



The utilization of Fe-doped g-C₃N₄ in a heterogeneous photo-Fenton-like catalytic system: the effect of different parameters and a system mechanism investigation

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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**

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Abstract

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

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

1. Introduction

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

and easy handling ¹⁻⁵. Among various AOPs, visible light-induced heterogeneous photo-Fenton-like process has been taken into account as an effective way for pollutants treatment. Compared with the traditional Fenton and photo-Fenton process in homogeneous system, it showed many advantages, such as efficient mineralization of organic pollutants, lower cost, reuse, good chemical stability and small amounts of iron precipitation ⁶. However, the rigorous pH range (acidic or near-neutral conditions), high iron leaching (>2 ppm), fewer iron active sites and low efficiency cycling of $\text{Fe}^{3+}/\text{Fe}^{2+}$ limited the application of this process ⁷. Therefore, exploring a highly efficient and low-cost catalyst for this system is essential.

Polymeric graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) as a visible-light-driven photocatalyst has been applied worldwide in water splitting, organic degradation, and conversion of CO_2 ⁸⁻¹⁰. However, the rapid charge recombination has limited its application in AOPs^{11, 12}. To overcome this drawback, the external element doped and copolymerized are taken into account and proved to be applicable ¹³⁻¹⁶. Fe is an environmentally friendly and abundant element in the earth. It has been extensively investigated to improve the photocatalytic performance of $\text{g-C}_3\text{N}_4$ by element doping way. Meanwhile, it was certified in previous studies that the photocatalytic activity of $\text{g-C}_3\text{N}_4$ towards dye degradation can be remarkably improved by Fe doping and Fe existed in $\text{Fe-C}_3\text{N}_4$ by Fe-N ligand ¹⁷⁻²⁰. Besides, the photo-induced electrons from $\text{Fe-C}_3\text{N}_4$ can reduce Fe^{3+} to Fe^{2+} under visible light illumination ²¹. Thence, $\text{Fe-C}_3\text{N}_4$ can work as an efficient catalyst in the heterogeneous photo-Fenton-like system. It has been already reported that the $\text{Fe-C}_3\text{N}_4$ is an efficient catalyst for removal of organic pollutants in photo-Fenton system. Previous studies have focused on the preparation and optimization of $\text{Fe-C}_3\text{N}_4$ or coupled $\text{Fe-C}_3\text{N}_4$ material. The influence of reaction parameters especial for various inorganic ions in natural water on activity and the degradation pathway of specific contaminant (MB) in $\text{Fe-C}_3\text{N}_4$ based photo-Fenton

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

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

2. Experimental

2.1 Materials

The chemicals were of commercially available analytical grade used as purchased without further purification. Melamine, ferric nitrate (Fe(NO₃)₃·9H₂O), Hydrogen Peroxide (H₂O₂, 30%, w/w), sodium hydroxide (NaOH), hydrochloric acid (HCl), tertiary butanol (TBA), p-benzoquinone, sodium chloride (NaCl), sodium bicarbonate (NaHCO₃), sodium nitrate (NaNO₃), calcium chloride (CaCl₂, P96.0%), magnesium chloride (MgCl₂, P98.0%), aluminum chloride (AlCl₃, P97.0%), Potassium iodide (KI), and methylene blue (MB) were supplied by Nanning Lantian Experiment Equipment Co., Ltd (Nanning, China).

2.2 Synthesis of Fe-C₃N₄

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

2.3 Characterization of catalyst

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

2.4 Experimental procedures

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

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

2.5 Analytical methods

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

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

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

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

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

referred to previous report ²⁴.

3. Results and discussion

3.1 Characterization of g-C₃N₄ and Fe-C₃N₄

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

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

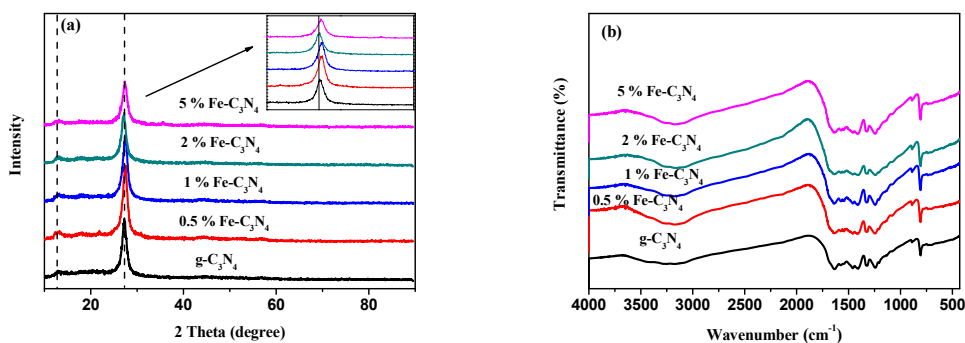


Fig.1. XRD patterns (a) and FT-IR spectra (b) of g-C₃N₄ and Fe-C₃N₄ samples.

