Photocatalysis-self-Fenton system with high-fluent degradation and high mineralization ability

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ABSTRACT

Fenton technology has been seriously restricted by the external addition of H2O2 and low mineralization efficiency for organic pollutants. Herein, a photocatalysis-self-Fenton system was constructed to achieve high-fluent degradation and high mineralization performance, based on in-situ generated H2O2 over graphitic carbon nitride (g-C3N4) under visible-light irradiation. The degradation activity for 2,4-dichlorophenol (2,4-DCP) was enhanced by 20.5 and 3.7 times, compared to bulk-g-C3N4 photocatalysis and Fenton technology, respectively. Meanwhile, the corresponding mineralization degree was 22.5 and 3.8 times higher, respectively. The high-fluent degradation and high mineralization ability were ascribed to the highly efficient utilization of H2O2 via in-situ generation and consumption, which sustainably produced abundant `OH radicals. Briefly, the photocatalysis-self-Fenton system proposed here provides new insight into effectively and environmentally friendly removing the organic containment.

1. Introduction

Nowadays, environmental pollution originated from organic pollutants have attracted increasing attention from the public, on account of their toxic and degradation-resistant properties [1–4]. Fenton technology, as an advanced oxidation processes (AOPs), has attracted increasing attention in the field of environmental protection and pollution remediation. Since 'OH radical, originated from Fenton technology, could degrade and even mineralize organic pollutant without selectivity owning to its extra high oxidizing ability [5–7]. However, Fenton technology requires external addition of H2O2 and always exhibits low mineralization for organic pollutant, seriously retarding its extensive application. Noteworthily, in-situ generation and utilization of H2O2 could considerably reduce the risk and cost for H2O2 synthesis, transport and storage. Therefore, exploring Fenton technology without the external addition of H2O2 and with significantly improved degradation and mineralization performance seems significant.

For this purpose, photocatalysis-self-Fenton system constructed by coupling photocatalysis and Fenton technology was presented. Solar light is regarded as suitable diving force since it is inexhaustible and sustainable. In this system, H2O2 generated in-situ under visible light irradiation was utilized to produce `OH radicals via Fenton reaction. As we all known that the Fenton technology is remarkably restarted by Fe (III)/Fe(II) recycle [8]. A high degradation activity could be obtained if Fe(III) could be effectively reduced by photo-generated electron [9]. Particularly, CdS/rGO/Fe2+ system, developed by Jinlong Zhang group, exhibited a satisfactory degradation efficiency for organic pollutant represented by phenol, in which CdS was utilized for in-situ generation of H2O2 [10]. In the system, phenol was efficiently degraded under visible light irradiation for 1 h without the external addition of H2O2. However, potential environmental pollution may be caused since CdS is chemically unstable and biologically toxic. Meanwhile, the employment of noble metal would lead to a relatively high fabrication cost, which seriously restrict their actual application. Particularly, the intrinsic mechanism was ambiguous.

Graphite carbon nitride (g-C3N4), a polymer semiconductor, has become one of the research hotspots in recent years due to its enormous advantages, including strong visible light responsibility, controllable structure and morphology, environmental benign and feasible fabrication method [11–13]. Therefore, g-C3N4 has been widely applied in the field of hydrogen peroxide generation [14,15], pollutant degradation [16], water decomposition [17], carbon dioxide reduction [18],
nitrogen fixation [19] and sterilization [20]. Photocatalytic generation of H$_2$O$_2$ via dioxygen reduction in alcohol/water mixture (9/1 v/v) under visible light over g-C$_3$N$_4$ was firstly reported by Yasuhiro Shiraishi group in 2014 [21]. Two electron reduction of dioxygen in aqueous solution with high selectivity towards H$_2$O$_2$ was obtained, through forming 1,4-endoperoxide species on the melem unit of g-C$_3$N$_4$. The accumulated concentration reached up to 30 μmol after irradiation for 12 h under visible light. Furthermore, the photocatalytic performance for H$_2$O$_2$ generation could be further improved by tremendous efforts, including doping metal/nonmetal elements [22,23], tailoring the nanostructure and surface properties [24,25], and compositing with other semiconductors [26]. Therefore, g-C$_3$N$_4$ based photocatalyst is regarded as a suitable candidate for the construction of photocatalysis-self-Fenton system.

