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1 **Utilization of Fe doped g-C₃N₄ in heterogeneous photo-Fenton-**
2 **like catalytic system: different parameters effect and system**
3 **mechanism investigation**

4

5 Wei Luo^a, Wenyu Huang^{a,b,*}, Xiaoqing Feng^a, Ying Huang^a, Xiongwei Song^a, Hongfei Lin^b, Shuangfei

6 Wang^{b,c} and Gilles Mailhot^d

7 ^a College of Resources, Environment and Materials, Guangxi University, Nanning 530004, PR China

8 ^b Guangxi Bossco Environmental Protection Technology Co., Ltd, Nanning, 530007, China

9 ^c Guangxi Key Laboratory of Clean Pulp & Papermaking and Pollution Control, Guangxi University,

10 Nanning 530004, China

11 ^d Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de Clermont-Ferrand, F-

12 63000 Clermont-Ferrand, France

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* Corresponding author.

E-mail address: huangwenyu@gxu.edu.cn (Wenyu Huang)

23 **Abstract**

24 In this study, a series of Fe-doped g-C₃N₄ (Fe-C₃N₄) was synthesized and characterized by X-ray
25 powder diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR), X-
26 ray photoelectron spectroscopy (XPS), UV–vis diffuse reflection spectra (UV-vis DRS), and
27 fluorescence spectra (PL). The photocatalytic activity of the synthesized catalyst was investigated on
28 methylene blue (MB) degradation with hydrogen peroxide (H₂O₂) assisting. Results showed that the Fe-
29 C₃N₄ heterogeneous photo-Fenton-like system showed a good catalytic performance when the pH value
30 varies from 3.0 to 9.0. For the effect of various inorganic anions in the Fe-C₃N₄ heterogeneous photo-
31 Fenton-like system, HCO₃⁻ showed a dual effect on MB degradation. Cl⁻ and NO₃⁻ showed an inhibited
32 effect on MB degradation. For the effect of inorganic cations, Al³⁺, Mg²⁺, and Ca²⁺ showed a strong
33 inhibition in MB degradation. The recycling experiment demonstrated that Fe-C₃N₄ possesses good
34 reusability and stability. The quenching experiment was carried out and it was found that hydroxyl radical
35 ([•]OH) was the major active species in the system. Besides, nine intermediates were identified by LC/MS
36 and a possible pathway of MB degradation in the system was proposed. This study could promote the
37 application of the Fe-C₃N₄ heterogeneous photo-Fenton-like system in realistic dye wastewater.

38

39 **Key words** Fe doped g-C₃N₄, H₂O₂, Methylene blue, Heterogeneous photo-Fenton-like reaction,
40 Inorganic ions, Degradation pathway

41

42 **1. Introduction**

43 Nowadays, advanced oxidation processes (AOPs) are commonly recognized as potential alternative
44 technologies for the treatment of refractory organic pollutants, because of their simplicity, high efficiency

45 and easy handling ¹⁻⁵. Among various AOPs, visible light-induced heterogeneous photo-Fenton-like
46 process has been taken into account as an effective way for pollutants treatment. Compared with the
47 traditional Fenton and photo-Fenton process in homogeneous system, it showed many advantages, such
48 as efficient mineralization of organic pollutants, lower cost, reuse, good chemical stability and small
49 amounts of iron precipitation ⁶. However, the rigorous pH range (acidic or near-neutral conditions), high
50 iron leaching (>2 ppm), fewer iron active sites and low efficiency cycling of Fe³⁺/Fe²⁺ limited the
51 application of this process ⁷. Therefore, exploring a highly efficient and low-cost catalyst for this system
52 is essential.

53 Polymeric graphitic carbon nitride (g-C₃N₄) as a visible-light-driven photocatalyst has been applied
54 worldwide in water splitting, organic degradation, and conversion of CO₂ ⁸⁻¹⁰. However, the rapid charge
55 recombination has limited its application in AOPs^{11,12}. To overcome this drawback, the external element
56 doped and copolymerized are taken into account and proved to be applicable ¹³⁻¹⁶. Fe is an
57 environmentally friendly and abundant element in the earth. It has been extensively investigated to
58 improve the photocatalytic performance of g-C₃N₄ by element doping way. Meanwhile, it was certified
59 in previous studies that the photocatalytic activity of g-C₃N₄ towards dye degradation can be remarkably
60 improved by Fe doping and Fe existed in Fe-C₃N₄ by Fe-N ligand ¹⁷⁻²⁰. Besides, the photo-induced
61 electrons from Fe-C₃N₄ can reduce Fe³⁺ to Fe²⁺ under visible light illumination ²¹. Thence, Fe-C₃N₄ can
62 work as an efficient catalyst in the heterogeneous photo-Fenton-like system. It has been already reported
63 that the Fe-C₃N₄ is an efficient catalyst for removal of organic pollutants in photo-Fenton system.
64 Previous studies have focused on the preparation and optimization of Fe-C₃N₄ or coupled Fe-C₃N₄
65 material. The influence of reaction parameters especial for various inorganic ions in natural water on
66 activity and the degradation pathway of specific contaminant (MB) in Fe-C₃N₄ based photo-Fenton

67 system have not been systematically studied. It has been already reported that the Fe-C₃N₄ is an efficient
68 catalyst for removal of organic pollutants in photo-Fenton system. However, previous studies have
69 focused on the preparation and optimization of Fe-C₃N₄ or coupled Fe-C₃N₄ material. The influence of
70 reaction parameters especially for various inorganic ions in natural water on activity and the degradation
71 pathway of specific contaminant (MB) in Fe-C₃N₄ based photo-Fenton system have not been
72 systematically studied.

73 In this study, Fe-C₃N₄ was reported as an effectual photo-Fenton-like photocatalyst for MB
74 degradation under simulated sunlight. Various Fe-C₃N₄ catalysts with different Fe doping amounts were
75 synthesized and characterized. The effect of important parameters including Fe doping amounts, H₂O₂
76 concentration, catalyst dosage, pH, MB concentration, naturally occurring inorganic ions (Cl⁻, NO₃⁻,
77 HCO₃⁻, Al³⁺, Mg²⁺, and Ca²⁺) and the stability of Fe-C₃N₄ were investigated. Besides, scavenging tests
78 were conducted to identify the active species for MB degradation in this catalytic process, and coupling
79 with the intermediate determined by LC-MS, a possible degradation pathway of MB was proposed.

80 **2. Experimental**

81 **2.1 Materials**

82 The chemicals were of commercially available analytical grade used as purchased without further
83 purification. Melamine, ferric nitrate (Fe(NO₃)₃·9H₂O₂), Hydrogen Peroxide (H₂O₂, 30%, w/w), sodium
84 hydroxide (NaOH), hydrochloric acid (HCl), tertiary butanol (TBA), p-benzoquinone, sodium chloride
85 (NaCl), sodium bicarbonate (NaHCO₃), sodium nitrate (NaNO₃), calcium chloride (CaCl₂, P96.0%),
86 magnesium chloride (MgCl₂, P98.0%), aluminum chloride (AlCl₃, P97.0%), Potassium iodide (KI), and
87 methylene blue (MB) were supplied by Nanning Lantian Experiment Equipment Co., Ltd (Nanning,
88 China).