To analyze the elemental composition and the surface states of x wt% Fe-C₃N₄, the XPS of 5 wt% Fe-C₃N₄ were investigated. As shown in Fig.2(a), four elements were present in the XPS survey spectra of 5% Fe-C₃N₄ including C, N, O and Fe. This result was the same as to the EDS analysis that Fe was successfully doped into the structure of 5 wt% Fe-C₃N₄ (Fig. S2). The signal of O was ascribed to O₂ or H₂O absorbed in the surface of 5 wt% Fe-C₃N₄²⁹. The signal of Fe was weak because of the low amount of Fe doping. The C 1s XPS spectra was deconvoluted into two peaks at binding energies of 283.7 and 287.3 eV, as shown in Fig.2(b). The peak at 283.7 eV was the characteristic peak of graphitic carbon 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 the N 1s XPS spectra was deconvoluted into three peaks at binding energies of 397.9, 399.1, and 400.4 eV, respectively. The main peak at 397.9 eV due to the sp²-bonded N atoms in the triazine rings. The 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 ascribed to the groups of -NH₂ or =NH³¹. From Fig. 2(d), the O 1s spectrum exhibits one characteristic peaks at 531.39 eV which was ascribed to surface adsorbed water in the Fe-C₃N₄. The Fe-O-Fe and Fe-OH were not found in the Fe-C₃N₄ due to the characteristic diffraction peak of Fe-O-Fe and Fe-OH at 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 Fig.2(e). The binding energy peak of Fe³⁺ at the range from 710.3 to 711.8 eV. Thus, the primary Fe state

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

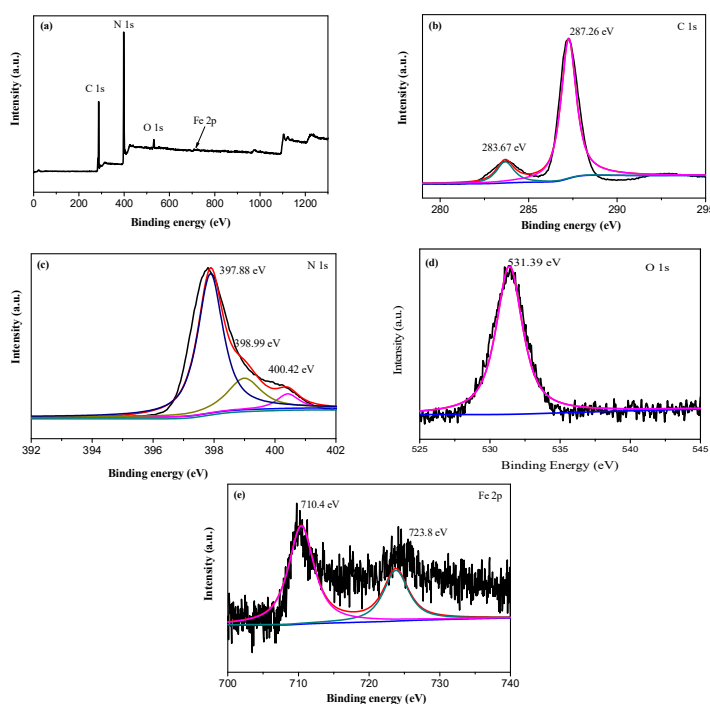


Fig.2. XPS spectra of 5 wt% Fe-C₃N₄ sample: (a) survey scan, (b) C 1s, (c) N 1s, (d) O 1s, and (e) Fe 2p.

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

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

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

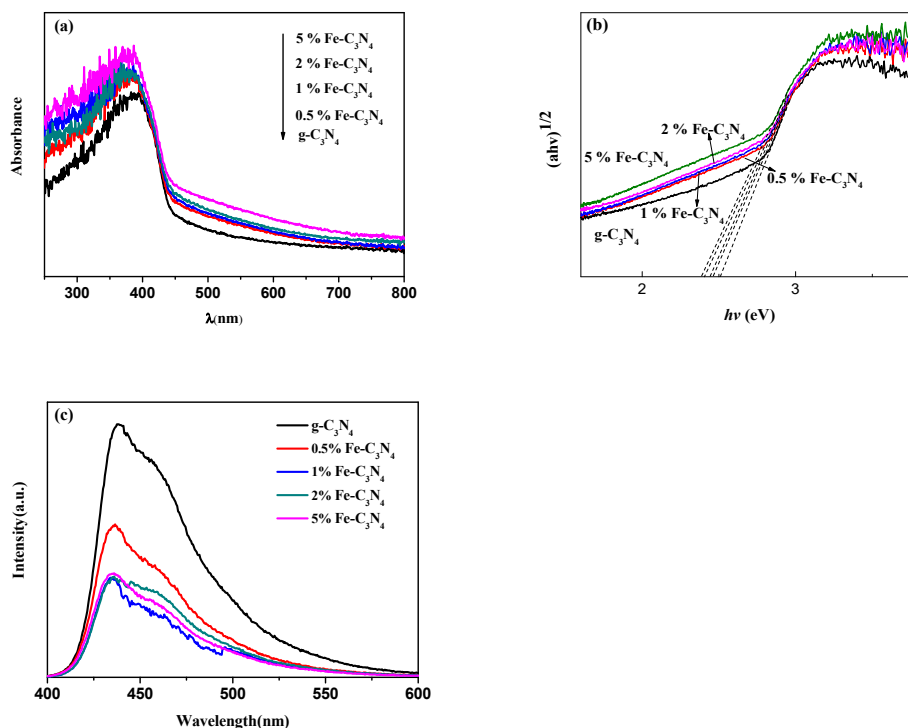
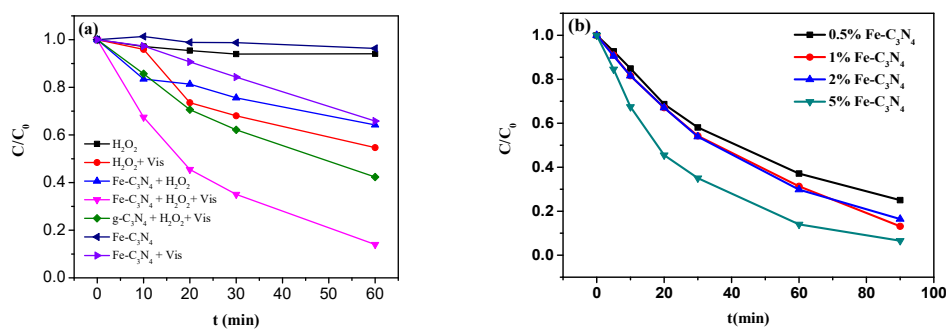