With these motivations, herein, photocatalysis-self-Fenton system was constructed based on g-C$_3$N$_4$. The system exhibited significantly high-fluent degradation and high mineralization performance for organic pollutants, including 2,4-DCP, compared with g-C$_3$N$_4$ based photocatalysis and Fenton technology. Finally, the intrinsic mechanism for the system was unambiguously disclosed. The photocatalysis-self-Fenton system presented here provides new insight for the effective and environmentally friendly removal of organic pollutants.

2. Experimental sections

2.1. Preparation of P-g-C$_3$N$_4$ catalyst

P-g-C$_3$N$_4$ was prepared through the second thermal treatment of the mixture of g-C$_3$N$_4$ nanosheet and NaH$_2$PO$_2$ at controlled temperature of 400 °C for under Nz atmosphere 1 h. PH$_3$ gas originated from NaH$_2$PO$_2$ decomposition possess high reactive activity towards g-C$_3$N$_4$ nanosheet, resulting in P heteroatom doping in the framework of g-C$_3$N$_4$. Thereupon, it was thoroughly washed with deionized water and dried in vacuum. The P-doped g-C$_3$N$_4$ catalyst was labeled as P-g-C$_3$N$_4$-(x) (x represents weight percent of NaH$_2$PO$_2$ to g-C$_3$N$_4$ nanosheet). For comparison, bulk-C$_3$N$_4$ was prepared by a thermal polymerization method of dicyandiamide at 550 °C for 4 h at a ramping rate of 2.3 °C/min. g-C$_3$N$_4$ nanosheet was prepared by a thermal polymerization method. The mixture of ammonium chloride and dicyandiamide (weight ratio 1:5) were thoroughly blended in mortar, then thermally treated at 550 °C at a ramping rate of 2.3 °C/min for 4 h. Dicyandiamide was utilized as g-C$_3$N$_4$ precursor and NH$_4$Cl as template. After cooling, the product was rinsed twice with deionized water and dried in vacuum. The P-doped g-C$_3$N$_4$ catalyst was labeled as P-g-C$_3$N$_4$-(x).

2.2. Characterization of materials

The structural and optical properties of P doped g-C$_3$N$_4$ were thoroughly characterized by FE-SEM, TEM, XPS, FT-IR, XRD and UV–vis. The morphology of the materials prepared were observed by the scanning electron microscope (FE-SEM, Hitachi SU-8010) and the transmission electron microscope (TEM, Hitachi HT7700). X-ray photoelectron spectroscopy (XPS) was performed on the ULVAC-PHI-Quantera spectrometer. The FT-IR spectra was measured by a Bruker V70 spectrometer. The crystalinity of the samples was characterized by X-ray diffraction (XRD, Rigaku D/max-2500) with Cu Kα radiation ($\lambda=1.5406\text{Å}$) at 40 kV and 200 mA with a scan step of 0.02°. UV–vis spectrophotometer (Hitachi U-3010) were used to obtain the UV–vis diffuse reflection spectra (DRS) of the samples. The reflectance standard was BaSO$_4$. The mainly active species were detected by radical scavenger experiment, EPR measure of DMPO-·OH (electron paramagnetic resonance, JES-FA200) and PL analysis.