89 **2.2 Synthesis of Fe-C₃N₄**

90 The Fe-C₃N₄ catalyst was synthesized according to the method reported ^{22, 23}. Typically, 6 g
91 melamine was dispersed in 30 ml deionized water under stirring magnetically. Then different dosage of
92 ferric nitrate (0.03, 0.06, 0.12, and 0.3 g) was added. The mixture was heated to 100 °C to remove the
93 water. The obtained solid product was milled and put into 25 mL crucible, placed into a muffle furnace
94 and heated to 520 °C maintaining 2 h. Finally, yellow powder of Fe-C₃N₄ was obtained. The products
95 were labeled x wt% Fe-C₃N₄, where x was the mass percent of ferric nitrate to melamine. The pristine g-
96 C₃N₄ was synthesized by heating melamine directly under the same conditions without ferric nitrate.

97 **2.3 Characterization of catalyst**

98 XRD at a 40 KV operating voltage and 300 mA current (DX-2700A) was applied to determine the
99 crystal structure of g-C₃N₄ and x wt% Fe-C₃N₄. The morphology of all catalysts was characterized by S-
100 3400N scanning electron microscopy. The functional groups and chemical states of C, N and Fe on the
101 catalyst surface were analyzed by Nicolet iS 50 Fourier transform infrared spectroscopy and ESCALAB
102 250XI+ X-ray photoelectron spectroscopy. UV-vis absorption spectra were investigated by UV-2501 PC
103 to determine the light adsorption region of catalysts. Photoluminescence were investigated by the ZLX-
104 PL-I fluorescence spectrometer to evaluate the reduction of charge carrier recombination of prepared
105 catalysts.

106 **2.4 Experimental procedures**

107 MB was chosen as the model compound to evaluate the efficiency of heterogeneous photo-Fenton-
108 like system. Investigation for the degradation of MB was conducted in a 250 mL quartz reactor at room
109 temperature under stirring magnetically. The MB solutions with different concentrations (20, 30, and 40
110 mg·L⁻¹) were prepared. During each experiment, 200 mL MB was placed in the reactor. The initial pH of

111 the MB solution was not adjusted (initial pH of 6.86) or adjusted with 1 M NaOH and HCl solutions. To
112 achieve the adsorption equilibrium, the catalyst was added into the MB solution at the same time with
113 constant stirring for 30 min without light irradiation. After that, H₂O₂ was added and the suspension was
114 exposed to a 150 W xenon lamp. At a given time, about 5 ml of the suspension was removed. The
115 suspension was filtered with 0.22 um the filter heading immediately. To investigate the influence of
116 inorganic ions on MB degradation, the altered concentrations of NaCl, NaNO₃, NaHCO₃, CaCl₂, MgCl₂,
117 and AlCl₃ with were added. To carry out recycling experiment, the Fe-C₃N₄ was removed from the
118 solution by centrifugation. Then Fe-C₃N₄ was washed, dried and applied in the next experiment without
119 purification.

120 **2.5 Analytical methods**

121 The absorbance of MB solution was obtained by a 722N Vis spectrophotometer at the wavelength
122 of 665 nm. The removal efficiency of MB was calculated by the following [equation \(1\)](#), where C₀ and C
123 were the initial concentration of MB and the concentration of MB after irradiation for a given time,
124 respectively.

$$125 \quad \text{Degradation efficiency(\%)} = \frac{C_0 - C}{C_0} * 100 \quad (1)$$

126 The kinetic analysis of MB degradation used the pseudo-first-order rate model by [equation \(2\)](#),
127 where *k* was the pseudo-first-order rate constant.

$$128 \quad \ln\left(\frac{C_0}{C}\right) = kt + \text{constant} \quad (2)$$

129 The reactive species were investigated by trapping experiment. In this section, 2 mM TBA, 2 mM
130 p-benzoquinone and 2 mM KI were used as the quenchers of ·OH, ·O₂⁻ and h⁺, respectively. The liquid
131 chromatography coupled with tandem mass spectrometer (LC/MS, AGILENT 6460, America) was
132 applied to analyze the reaction intermediates formed from MB degradation. The related test parameters

133 referred to previous report ²⁴.

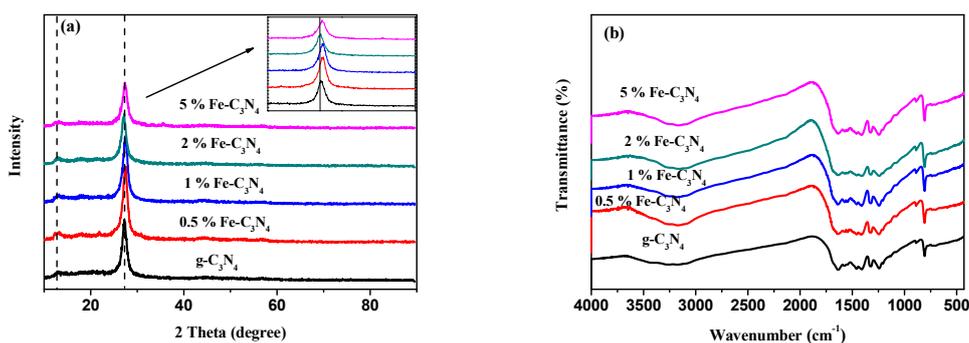
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135 **3. Results and discussion**

136 **3.1 Characterization of g-C₃N₄ and Fe-C₃N₄**

137 The morphology and structure of g-C₃N₄ and x% Fe-C₃N₄ was observed by SEM (Fig. S1). The
138 result revealed a typical layered structure of all prepared samples. The crystal phase structure of g-C₃N₄
139 and x wt% Fe-C₃N₄ was investigated by XRD as displayed in Fig.1 (a). Two typical peaks were observed
140 obviously in the XRD patterns of all catalysts. The weak peak at 13.2° and 27.4° was the (100) and (002)
141 facet diffraction peak of the g-C₃N₄²⁵. With the increase of Fe doping, the diffraction peaks intensities of
142 the (002) facets were gradually weakened. This phenomenon indicated the inhibitory effect of Fe species
143 on polymeric condensation and the host-guest interaction ²³. Furthermore, other characteristic peaks of
144 Fe species were not found that may be caused by limited content of doped iron. Therefore, Fe was
145 probably chemically coordinated to the g-C₃N₄ structure in the form of Fe-N bonds ²⁶.

146 The chemical composition and structure of pristine g-C₃N₄ and x wt% Fe-C₃N₄ samples were
147 investigated by the FT-IR spectroscopy. As shown in Fig.1(b), all materials exhibited characteristic peaks
148 near 3000-3300, 1200-1700, 892, and 806 cm⁻¹. Pristine g-C₃N₄ and x wt% Fe-C₃N₄ samples had similar
149 characteristic peak. This result indicated that the Fe-C₃N₄ and pristine g-C₃N₄ had the same structure.
150 The broad peak between 3000 and 3300 cm⁻¹ was indicative of the terminal N-H stretching vibration.
151 The peaks from 1200 to 1700 cm⁻¹ due to the characteristic breathing modes of tri-s-triazine rings. The
152 peak at 892 cm⁻¹ was assigned to the cross-linked deformation mode of N-H. Additionally, the peak at
153 806 cm⁻¹ due to the tri-s-triazine ring breathing vibration ^{27,28}.