Fig.3. UV-vis diffuse reflectance spectra (a), the Tauc's plot (b), and photoluminescence emission spectra (c) of g-C₃N₄ and Fe-C₃N₄ samples.

3.2 Catalytic performance of Fe doped g-C₃N₄

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

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



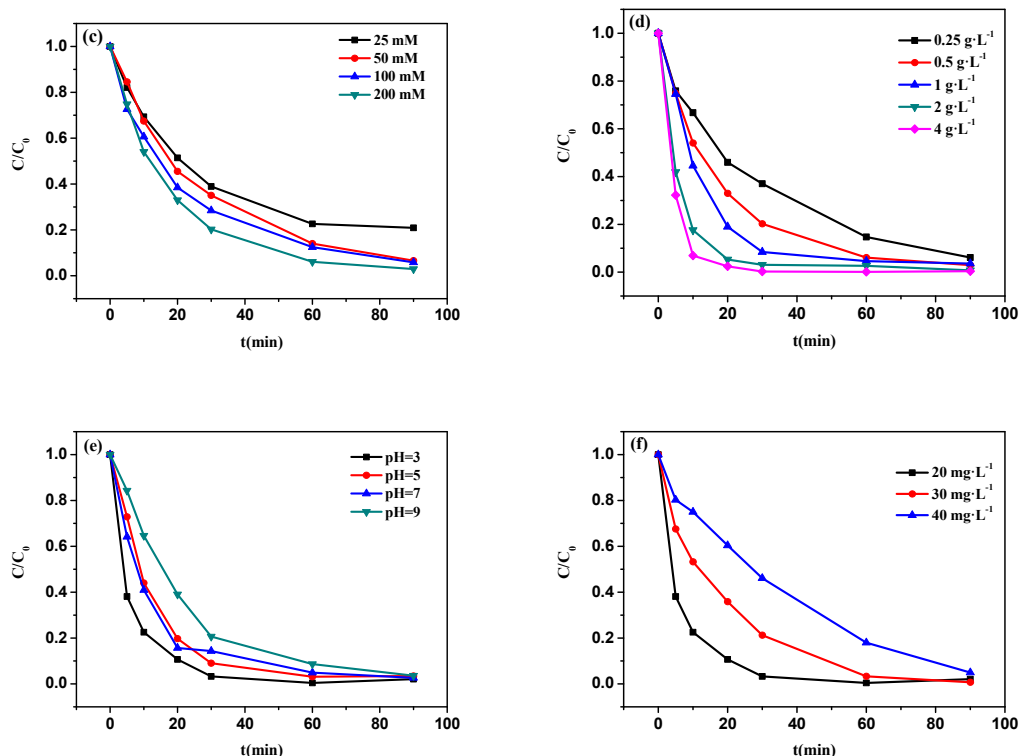


Fig. 4. Decolorization of MB under different system (a), effect of Fe doped amounts (b), effect of H₂O₂ concentration (c), effect of catalyst dosage (d), effect of pH (e), effect of MB initial concentration (f). Experimental condition: For (a), [MB] = 20 mg·L⁻¹, [5 wt% Fe-C₃N₄] = 0.5 g·L⁻¹, [H₂O₂] = 50 mM, pH = 6.86. For (b), [MB] = 20 mg·L⁻¹, [Fe-C₃N₄] = 0.5 g·L⁻¹, [H₂O₂] = 50 mM, pH = 6.86. For (c), [MB] = 20 mg·L⁻¹, [5 wt% Fe-C₃N₄] = 0.5 g·L⁻¹, pH = 6.86. For (d), [MB] = 20 mg·L⁻¹, [H₂O₂] = 200 mM, pH = 6.86. For (e), [MB] = 20 mg·L⁻¹, [5 wt% Fe-C₃N₄] = 2 g·L⁻¹, [H₂O₂] = 200 mM. For (f), [5 wt% Fe-C₃N₄] = 2 g·L⁻¹, [H₂O₂] = 200 mM, pH = 3.

