Eq. (1)). There was a synergy between photocatalysis and PS activation process (Eq. (2)). Fe<sup>3+</sup> and O<sub>2</sub> were reduced by e<sup>-</sup> to Fe<sup>2+</sup> and •O<sub>2</sub><sup>-</sup>. The produced ferrous ions, superoxide radicals and holes could effectively activate PS under visible light to produce sulfate radicals (SO<sub>4</sub><sup>•-</sup>) and hydroxyl radicals (•OH) (Eqs. (2) and (3)). The introduction of ferrocene and the conversion between ferrous ions and ferric ions also promoted the activation of persulfate (Eqs. (3) and (4)). Strong oxidizing SO<sub>4</sub><sup>•-</sup> could effectively remove tetracycline, oxidize and decompose it into carbon dioxide, water and other by-products, and reduce water toxicity (Eqs. (5–7)). Therefore, SO<sub>4</sub><sup>•-</sup>, h<sup>+</sup>, and •OH were the main active substances in the Fe/g-C<sub>3</sub>N<sub>4</sub>

composite material in the visible light activation of PS to remove tetracycline, which could eventually degrade tetracycline into small molecular compounds, and even mineralize it into CO<sub>2</sub>, H<sub>2</sub>O, etc.

#### 4. Conclusions

In summary, Fe/g-C<sub>3</sub>N<sub>4</sub> catalysts with various doping ratio were successfully prepared by the calcination method. This study comprehensively explored their catalytic performance toward PS activation under visible light evaluated by TC degradation. Fe/g-C<sub>3</sub>N<sub>4</sub> with good photocatalytic performance was synthesized by calcination method, effectively helped the separation of photogenerated carriers, and was beneficial to the activation of PS. When the PS concentration reached 2.5 mM, the Fe/g-C<sub>3</sub>N<sub>4</sub>/PS/Vis system had a removal rate of 93% for tetracycline after 60 min of visible light reaction. The effects of different ferrocene doping proportions, initial TC concentration, catalyst dosage, PS concentration and pH on the removal of tetracycline by photocatalytic activation of PS were explored. The experimental results showed that when the PS reached 2.5 mM, the catalyst amount was 1 g L<sup>-1</sup>, and the iron doping amount was 10%, the catalytic activation performance of the composite catalyst was the best. The catalyst had