154
155 **Fig.1.** XRD patterns (a) and FT-IR spectra (b) of g-C₃N₄ and Fe-C₃N₄ samples.
156

157 To analyze the elemental composition and the surface states of x wt% Fe-C₃N₄, the XPS of 5 wt%

158 Fe-C₃N₄ were investigated. As shown in Fig.2(a), four elements were present in the XPS survey spectra

159 of 5% Fe-C₃N₄ including C, N, O and Fe. This result was the same as to the EDS analysis that Fe was

160 successfully doped into the structure of 5 wt% Fe-C₃N₄ (Fig. S2). The signal of O was ascribed to O₂ or

161 H₂O absorbed in the surface of 5 wt% Fe-C₃N₄²⁹. The signal of Fe was weak because of the low amount

162 of Fe doping. The C 1s XPS spectra was deconvoluted into two peaks at binding energies of 283.7 and

163 287.3 eV, as shown in Fig.2(b). The peak at 283.7 eV was the characteristic peak of graphitic carbon

164 C=C and the peak at 287.3 eV was ascribed to the sp² bonded carbon N-C=C^{3,30}. Fig.2(c) showed that

165 the N 1s XPS spectra was deconvoluted into three peaks at binding energies of 397.9, 399.1, and 400.4

166 eV, respectively. The main peak at 397.9 eV due to the sp²-bonded N atoms in the triazine rings. The

167 peak at 399.1 eV was attributed to the presence of N-(C)₃ or H-N-(C)₂. The weaker peak at 400.4 eV was

168 ascribed to the groups of -NH₂ or =NH³¹. From Fig. 2(d), the O 1s spectrum exhibits one characteristic

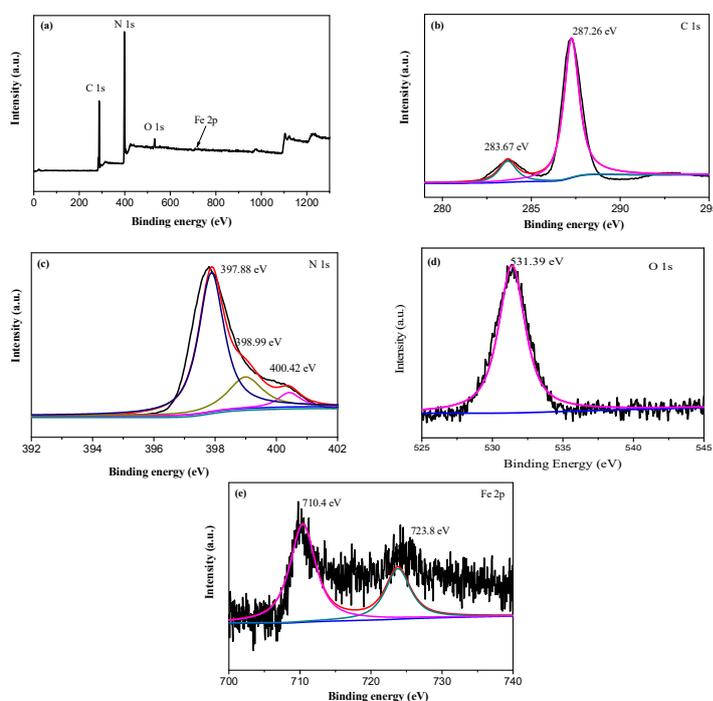
169 peaks at 531.39 eV which was ascribed to surface adsorbed water in the Fe-C₃N₄. The Fe-O-Fe and Fe-

170 OH were not found in the Fe-C₃N₄ due to the characteristic diffraction peak of Fe-O-Fe and Fe-OH at

171 529.8 eV. The Fe 2p_{3/2} XPS spectrum of 5% Fe-C₃N₄ showed a peak centered at 710.4 eV, as shown in

172 Fig.2(e). The binding energy peak of Fe³⁺ at the range from 710.3 to 711.8 eV. Thus, the primary Fe state

173 on the surface of Fe-C₃N₄ was Fe³⁺^{23, 32, 33}. Meanwhile, the binding energy of Fe species stabilized in
174 the g-C₃N₄ structure through Fe-N bonds were close to 710.4 eV^{19, 34}. Therefore, Fe had been
175 successfully doped into g-C₃N₄ and the Fe³⁺ connected to the N atom by Fe-N(III) coordinate bonds.

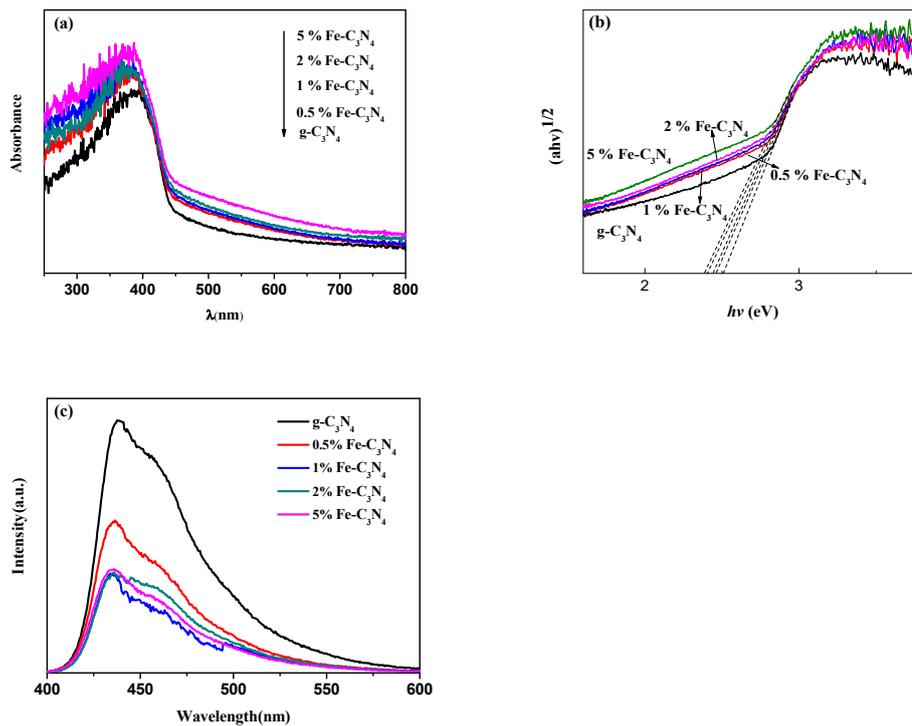


176
177 **Fig.2.** XPS spectra of 5 wt% Fe-C₃N₄ sample: (a) survey scan, (b) C 1s, (c) N 1s, (d) O 1s, and (e) Fe
178 2p.

179
180 To estimate the optical properties of all samples, UV-vis DRS was conducted. Fig.3(a) showed the
181 UV-vis DRS spectra of g-C₃N₄ and x wt% Fe-C₃N₄. Light absorbance of all samples was observed over
182 the range of 250-800 nm. As the amount of iron doping increasing, the absorption range of light gradually
183 increased. This phenomenon indicated that the Fe doping could enhance the light harvesting ability
184 effectively for g-C₃N₄. The pristine g-C₃N₄ showed an apparent absorption edge at approximately 456
185 nm. With the increasing of Fe doping, the adsorption edge of Fe-C₃N₄ displayed an obvious redshift from
186 456 to 477 nm. This result was caused by the impurity energy level formation due to Fe doping²².