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

The effect of Fe doping amounts on the MB degradation were investigated in the range of 0.5-5 wt% and the result was shown in Fig.4(b). From the result, Fe doping amounts had an obviously promoted effect on the degradation of MB. With the increase of Fe doping amounts from 0.5 wt% to 5 wt%, the degradation efficiency of MB increased from 75% to 95%. This result demonstrated that the Fe doping amounts played a major role in degradation of MB and the Fe-N bond in the catalyst can activate the

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

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

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

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

Fenton-like system was investigated. As shown in Fig. 4(e), the catalyst remains highly active towards MB degradation over an initial broad pH range from 3 to 9. When pH increased from 3 to 9, the efficiency of MB degradation decreased slightly. Interestingly, at first 30 min, the heterogeneous photo-Fenton-like system degradation efficiency at pH=3, 5, 7 and 9 was 97%, 91%, 85% and 79%, respectively. This phenomenon was attributed to different Fe-N ligands formed in the system. At acidic condition, the produced Fe-N ligands was more conducive to activate H_2O_2 compared to the ligands formed under alkaline conditions. Besides, the H_2O_2 can be consumed and decomposed to H_2O and O_2 under alkaline conditions. In general, at 90 min, all the decolorization ratio of MB with pH rising from 3 to 9 was more than 90%. Hence, Fe- C_3N_4 heterogeneous photo-Fenton-like system showed a wide pH range compared to the conventional Fenton system.

The effect of initial MB concentration on the degradation was examined in the range of 20 to 40 $\text{mg}\cdot\text{L}^{-1}$. As shown in Fig. 4(f), the degradation efficiency of MB within 90 min reached to almost 100% with increasing MB concentration from 20 to 40 $\text{mg}\cdot\text{L}^{-1}$. However, at first 30 min, the degradation efficiency decreased from 96.7% to 53.9% with the increase of MB concentration from 20 to 40 $\text{mg}\cdot\text{L}^{-1}$. This result was attributed to the amounts of the active species. With the increase of initial MB concentration, the more active species were required for the degradation of MB. However, the active species in the system were theoretically constant at the fixed Fe- C_3N_4 dosage, H_2O_2 concentration and light intensity. Thus, the active species were inadequate for higher MB concentration.