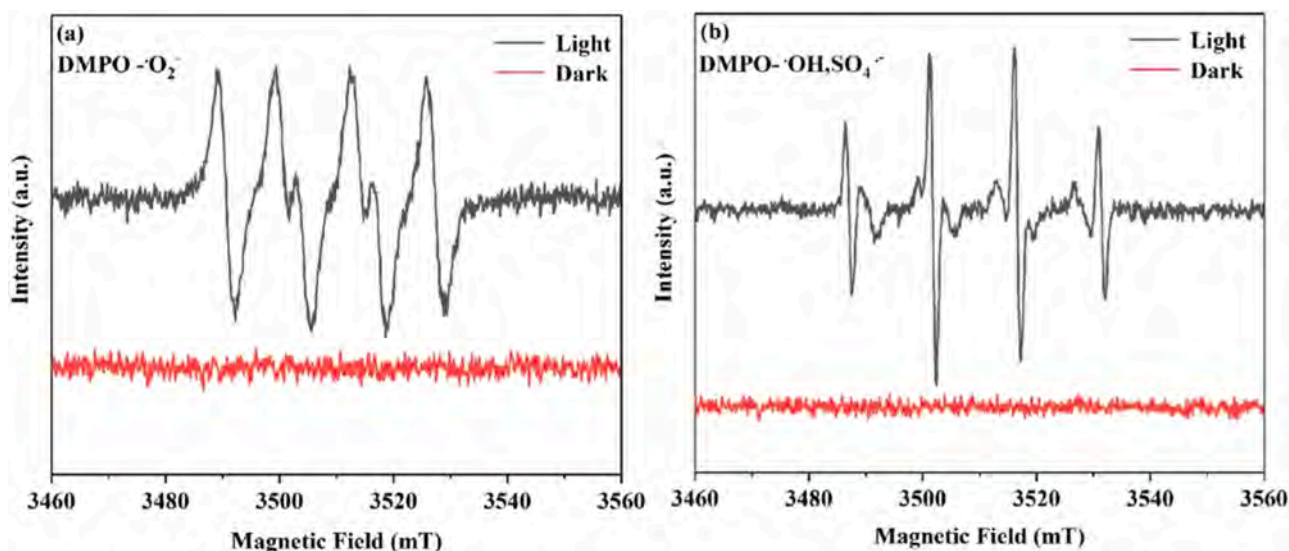
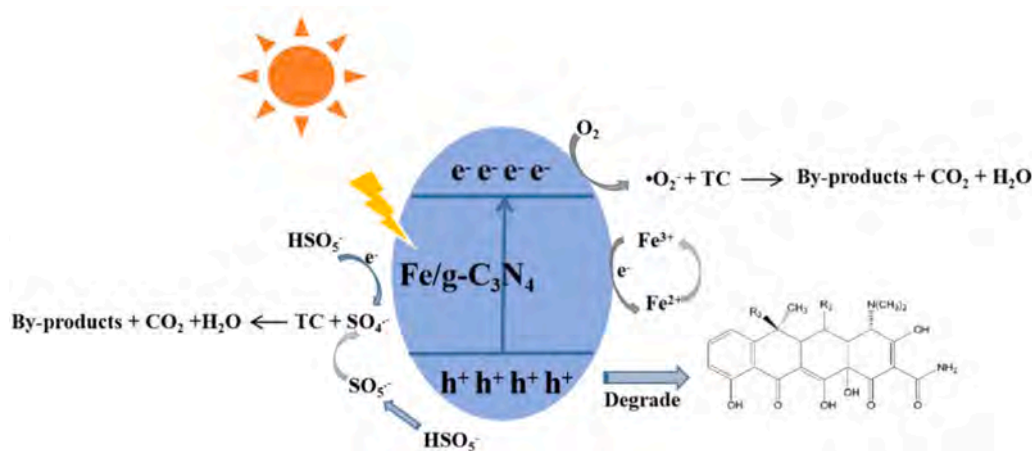


Fig. 16. (a) In methanol dispersion for DMPO- $\bullet\text{O}_2$  and (b) in aqueous dispersion for DMPO- $\bullet\text{OH}$  and  $\text{SO}_4^{\bullet-}$ .



Scheme 1. Degradation mechanisms of TC by Fe-g-C<sub>3</sub>N<sub>4</sub> /PMS/Vis process.

good stability in a wide pH range, where in acidic and neutral conditions were more conducive to the removal of tetracycline.

In the reaction system, the main active species involved in  $\text{SO}_4^{\bullet-}$ ,  $\bullet\text{OH}$  and  $\text{h}^+$ , of which holes contributed the most. Photocurrent experiments had proved that the modification of ferrocene was beneficial to the separation of photogenerated carriers in g-C<sub>3</sub>N<sub>4</sub> and promoted the photocatalytic reaction. As the result of BET, the specific surface area of the composite material was larger, which provided a larger attachment space for the reaction and facilitated the removal of pollutants. Fe/g-C<sub>3</sub>N<sub>4</sub> had good stability and recyclability, and its chemical structure was quite stable. It is an effective catalyst for activating PS under visible light to effectively remove tetracycline from water.

#### CRediT authorship contribution statement

Zixuan Wang, Han Wang, Ziwei Wang: Responsible for writing papers and conducting experiments. Danlian Huang: Responsible for the analysis of the characterization part. Hong Qin, Yangzhuo He: Responsible for drawing the chart. Ming Chen, Guangming Zeng, Piao Xu: Responsible for the revision and typesetting of the paper.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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