187 The transfer and separation efficiency of photogenerated charge carriers of g-C₃N₄ and Fe-C₃N₄

188 were investigated by Photoluminescence (PL) measurements. As shown in Fig.3(b), all samples showed
 189 a broad emission peak centered at approximately 438 nm. This result was formed due to the characteristic
 190 band-band PL phenomenon of the photoexcited charge carriers for g-C₃N₄. The peak intensities of Fe-
 191 C₃N₄ were far weaker than pristine g-C₃N₄ obeying the order of g-C₃N₄ > 0.5 % Fe-C₃N₄ > 5 % Fe-C₃N₄ >
 192 1 % Fe-C₃N₄ ≈ 2 % Fe-C₃N₄. Thus, the separation and transport efficiency of the photoexcited carriers
 193 was enhanced by Fe doping. This result attributed that the Fe doping site in catalyst could trap
 194 photogenerated electrons and reduced recombination of photogenerated electron-hole pairs²³. However,
 195 when the doping content of Fe was excessive, a recombination center of electrons and holes may be
 196 generated to suppress the separation of photogenerated charges³⁵.



197

198

199 **Fig.3.** UV-vis diffuse reflectance spectra (a), the Tauc's plot (b), and photoluminescence emission
 200 spectra (c) of g-C₃N₄ and Fe-C₃N₄ samples.

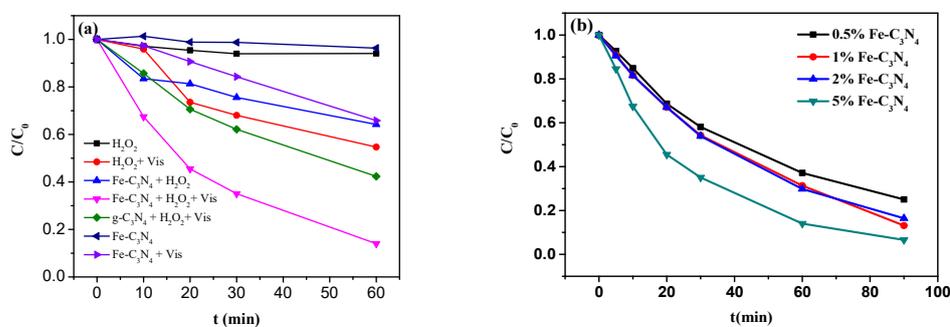
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202 3.2 Catalytic performance of Fe doped g-C₃N₄

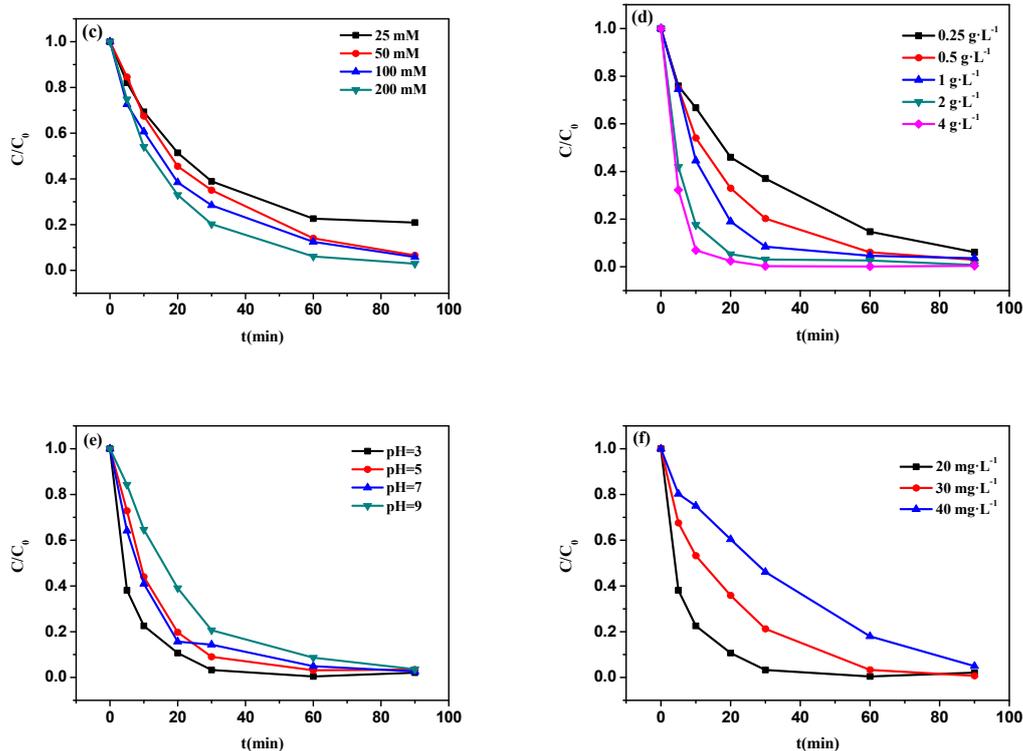
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From the results of XPS, synthesized Fe-C₃N₄ materials had large amounts of Fe-N sites. Therefore,

204 it was expected that Fe-C₃N₄ would show a good performance for removal of organic molecules in the
 205 photo-Fenton-like system. The cationic MB was chosen as a model pollutant for evaluating catalytic
 206 activity of synthesized materials. Experiments of MB oxidation were conducted without pH control
 207 (initial pH=6.86) and the results were shown in Fig.4(a). The degradation efficiency of MB by H₂O₂ in
 208 the dark, H₂O₂ under simulated sun-light irradiation, Fe-C₃N₄ in the dark, Fe-C₃N₄ under irradiation, and
 209 Fe-C₃N₄ assisting with H₂O₂ in the dark was 5.9%, 45.3%, 4.7%, 42.8% and 35.8%, respectively. Besides,
 210 the degradation efficiency of MB in g-C₃N₄, H₂O₂ and simulated sun-light irradiation system was 71.6%.
 211 Obviously, the Fe-C₃N₄ heterogeneous photo-Fenton-like system displayed an excellent performance
 212 towards MB degradation compared to other reaction systems and the degradation efficiency reached to
 213 85.9%. From the results, it was inferred that the synergetic effect was formed between Fe-C₃N₄ and H₂O₂
 214 under simulated sun light irradiation. The high removal efficiency of MB in Fe-C₃N₄ heterogeneous
 215 photo-Fenton-like system may be contributed from these reasons as follow: (1) The photocatalytic
 216 efficiency of g-C₃N₄ was improved by Fe doping. (2) The photo-generated electrons of Fe-C₃N₄ were
 217 captured by H₂O₂, and the separation of photo-generated electron and hole was enhanced. (2) The H₂O₂
 218 was activated to generate ·OH by the photo-generated electron and Fe³⁺/Fe²⁺ cycle under light irradiation.
 219



220



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222

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Fig. 4. Decolorization of MB under different system (a), effect of Fe doped amounts (b), effect of H_2O_2 concentration (c), effect of catalyst dosage (d), effect of pH (e), effect of MB initial concentration (f).

225

Experimental condition: For (a), $[MB] = 20 \text{ mg}\cdot\text{L}^{-1}$, $[5 \text{ wt}\% \text{ Fe-C}_3\text{N}_4] = 0.5 \text{ g}\cdot\text{L}^{-1}$, $[H_2O_2] = 50 \text{ mM}$, pH

226

$= 6.86$. For (b), $[MB] = 20 \text{ mg}\cdot\text{L}^{-1}$, $[Fe-C_3N_4] = 0.5 \text{ g}\cdot\text{L}^{-1}$, $[H_2O_2] = 50 \text{ mM}$, pH $= 6.86$. For (c), $[MB] =$

227

$20 \text{ mg}\cdot\text{L}^{-1}$, $[5 \text{ wt}\% \text{ Fe-C}_3\text{N}_4] = 0.5 \text{ g}\cdot\text{L}^{-1}$, pH $= 6.86$. For (d), $[MB] = 20 \text{ mg}\cdot\text{L}^{-1}$, $[H_2O_2] = 200 \text{ mM}$, pH $=$

228

6.86 . For (e), $[MB] = 20 \text{ mg}\cdot\text{L}^{-1}$, $[5 \text{ wt}\% \text{ Fe-C}_3\text{N}_4] = 2 \text{ g}\cdot\text{L}^{-1}$, $[H_2O_2] = 200 \text{ mM}$. For (f), $[5 \text{ wt}\% \text{ Fe-C}_3\text{N}_4]$

229

$= 2 \text{ g}\cdot\text{L}^{-1}$, $[H_2O_2] = 200 \text{ mM}$, pH $= 3$.