3.4 Effect of inorganic ions on the degradation of MB

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

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

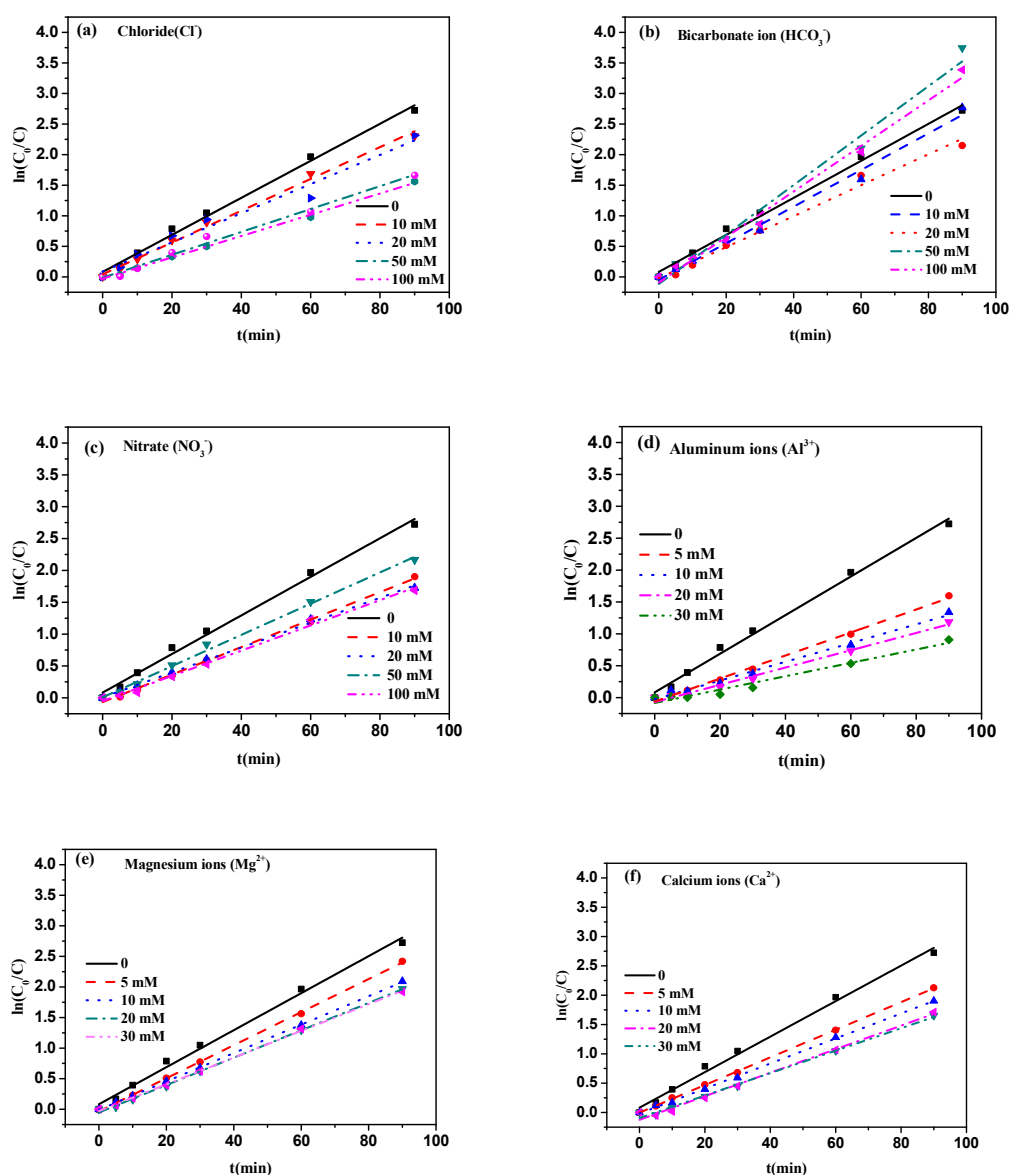


Fig. 5. Effect of inorganic anions and cations on MB degradation under simulated solar light irradiation (a-e). Experimental condition : $[\text{MB}] = 20 \text{ mg}\cdot\text{L}^{-1}$, $[5 \text{ wt\% Fe-C}_3\text{N}_4] = 0.5 \text{ g}\cdot\text{L}^{-1}$, no pH adjustment and

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 $[\text{Ca}^{2+}] = 5, 10, 20, 30 \text{ mM}$.

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

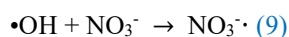
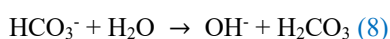
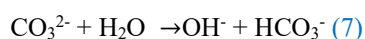
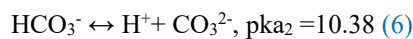
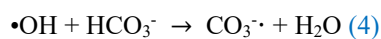
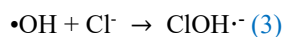
Fig.5(b) showed that the effect of HCO_3^- on MB degradation in the Fe- C_3N_4 heterogenous photo-Fenton-like system. With the increase of HCO_3^- concentrations from 0 to 20 mM, the k values of MB degradation rate decreased from 0.0303 to 0.0299 min^{-1} (Table S1). However, the k values improved with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

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

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

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

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



3.5 Stability of Fe-C₃N₄ catalyst

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

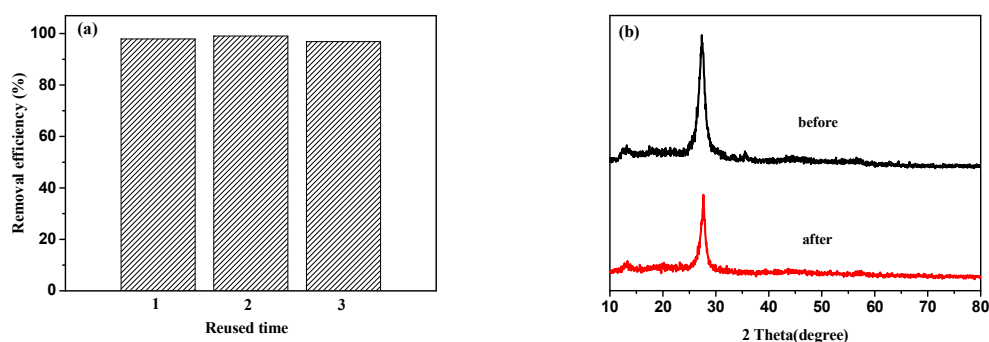


Fig. 6. The degradation efficiency of MB under recycling experiment **(a)** and XRD survey of Fe-C₃N₄ before and after decolorization of MB in the Fe-C₃N₄ heterogenous photo-Fenton-like system **(b)**. Experimental condition: For **(a)** and **(b)**, [MB] = 20 mg·L⁻¹, [5 wt% Fe-C₃N₄] = 2 g·L⁻¹, [H₂O₂]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

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

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

significantly inhibited effect on MB degradation. The result implied the fact that $\bullet\text{OH}$ was a major active species in the system. When 1,4-benzoquinone was added in the reaction system, the degradation efficiency of MB was affected but without decreasing within 30 min, and was nearly similar to the performance of control experiment. This result demonstrated that $\text{O}_2^{\cdot-}$ rarely or not formed during this reaction system. However, the MB degradation efficiency has an enhancement when 1,4-benzoquinone was added into catalytic system at the first 20 min. This phenomenon may be due to the activation of H_2O_2 by 1,4-benzoquinone. Several literatures have reported that peroxydisulfate and H_2O_2 can be activated by organic quinones. For instance, Zhou et al found that peroxymonosulfate could be activated by benzoquinone⁴⁹. Fang et al reported that 1,4-benzoquinone, 2-methyl-1,4-benzoquinone or 2-chloro-1,4-benzoquinone could enhance the degraded efficiency of 2,4,4'-trichlorobiphenyl by peroxydisulfate⁵⁰. Zhu et al reported that halogenated quinones could activate H_2O_2 to produce $\bullet\text{OH}$ ⁵¹. Besides, Chen et al investigated the degradation of tetracycline by H_2O_2 alone, and similar phenomenon was found that the tetracycline degradation efficiency has an enhancement when benzoquinone was added into catalytic system at the first 45 min⁵².