2.3. Photocatalysis-self-Fenton degradation of organic pollutants

The Photocatalysis-self-Fenton performances were evaluated through 2,4-DCP degradation in a multi-tube agitated reactor under visible-light irradiation (λ > 420 nm). 30 mg catalyst was added into 30 mL 2,4-DCP solution (20 ppm), then ultrasonically dispersed for 30 min. The suspension was kept O$_2$-pumping under constant stirring in the dark to reach the adsorption equilibrium and dioxygen saturation. Then 10 mg FeSO$_4$·7H$_2$O was added and 500 W metal halide lamp (with a filter above 420 nm) was turned on as the light source to trigger the photocatalytic reaction. Took 2 mL of the reaction solution at regular intervals and centrifuged to remove the photocatalytic material. Finally, the concentration of organic pollutant was analyzed by gas chromatograph (GC) or high performance liquid chromatography (HPLC). For degradation of other organic pollutants, such as antibiotics (ciprofloxacin), chloride-contained organics (chlorophenols, 4-chlorophenol, 2,4,6-trichlorophenol) and carcinogenic drugs (sulfamethoxazole, metronidazole), the experimental condition was similar to that for 2,4-dichlorophenol degradation. The liquid chromatography condition for the organic pollutant illustrated as Table S1.

3. Results and discussion

3.1. Construction of photocatalysis-self-Fenton system

Photocatalysis-self-Fenton system is based on the Fenton reaction between the H$_2$O$_2$ in-situ generated and Fe(II). According to the report by Choi, H$_2$O$_2$ was generated over P doped g-C$_3$N$_4$ with a maximum concentration of 1.0 mM [27]. The morphology, structural properties and band structure of P doped g-C$_3$N$_4$ fabricated are illustrated as Fig. 1 and Fig. S1 – 4 and Table S2. And the improved photocatalytic performance for H$_2$O$_2$ generation over P-g-C$_3$N$_4$-10 is shown in Fig. S5. The scheme of photocatalysis-self-Fenton degradation is proposed as Fig. 2a. H$_2$O$_2$ is firstly in-situ generated in the framework of P doped g-C$_3$N$_4$, followed by abundant OH radicals are generated via Fenton re-action in the presence of Fe(II), thereby resulting in effective degradation and mineralization performance. Since the photocatalysis-self-Fenton degradation performance highly depend on the amount of H$_2$O$_2$ generated in-situ, the effect of P dopant on the accumulated amount of H$_2$O$_2$ was firstly investigated (Fig. 2b). The catalytic activity for H$_2$O$_2$ generation over pristine g-C$_3$N$_4$ was poor, with an accumulation concentration of H$_2$O$_2$ of only 10.4 μM after visible-light irradiation for 3 h. Interestingly, the activity for H$_2$O$_2$ generation increased with P dosage, reaching a maximum amount of 70.5 μM over P-g-C$_3$N$_4$-10, nearly 7.0-fold increase in comparison with the pristine g-C$_3$N$_4$. Considering that Fe(II) will hydrolyze to form FeOOH once pH is above 3.0 [28], thus the effect of pH value and usage of FeSO$_4$ on photocatalysis-self-Fenton degradation activity was also investigated. As shown in Fig. 2c, when pH value was controlled as 3.0, 2.4-DCP was almost completely degraded, with a rate constant was 0.91 h$^{-1}$. Even the pH value was controlled at 6.4 and 9.0, satisfactory degradation performance was remained, with rate constant being 0.82 h$^{-1}$ and 0.62 h$^{-1}$, respectively, indicating that photocatalysis-self-Fenton degradation could be effectively performed via both Fenton and Fenton-like reaction. Meanwhile, the effect of FeSO$_4$ usage on photocatalysis-self-Fenton degradation activity was investigated (Fig. 2d). When the addition amount was 5.0 mg, the system exhibited a degradation rate constant of 0.61 h$^{-1}$. With the addition amount increased to 10.0 mg, the degradation activity was promoted to be 0.82 h$^{-1}$, which may be ascribed to the improved utilization efficiency of H$_2$O$_2$. However, the degradation activity declined to be 0.48 h$^{-1}$ when the usage increased to be 15.0 mg, which may be stemmed from the decreased light penetrability caused by excessive formation of FeOOH.