230

231

3.3 Effect of reagent doses and pH on the degradation of MB

232

The effect of Fe doping amounts on the MB degradation were investigated in the range of 0.5-5 wt%

233

and the result was shown in Fig.4(b). From the result, Fe doping amounts had an obviously promoted

234

effect on the degradation of MB. With the increase of Fe doping amounts from 0.5 wt% to 5 wt%, the

235

degradation efficiency of MB increased from 75% to 95%. This result demonstrated that the Fe doping

236

amounts played a major role in degradation of MB and the Fe-N bond in the catalyst can activate the

237 H₂O₂ to produce hydroxyl radicals. With the content of Fe³⁺ doping improving, the more ·OH was
238 generated in the system for degradation of MB.

239 The effect of H₂O₂ concentration was investigated in the range of 25 to 200 mM as shown in Fig.4(c).
240 The degraded performance of MB was obviously enhanced by increased the concentration of H₂O₂.
241 Degradation efficiency increased from 79.2% to 97.1% when the concentration of H₂O₂ increased from
242 25 to 200 mM. This result may be attributed to an increase in the rate of ·OH produced by Fe-C₃N₄ and
243 H₂O₂ under simulation sunlight irradiation. However, the degradation efficiency had little change when
244 the dosage of H₂O₂ from 100 to 200 mM. Therefore, there was no requirement to continue increasing the
245 concentration of H₂O₂.

246 To investigate the influence of the dosage of Fe-C₃N₄, five different values were tested as shown in
247 Fig.4(d). Apparently, the increase of Fe-C₃N₄ dosage from 0.25 to 2 g·L⁻¹ had a promoted effect on the
248 degradation of MB. The degradation efficiency increased significantly from 62.99% to 96.95% within
249 30 minutes. The amounts of active sites in the Fe-C₃N₄ heterogenous photo-Fenton-like system affected
250 the degradation rate of MB, and the degradation rate was limited to low Fe-C₃N₄ dosage by reason of not
251 enough active sites. However, with the increase of Fe-C₃N₄ dosage from 2 to 4 g·L⁻¹, the MB degradation
252 curves showed very similar profiles within 90 minutes. The photocatalytic degradation performance of
253 MB was determined by the amounts of active sites on the catalyst and the penetration of simulated solar
254 irradiation. With increasing the dosage of Fe-C₃N₄, the number of active sites would increase and more
255 photoelectron could be generated resulted to more ·OH produced from H₂O₂. However, the light
256 reflectance and shielding effect would occur by the excess Fe-C₃N₄ dosages. Therefore, the degradation
257 efficiency of MB had no obvious change with increase of Fe-C₃N₄ from 2 to 4 g·L⁻¹.

258 The effect of pH within ranges 3-9 on the MB degradation in the Fe-C₃N₄ heterogeneous photo-

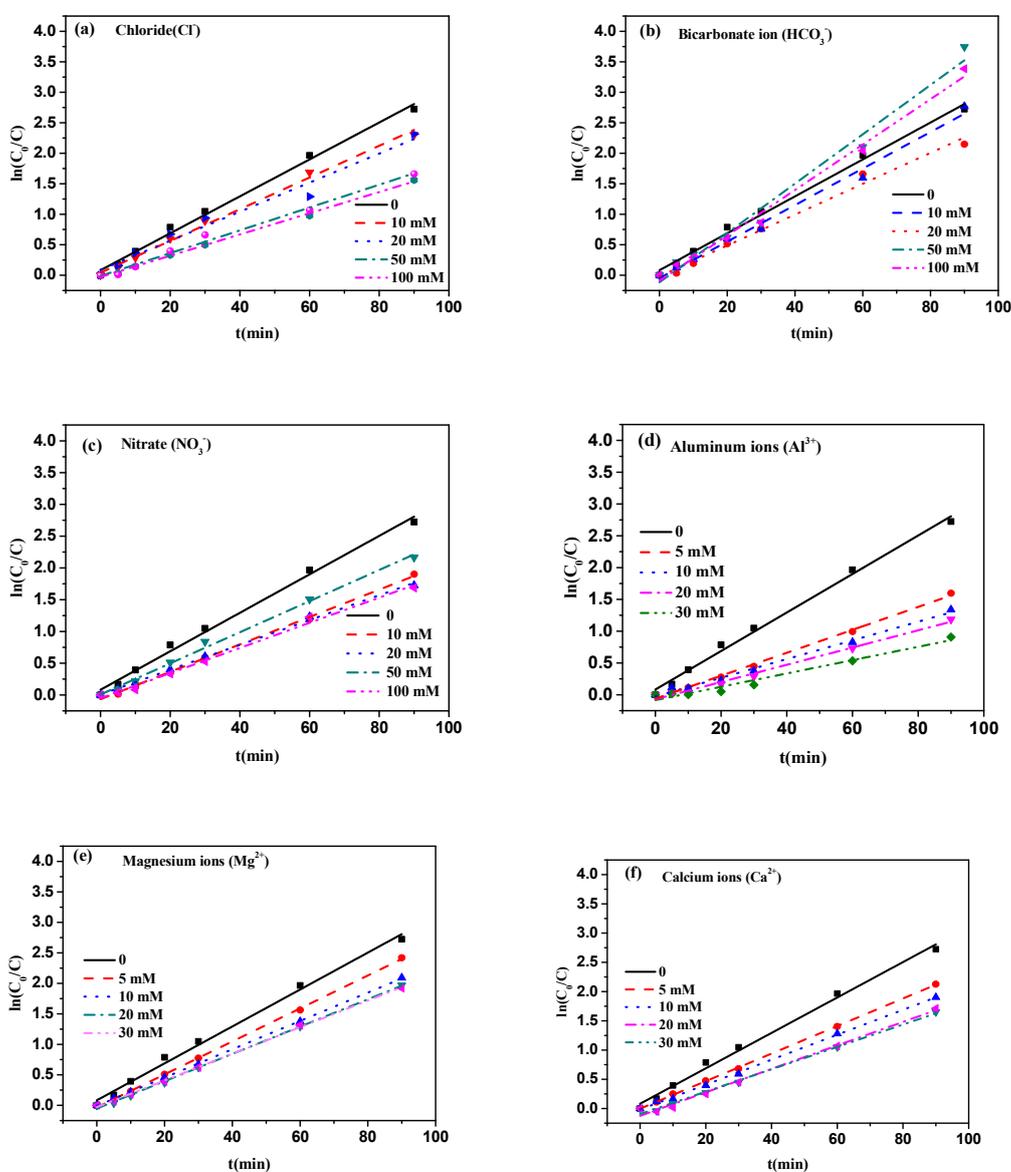
259 Fenton-like system was investigated. As shown in Fig. 4(e), the catalyst remains highly active towards
260 MB degradation over an initial broad pH range from 3 to 9. When pH increased from 3 to 9, the efficiency
261 of MB degradation decreased slightly. Interestingly, at first 30 min, the heterogeneous photo-Fenton-like
262 system degradation efficiency at pH=3, 5, 7 and 9 was 97%, 91%, 85% and 79%, respectively. This
263 phenomenon was attributed to different Fe-N ligands formed in the system. At acidic condition, the
264 produced Fe-N ligands was more conducive to activate H₂O₂ compared to the ligands formed under
265 alkaline conditions. Besides, the H₂O₂ can be consumed and decomposed to H₂O and O₂ under alkaline
266 conditions. In general, at 90 min, all the decolorization ratio of MB with pH rising from 3 to 9 was more
267 than 90%. Hence, Fe-C₃N₄ heterogeneous photo-Fenton-like system showed a wide pH range compared
268 to the conventional Fenton system.