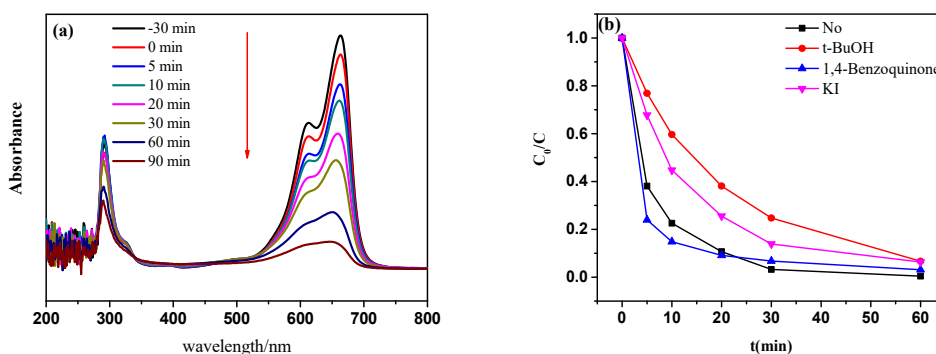


Fig. 7. Temporal evolution of the UV-vis spectra during decolorization of MB in the $\text{Fe-C}_3\text{N}_4$ heterogenous photo-Fenton-like system (a) and influences of radical scavengers on decolorization of MB (b). Experimental condition: For (a), $[\text{MB}] = 20 \text{ mg}\cdot\text{L}^{-1}$, $[5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

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

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

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

organics, inorganic ions, CO₂ and H₂O.

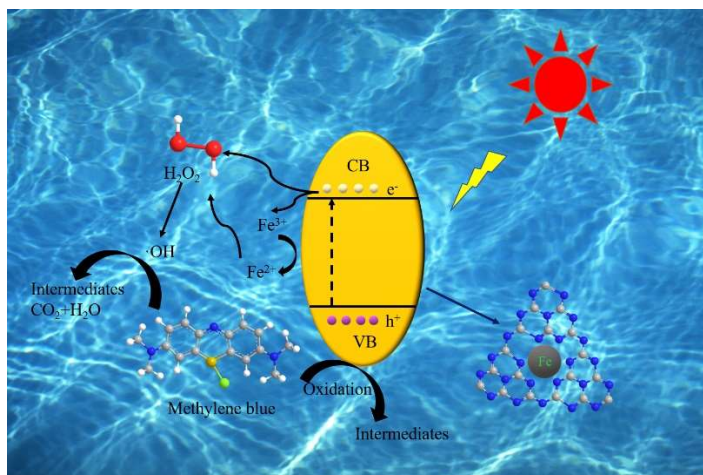
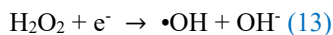
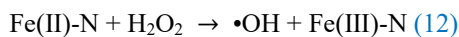
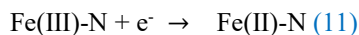


Fig.8. Schematic diagram of Fe-C₃N₄ catalyzed heterogeneous photo-Fenton-like reaction.

4. Conclusions

In this study, Fe-C₃N₄ was fabricated and applied in the heterogeneous photo-Fenton-like system. Fe-C₃N₄ exhibited superb performance for degradation of MB in the pH range of 3-9. The effect of various inorganic ions on the degradation of MB was studied where Cl⁻ and NO₃⁻ inhibited the degradation of MB, HCO₃⁻ exhibited a dual effect. The presence of cations (Al³⁺, Mg²⁺, Ca²⁺) inhibits the degradation of MB, and the order of the inhibitory effect was: Al³⁺ > Ca²⁺ > Mg²⁺. The catalyst cycle experiment illustrated that Fe-C₃N₄ was highly stable with consistently high degradation of MB. According to the quenching experiment, dominated activated species was •OH. In short, this photo assisted heterogeneous Fenton-like process had a highly efficient removal of MB while overcame the common questions in conventional Fenton system.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1. D. B. Miklos, C. Remy, M. Jekel, K. G. Linden, J. E. Drewes and U. Hübner, *Water Research*, 2018, **139**, 118-131.
2. T. Guo, K. Wang, G. Zhang and X. Wu, *Applied Surface Science*, 2019, **469**, 331-339.
3. Z. Xiong, Z. Wang, M. Muthu and Y. Zhang, *Journal of Hazardous Materials*, 2019, **373**, 565-571.
4. S. Yang, P. Wu, J. Liu, M. Chen, Z. Ahmed and N. Zhu, *Chemical Engineering Journal*, 2018, **350**, 484-495.
5. J. Liu, P. Wu, S. Yang, S. Rehman, Z. Ahmed, N. Zhu, Z. Dang and Z. Liu, *Applied Catalysis B: Environmental*, 2020, **261**, 118232.
6. C. Cai, Z. Zhang, J. Liu, N. Shan, H. Zhang and D. D. Dionysiou, *Appl. Catal. B-Environ.*, 2016, **182**, 456-468.
7. X. Y. Li, Y. H. Pi, L. Q. Wu, Q. B. Xia, J. L. Wu, Z. Li and J. Xiao, *Appl. Catal. B-Environ.*, 2017, **202**, 653-663.
8. J. Fu, J. Yu, C. Jiang and B. Cheng, *Advanced Energy Materials*, 2018, **8**, 1701503.
9. Z. Sun, H. Wang, Z. Wu and L. Wang, *Catalysis Today*, 2018, **300**, 160-172.
10. X. Zhang, X. Zhang, J. Li, J. Sun, J. Bian, J. Wang, Y. Qu, R. Yan, C. Qin and L. Jing, *Applied Catalysis B: Environmental*, 2018, **237**, 50-58.
11. A. Nikokavoura and C. Trapalis, *Applied Surface Science*, 2018, **430**, 18-52.
12. Y. Yu, W. Yan, X. Wang, P. Li, W. Gao, H. Zou, S. Wu and K. Ding, *Adv. Mater.*, 2018, **30**, 1705060.
13. X. Ma, Y. Lv, J. Xu, Y. Liu, R. Zhang and Y. Zhu, *The Journal of Physical Chemistry C*, 2012, **116**, 23485-23493.
14. J. Jiang, S. Cao, C. Hu and C. Chen, *Chinese Journal of Catalysis*, 2017, **38**, 1981-1989.
15. W. Yan, L. Yan and C. Jing, *Applied Catalysis B: Environmental*, 2019, **244**, 475-485.
16. Y. Wang, S. Zhao, Y. Zhang, W. Chen, S. Yuan, Y. Zhou and Z. Huang, *Applied Surface Science*, 2019, **463**, 1-8.
17. S. Hu, L. Ma, J. You, F. Li, Z. Fan, G. Lu, D. Liu and J. Gui, *Applied Surface Science*, 2014, **311**, 164-171.
18. Q. Liu, T. Chen, Y. Guo, Z. Zhang and X. Fang, *Applied Catalysis B: Environmental*, 2017, **205**, 173-181.