269 The effect of initial MB concentration on the degradation was examined in the range of 20 to 40
270 mg·L⁻¹. As shown in Fig. 4(f), the degradation efficiency of MB within 90 min reached to almost 100%
271 with increasing MB concentration from 20 to 40 mg·L⁻¹. However, at first 30 min, the degradation
272 efficiency decreased from 96.7% to 53.9% with the increase of MB concentration from 20 to 40 mg·L⁻¹.
273 This result was attributed to the amounts of the active species. With the increase of initial MB
274 concentration, the more active species were required for the degradation of MB. However, the active
275 species in the system were theoretically constant at the fixed Fe-C₃N₄ dosage, H₂O₂ concentration and
276 light intensity. Thus, the active species were inadequate for higher MB concentration.

277 **3.4 Effect of inorganic ions on the degradation of MB**

278 Various inorganic ions may co-exist with dye waste water. Thus, to examine the effect of co-existing
279 ions on the MB degradation is very important and benefit of realistic dye treatment process. Previous
280 studies have confirmed that the presence of some inorganic ions in the photocatalytic system can affect

281 the degradation of MB ³⁶⁻³⁹. To investigate the effect of the co-existing various inorganic ions on the MB
 282 degradation, photocatalytic degradation of MB was conducted with six typical inorganic ions of nitrate
 283 (NO_3^-), chloride (Cl^-), bicarbonate ions (HCO_3^-), aluminum ions (Al^{3+}), magnesium ions (Mg^{2+}) and
 284 calcium ions (Ca^{2+}). Considering that natural water does not contain buffer solution and the introduction
 285 of buffer solution will make the system more complicated, the influence of inorganic ions was not
 286 investigated in buffer solution.



290 **Fig. 5.** Effect of inorganic anions and cations on MB degradation under simulated solar light irradiation
 291 (a-e). Experimental condition : $[\text{MB}] = 20 \text{ mg}\cdot\text{L}^{-1}$, $[\text{5 wt\% Fe-C}_3\text{N}_4] = 0.5 \text{ g}\cdot\text{L}^{-1}$, no pH adjustment and

292 original pH=6.86, $[\text{Cl}^-]$, $[\text{HCO}_3^-]$ and $[\text{NO}_3^-] = 10, 20, 50, 100 \text{ mM}$, $[\text{Al}^{3+}]$, $[\text{Mg}^{2+}]$ and $[\text{Ca}^{2+}] = 5, 10, 20,$
293 30 mM.

294

295 Effect of Cl^- on the degradation of MB in the Fe- C_3N_4 heterogenous photo-Fenton-like system was
296 investigated under different Cl^- concentrations from 0 to 100 mM. Fig.5(a) showed that efficient
297 degradation of MB was inhibited by the Cl^- . Adding concentrations of Cl^- obviously decreased the k
298 values of MB degradation rate (Fig. 5(a) and Table S1). The k values of MB degradation rate decreased
299 from 0.0302 to 0.0187 min^{-1} with increasing the concentration of Cl^- from 0 to 100 mM. This
300 phenomenon could be attributed to the reaction of $\cdot\text{OH}$ with Cl^- generated $\text{ClOH}\cdot$ (Eq. (3)) that the
301 reactivity is not as reactive $\cdot\text{OH}$. In this circumstance, Cl^- act as $\cdot\text{OH}$ scavenger, inhibiting the MB
302 degradation^[43].

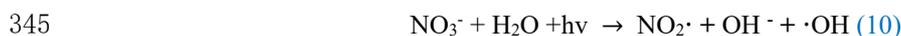
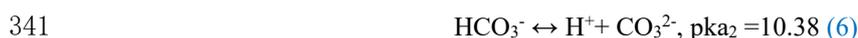
303 Fig.5(b) showed that the effect of HCO_3^- on MB degradation in the Fe- C_3N_4 heterogenous photo-
304 Fenton-like system. With the increase of HCO_3^- concentrations from 0 to 20 mM, the k values of MB
305 degradation rate decreased from 0.0303 to 0.0299 min^{-1} (Table S1). However, the k values improved with
306 the further increase of HCO_3^- concentration. It has been found that HCO_3^- could react with $\cdot\text{OH}$ to
307 produce the carbonate radical ($\text{CO}_3^{\cdot-}$) (Eq. (4)). Meanwhile, the ionization reactions of carbonic acid to
308 reach the equilibration would occur (Eq. (5)-(8))^[43], and the concentration of HCO_3^- could influence the
309 pH of the reaction system. Therefore, the effect of different HCO_3^- concentration on the degradation of
310 MB can be explained by these reasons. (1) At a low HCO_3^- concentration (10, 20 mM), the HCO_3^- may
311 mostly play the role of $\cdot\text{OH}$ scavenger and the produced $\text{CO}_3^{\cdot-}$ would not involve in the degradation of
312 MB. The degradation rate of MB decreased due to $\cdot\text{OH}$ scavenging. (2) At a high HCO_3^- concentration
313 (50, 100 mM), the degradation rate increased because the abundant of $\text{CO}_3^{\cdot-}$ was produced and
314 participated in the MB degradation. Besides, with the increase of the HCO_3^- concentration, the changed

315 pH of reaction system from neutral to alkaline could result in negative charge Fe-g-C₃N₄, and more MB
316 molecule could be contacted and degraded.

317 As for NO₃⁻, Fig.5(c) showed the MB degradation rate *k* values at different concentration from 0 to
318 100 mM. The NO₃⁻ showed an inhibition effect in the Fe-C₃N₄ heterogenous photo-Fenton system. With
319 the increase of NO₃⁻ concentration from 0 to 20 mM, the *k* values of MB degradation rate decreased from
320 0.0303 to 0.0195 min⁻¹ (Table.S1). This result might be attributed to the reaction between ·OH and NO₃⁻.
321 The ·OH could react with NO₃⁻ to produce the nitrate radical (NO₃[·]) (Eq. (9)) that the redox ability is
322 weaker than ·OH [43]. However, when the NO₃⁻ concentration was further increased from 20 to 50 mM,
323 the *k* values of MB degradation rate increased from 0.0195 to 0.0245 min⁻¹. When the concentrations of
324 NO₃⁻ were more than 20 mM, the *k* values of MB degradation were improved. This phenomenon might
325 be due to the formation of ·OH under simulated solar irradiation (Eq. (10)) [43]. Interestingly, further
326 increased of NO₃⁻ concentration to 100 mM, the *k* values of MB degradation rate decreased to 0.0198
327 min⁻¹. When the concentration of the NO₃⁻ further increased, more ·OH was consumed by NO₃⁻ rather
328 than produced. Therefore, MB removal efficiency exhibited an irregularly inhibition effects by NO₃⁻.

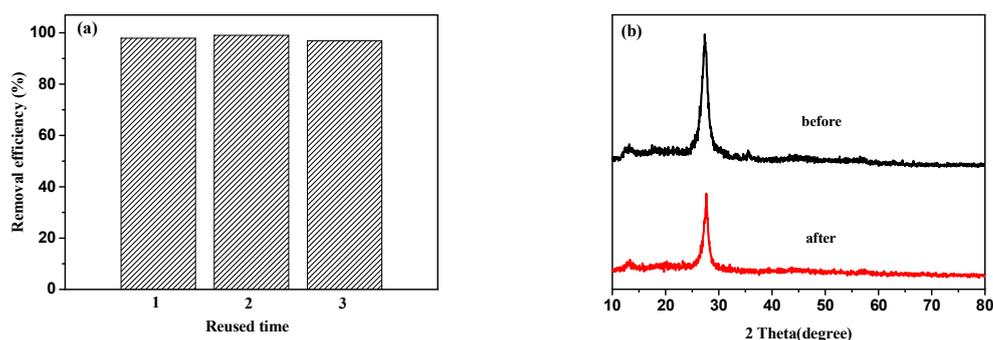
329 Influence of inorganic cations on the degradation of MB in the Fe-C₃N₄ heterogenous photo-Fenton
330 system was investigated under various concentrations from 0 to 30 mM. Inorganic cations including Al³⁺,
331 Mg²⁺, and Ca²⁺ exhibited an obviously inhibited effect on the degradation of MB, as shown in Fig. 5((d)-
332 (f)) and Table.S2. Among three kind of cations, the Al³⁺ ions showed a maximum negative effect on the
333 *k* values of MB degradation rate and the *k* value decreased from 0.0303 to 0.0105 min⁻¹ with increasing
334 concentration of Al³⁺ from 5 to 30 mM. Compared with the Mg²⁺ and Ca²⁺, the *k* value decreased 2.88
335 times with 30 mM Al³⁺ addition. This result could be explained by that Al³⁺, Mg²⁺ and Ca²⁺ were absorbed
336 onto Fe-C₃N₄ surface. At the same time, the accompanying shielding effect, reduction of active sites and

337 the penetration of light irradiation caused the low photocatalytic efficiency^{38, 40-43}.



346 3.5 Stability of Fe-C₃N₄ catalyst

347 With reference to the practical application of Fe-C₃N₄ heterogeneous photo-Fenton-like system, the
348 stability of the catalyst was examined. As the result shown in Fig. 6(a), MB degradation efficiency was
349 still more than 90% within 90 min after three cycles. The residual amount of iron ion in the solution after
350 the reaction was measured by an atomic absorption spectrophotometer (AA-700, Shimadzu International
351 Trading Co., Ltd.) and the concentration of iron ion was 0.4781 mg·L⁻¹. The concentration of leaching
352 Fe content was lower than the limitation in drinking-water in EU and US (< 2 ppm)^{32, 44, 45}. In addition,
353 the XRD result of the used catalyst as shown in Fig. 6(b) and the XRD patterns of Fe-C₃N₄ had no
354 obviously change. These results demonstrated that Fe-C₃N₄ has a good reusability and stability.



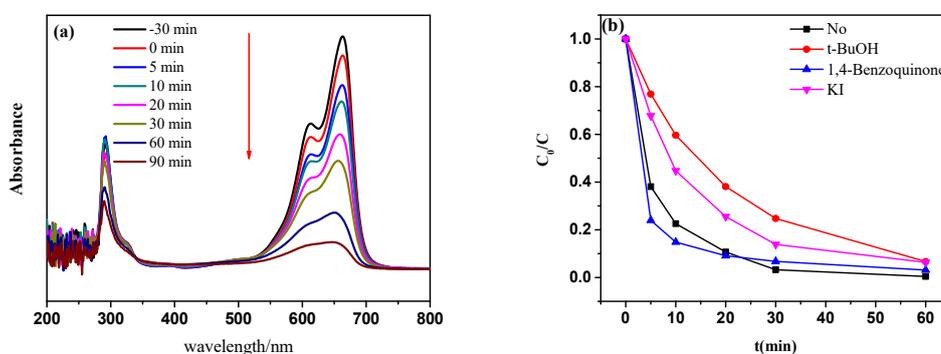
355
 356 **Fig. 6.** The degradation efficiency of MB under recycling experiment **(a)** and XRD survey of Fe-C₃N₄
 357 before and after decolorization of MB in the Fe-C₃N₄ heterogenous photo-Fenton-like system **(b)**.
 358 Experimental condition: For **(a)** and **(b)**, [MB] = 20 mg·L⁻¹, [5 wt% Fe-C₃N₄] = 2 g·L⁻¹, [H₂O₂] = 200
 359 mM, pH = 3.

360

361 **3.6 Degradation mechanism of Fe-C₃N₄ heterogeneous photo-Fenton-like system**

362 It was considered that MB molecule was broken and degraded into smaller molecules in the Fe-
 363 C₃N₄ heterogenous photo-Fenton-like system. To demonstrate this hypothesis, the UV-vis adsorption
 364 spectra was conducted as shown in Fig. 7(a). The result showed the absorption spectral variation of MB
 365 with irradiation time. Two main absorbance peaks were observed at 665 and 290 nm, respectively. The
 366 peak at 665 nm was attributed to the chromophore (-C=S) of MB and the peak at 290 nm was attributed
 367 to the unsaturated conjugate aromatic rings^{24, 46, 47}. It was obvious that the adsorption peaks at 665 and
 368 290 nm decreased significantly with irradiation time, suggesting that the conjugate structure of MB was
 369 destroyed and the aromatic rings of MB was degraded in the system. Besides, with the reaction time
 370 increasing, the position of maximum absorbance peak at 665 nm without shift. Related research showed
 371 that the peak at 665 nm of MB blue shifted was related to occurring of N-demethylation intermediates of
 372 MB²⁴. Thus, we inferred that the initial step of MB degradation in the Fe-C₃N₄ heterogeneous photo-
 373 Fenton system may not involve N-demethylation. To investigated the reactive species of MB degradation
 374 in the system, quenching experiments by TBA, KI and 1,4-benzoquinone were conducted⁴⁸. In this
 375 section, 2 mM TBA, 2 mM p-benzoquinone and 2 mM KI were used as the quenchers of ·OH, ·O₂⁻ and
 376 h⁺, respectively. As shown in Fig. 7(b), at first 30 min, the MB degradation efficiency decreased from
 377 96.7% to 93.2%, 86.1%, and 75.3% after adding 1,4-benzoquinone, KI, and TBA, respectively. It was
 378 found that 1,4-benzoquinone had little effect on MB removal in this system and TBA showed

379 significantly inhibited effect on MB degradation. The result implied the fact that $\bullet\text{OH}$ was a major active
 380 species in the system. When 1,4-benzoquinone was added in the reaction system, the degradation
 381 efficiency of MB was affected but without decreasing within 30 min, and was nearly similar to the
 382 performance of control experiment. This result demonstrated that $\text{O}_2^{\cdot-}$ rarely or not formed during this
 383 reaction system. However, the MB degradation efficiency has an enhancement when 1,4-benzoquinone
 384 was added into catalytic system at the first 20 min. This phenomenon may be due to the activation of
 385 H_2O_2 by 1,4-benzoquinone. Several literatures have reported that peroxydisulfate and H_2O_2 can be
 386 activated by organic quinones. For instance, Zhou et al found that peroxymonosulfate could be activated
 387 by benzoquinone⁴⁹. Fang et al reported that 1,4-benzoquinone, 2-methyl-1,4-benzoquinone or 2-chloro-
 388 1,4-benzoquinone could enhance the degraded efficiency of 2,4,4'-trichlorobiphenyl by peroxydisulfate
 389⁵⁰. Zhu et al reported that halogenated quinones could activate H_2O_2 to produce $\bullet\text{OH}$ ⁵¹. Besides, Chen et
 390 al investigated the degradation of tetracycline by H_2O_2 alone, and similar phenomenon was found that
 391 the tetracycline degradation efficiency has an enhancement when benzoquinone was added into catalytic
 392 system at the first 45 min⁵².