- 479 19. J. Gao, Y. Wang, S. Zhou, W. Lin and Y. Kong, *ChemCatChem*, 2017, **9**, 1708-1715.
- 480 20. W.-D. Oh, V. W. C. Chang, Z.-T. Hu, R. Goei and T.-T. Lim, *Chemical Engineering Journal*,
481 2017, **323**, 260-269.
- 482 21. X. Chen, J. Zhang, X. Fu, M. Antonietti and X. Wang, *Journal of the American Chemical*
483 *Society*, 2009, **131**, 11658-11659.
- 484 22. X. Song, H. Tao, L. Chen and Y. Sun, *Materials Letters*, 2014, **116**, 265-267.
- 485 23. S. Hu, R. Jin, G. Lu, D. Liu and J. Gui, *Rsc Advances*, 2014, **4**, 24863-24869.
- 486 24. Y. Liu, W. Jin, Y. Zhao, G. Zhang and W. Zhang, *Applied Catalysis B: Environmental*, 2017,
487 **206**, 642-652.
- 488 25. S. Yan, Z. Li and Z. Zou, *Langmuir*, 2009, **25**, 10397-10401.
- 489 26. H. Li, C. Shan and B. Pan, *Environmental Science & Technology*, 2018, **52**, 2197-2205.
- 490 27. K. Wang, Q. Li, B. Liu, B. Cheng, W. Ho and J. Yu, *Applied Catalysis B: Environmental*,
491 2015, **176-177**, 44-52.
- 492 28. Y. Cui, Z. Ding, P. Liu, M. Antonietti, X. Fu and X. Wang, *Phys. Chem. Chem. Phys.*, 2012,
493 **14**, 1455-1462.
- 494 29. S. Hu, X. Chen, Q. Li, F. Li, Z. Fan, H. Wang, Y. Wang, B. Zheng and G. Wu, *Applied*
495 *Catalysis B: Environmental*, 2017, **201**, 58-69.
- 496 30. X. Du, X. Yi, P. Wang, J. Deng and C.-c. Wang, *Chinese Journal of Catalysis*, 2019, **40**, 70-
497 79.
- 498 31. A. Mirzaei, Z. Chen, F. Haghighat and L. Yerushalmi, *Applied Catalysis B: Environmental*,
499 2019, **242**, 337-348.
- 500 32. J. Ma, Q. Yang, Y. Wen and W. Liu, *Applied catalysis B: environmental*, 2017, **201**, 232-240.
- 501 33. M. Chen, P. Wu, L. Yu, S. Liu, B. Ruan, H. Hu, N. Zhu and Z. Lin, *Journal of environmental*
502 *management*, 2017, **192**, 31-38.
- 503 34. X. Wang, X. Chen, A. Thomas, X. Fu and M. Antonietti, *Adv. Mater.*, 2009, **21**, 1609-1612.
- 504 35. W.-J. Ong, L.-L. Tan, Y. H. Ng, S.-T. Yong and S.-P. Chai, *Chemical reviews*, 2016, **116**, 7159-
505 7329.
- 506 36. C. Guillard, H. Lachheb, A. Houas, M. Ksibi, E. Elaloui and J.-M. Herrmann, *Journal of*
507 *Photochemistry and Photobiology A: Chemistry*, 2003, **158**, 27-36.
- 508 37. A.-G. Rincón and C. Pulgarin, *Applied Catalysis B: Environmental*, 2004, **51**, 283-302.
- 509 38. I. K. Konstantinou and T. A. Albanis, *Applied Catalysis B: Environmental*, 2004, **49**, 1-14.
- 510 39. C. Hu, J. C. Yu, Z. Hao and P. K. Wong, *Applied Catalysis B: Environmental*, 2003, **46**, 35-47.
- 511 40. X. Gao, X. Zhang, Y. Wang, S. Peng, B. Yue and C. Fan, *Chemical Engineering Journal*,
512 2015, **273**, 156-165.
- 513 41. S. Liu, P. Wu, M. Chen, L. Yu, C. Kang, N. Zhu and Z. Dang, *Environmental Pollution*, 2017,
514 **228**, 277-286.
- 515 42. C. Liu, P. Wu, Y. Zhu and L. Tran, *Chemosphere*, 2016, **144**, 1026-1032.
- 516 43. L. Chen, P. Wu, M. Chen, X. Lai, Z. Ahmed, N. Zhu, Z. Dang, Y. Bi and T. Liu, *Applied Clay*
517 *Science*, 2018, **159**, 74-82.
- 518 44. X.-j. Yang, X.-m. Xu, J. Xu and Y.-f. Han, *Journal of the American Chemical Society*, 2013,
519 **135**, 16058-16061.
- 520 45. X. Li, X. Liu, L. Xu, Y. Wen, J. Ma and Z. Wu, *Applied Catalysis B: Environmental*, 2015,
521 **165**, 79-86.
- 522 46. Y. Li and F.-S. Zhang, *Chemical Engineering Journal*, 2010, **158**, 148-153.