393
 394 **Fig. 7.** Temporal evolution of the UV-vis spectra during decolorization of MB in the $\text{Fe-C}_3\text{N}_4$
 395 heterogenous photo-Fenton-like system (a) and influences of radical scavengers on decolorization of MB
 396 (b). Experimental condition: For (a), $[\text{MB}] = 20 \text{ mg}\cdot\text{L}^{-1}$, $[5 \text{ wt}\% \text{ Fe-C}_3\text{N}_4] = 0.5 \text{ g}\cdot\text{L}^{-1}$, $[\text{H}_2\text{O}_2] = 50 \text{ mM}$,
 397 $\text{pH} = 3$. For (b), $[\text{MB}] = 20 \text{ mg}\cdot\text{L}^{-1}$, $[5 \text{ wt}\% \text{ Fe-C}_3\text{N}_4] = 2 \text{ g}\cdot\text{L}^{-1}$, $[\text{H}_2\text{O}_2] = 200 \text{ mM}$, $[\text{t-BuOH}] = 2 \text{ mM}$,
 398 $[1,4\text{-Benzoquinone}] = 2 \text{ mM}$, $[\text{KI}] = 2 \text{ mM}$, $\text{pH} = 3$.

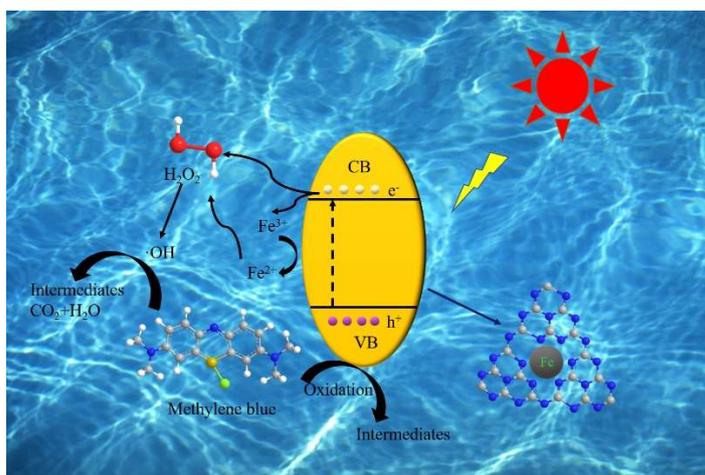
399

400 For degradation pathway analysis, the intermediate products resulting from MB degradation at 60
 401 min were analyzed by LC-MS. According to the results, nine main intermediate product ions at m/z

402 305.16, m/z 301.17, m/z 143.09, m/z 135.12, m/z 130.16, m/z 109.10, m/z 95.09, m/z 93.04 and m/z
403 75.03 were detected at different retention time, which probably corresponded to $C_{16}H_{23}N_3SO$,
404 $C_{16}H_{19}N_3SO$, $C_6H_6O_4$, C_7H_5NS , $C_6H_{13}NO_2$, C_6H_7NO , C_6H_6O , C_6H_7N and $C_2H_2O_3$, respectively (Table.
405 S3). It was confirmed that the benzene ring of MB could be hydroxylated by $\cdot OH$ in the previous work
406 24, 53, 54. However, we did not observe corresponding intense fragments in this study. Thus, the $\cdot OH$ may
407 played a role in aromatic ring opening and oxidation. Meanwhile, based on intermediates from previous
408 work 55-62, the possible pathway of MB degradation by Fe- C_3N_4 heterogenous photo-Fenton-like system
409 was proposed in Fig. S3. The Cl in the MB molecule was firstly ionized, after that $C-N^+=C$ and $C-S^+-C$
410 were destroyed. Then, $-N=(CH_3)_2$ groups were also degraded and induced the breakup of the aromatic
411 rings. In the process, produced intermediates such as DL-Norleucine, phenol and Benzothiadiazole,
412 which partly were further mineralized to carbon dioxide, water and inorganic anions (SO_4^{2-} , NH_4^+ and
413 NO_3^-).

414 The XPS results showed the Fe(III)-N was the main active sites for the photo-Fenton-like reaction.
415 By combining XPS results and previous works 32, 63, 64, we proposed a possible mechanism of this
416 catalytic system(Fig.8). There were two pathways to generate $\cdot OH$ (Eqs.(11)-(13)). (1) Fe- C_3N_4 was
417 excited to generate electrons and holes under simulated sunlight. The Fe(III)-N accepted electrons
418 transformed to Fe(II)-N. The Fe(II)-N and H_2O_2 combined to generated Fe(III)-N and $\cdot OH$ by electron
419 transfer. At the same time, a series of chain reactions were initiated, including the formation of redox
420 cycles of $\cdot OH$ and Fe(III)/Fe(II). (2) H_2O_2 decomposed to $\cdot OH$ under simulated sunlight. Theoretically,
421 the VB of g- C_3N_4 was +1.57 V and the redox potentials of $\cdot OH / OH^-$ was +1.99 V. Thus, $\cdot OH$ cannot
422 generated from VB holes in the g- C_3N_4 . In the Fe- C_3N_4 heterogenous photo-Fenton-like system, MB was
423 absorbed in the surface of Fe- C_3N_4 firstly. Then, MB attacked by $\cdot OH$ and transformed to small molecule

424 organics, inorganic ions, CO₂ and H₂O.



428

429 **Fig.8.** Schematic diagram of Fe-C₃N₄ catalyzed heterogeneous photo-Fenton-like reaction.

430

431 4. Conclusions

432 In this study, Fe-C₃N₄ was fabricated and applied in the heterogeneous photo-Fenton-like system.

433 Fe-C₃N₄ exhibited superb performance for degradation of MB in the pH range of 3-9. The effect of

434 various inorganic ions on the degradation of MB was studied where Cl⁻ and NO₃⁻ inhibited the

435 degradation of MB, HCO₃⁻ exhibited a dual effect. The presence of cations (Al³⁺, Mg²⁺, Ca²⁺) inhibits

436 the degradation of MB, and the order of the inhibitory effect was: Al³⁺ > Ca²⁺ > Mg²⁺. The catalyst cycle

437 experiment illustrated that Fe-C₃N₄ was highly stable with consistently high degradation of MB.

438 According to the quenching experiment, dominated activated species was •OH. In short, this photo

439 assisted heterogeneous Fenton-like process had a highly efficient removal of MB while overcame the

440 common questions in conventional Fenton system.

441 Conflicts of interest

442 There are no conflicts to declare.

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