- 523 47. B. Zhou, X. Zhao, H. Liu, J. Qu and C. P. Huang, *Applied Catalysis B: Environmental*, 2010,
524 **99**, 214-221.
- 525 48. J. Wang, Y. Xia, H. Zhao, G. Wang, L. Xiang, J. Xu and S. Komarneni, *Applied Catalysis B:*
526 *Environmental*, 2017, **206**, 406-416.
- 527 49. Y. Zhou, J. Jiang, Y. Gao, J. Ma, S.-Y. Pang, J. Li, X.-T. Lu and L.-P. Yuan, *Environmental*
528 *science & technology*, 2015, **49**, 12941-12950.
- 529 50. G. Fang, J. Gao, D. D. Dionysiou, C. Liu and D. Zhou, *Environmental science & technology*,
530 2013, **47**, 4605-4611.
- 531 51. B.-Z. Zhu, H.-T. Zhao, B. Kalyanaraman and B. Frei, *Free Radical Biology and Medicine*,
532 2002, **32**, 465-473.
- 533 52. Y.-Y. Chen, Y.-L. Ma, J. Yang, L.-Q. Wang, J.-M. Lv and C.-J. Ren, *Chemical Engineering*
534 *Journal*, 2017, **307**, 15-23.
- 535 53. L. C. A. Oliveira, M. Gonçalves, M. C. Guerreiro, T. C. Ramalho, J. D. Fabris, M. C. Pereira
536 and K. Sapag, *Applied Catalysis A: General*, 2007, **316**, 117-124.
- 537 54. H. A. Bicalho, J. L. Lopez, I. Binatti, P. F. R. Batista, J. D. Ardisson, R. R. Resende and E.
538 Lorençon, *Molecular Catalysis*, 2017, **435**, 156-165.
- 539 55. S. Xia, L. Zhang, G. Pan, P. Qian and Z. Ni, *Phys. Chem. Chem. Phys.*, 2015, **17**, 5345-5351.
- 540 56. M. A. Rauf, M. A. Meetani, A. Khaleel and A. Ahmed, *Chemical Engineering Journal*, 2010,
541 **157**, 373-378.
- 542 57. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard and J.-M. Herrmann, *Applied*
543 *Catalysis B: Environmental*, 2001, **31**, 145-157.
- 544 58. H. Huang, D. Y. C. Leung, P. C. W. Kwong, J. Xiong and L. Zhang, *Catalysis Today*, 2013,
545 **201**, 189-194.
- 546 59. A. Xu, X. Li, H. Xiong and G. Yin, *Chemosphere*, 2011, **82**, 1190-1195.
- 547 60. P. V. Bakre, P. S. Volvoikar, A. A. Vernekar and S. G. Tilve, *Journal of Colloid and Interface*
548 *Science*, 2016, **474**, 58-67.
- 549 61. K. Yu, S. Yang, C. Liu, H. Chen, H. Li, C. Sun and S. A. Boyd, *Environmental Science &*
550 *Technology*, 2012, **46**, 7318-7326.
- 551 62. Q. Wang, S. L. Tian and P. Ning, *Industrial & Engineering Chemistry Research*, 2014, **53**,
552 643-649.
- 553 63. J. Hu, P. Zhang, W. An, L. Liu, Y. Liang and W. Cui, *Applied Catalysis B: Environmental*,
554 2019, **245**, 130-142.
- 555 64. X. Qian, Y. Wu, M. Kan, M. Fang, D. Yue, J. Zeng and Y. Zhao, *Applied Catalysis B:*
556 *Environmental*, 2018, **237**, 513-520.
- 557