Therefore, the optimal experimental condition for constructing photocatalysis-self-Fenton system was determined as: P-g-C$_3$N$_4$-10 was utilized as catalyst for H$_2$O$_2$ generation, the usage amount of FeSO$_4$ was 10.0 mg, meanwhile needing not the adjustment of pH value.
Fig. 1. Doping site determination of P element. XPS spectra of (a) C1s and (b) P2p. (c) Solid-state $^{31}$P NMR spectra. (d) $^{13}$C MAS NMR spectra and the proposed structure of P-g-C$_3$N$_4$-10.

Fig. 2. Construction of photocatalysis-self-Fenton system. (a) Schematic illustration for photocatalysis-self-Fenton system. Optimal condition for photocatalysis-self-Fenton degradation: (b) P dopant amount, (c) pH value and (d) the usage of FeSO$_4$. 

J. Ma, et al. Applied Catalysis B: Environmental 276 (2020) 119150
3.2. Photocatalysis-self-Fenton degradation and mineralization performance

The photocatalysis-self-Fenton degradation and mineralization ability for organic pollutant presented by 2,4-DCP was thoroughly investigated, through comparing with photocatalysis and Fenton technology.

As illustrated in Fig. 3a, the photocatalytic degradation activity for 2,4-DCP was poor over three kinds of catalysts, including bulk-C3N4, g-C3N4 and P-g-C3N4-10. The apparent reaction rate constant (k) was only 0.04, 0.05 and 0.17 \( \mu \text{mol h}^{-1} \), respectively. Interestingly, for the photocatalysis-self-degradation, k value over the three catalysts were all strikingly increased. Especially, the k value over photocatalysis-self-Fenton system based on P-g-C3N4-10 increased as high as 0.82 \( \mu \text{mol h}^{-1} \), nearly 20.5 times higher than photocatalysis over bulk-g-C3N4, and even being superior to the g-C3N4 based photocatalysts reported to date (Table S3). Meanwhile, it is well known that total organic carbon (TOC) is vital index to evaluate the mineralization ability. As expected, the TOC removal rate in photocatalysis-self-Fenton system were significantly higher than photocatalysis (Fig. 3b). The TOC removal rate for 2,4-DCP over photocatalysis-self-Fenton system was 42.7% after reaction for 3 h when P-g-C3N4-10 acted as catalyst, nearly 22.5 times higher than photocatalysis in which bulk-C3N4 was employed. The increased magnitude of TOC was close to that of k value, indicating that the degradation and mineralization took place simultaneously. Therefore, compared with photocatalytic degradation, satisfactory degradation and mineralization ability were demonstrated over photocatalysis-self-Fenton system, which may be originated from more ·OH radicals were generated.

Photocatalysis-self-Fenton degradation performance was further compared with Fenton technology. Since the accumulated concentration of \( \text{H}_2\text{O}_2 \) was 2.0 \( \mu \text{mol} \) after visible-light irradiation for 3 h over P-g-C3N4-10 (Fig. S5a), the externally added amount of \( \text{H}_2\text{O}_2 \) into Fenton technology was designed as 2.0, 10.0 and 20.0 \( \mu \text{mol} \), respectively, being 1, 5, and 10-fold higher than the amount of \( \text{H}_2\text{O}_2 \) photo-generated in situ over P-g-C3N4-10. As shown in Fig. 3c, when 2.0 \( \mu \text{mol} \) of \( \text{H}_2\text{O}_2 \) was added into Fenton system, 30% of degradation yield was obtained after 0.5 h, but stopped increasing with a prolonged degradation time. Surprisingly, even if the addition amount of \( \text{H}_2\text{O}_2 \) was increased to 20 \( \mu \text{mol} \), still no obviously improved degrading efficiency was observed. In comparison, k value in photocatalysis-self-Fenton was 0.82 \( \mu \text{mol h}^{-1} \), nearly 3.7 times higher than Fenton degradation when 20.0 \( \mu \text{mol} \) \( \text{H}_2\text{O}_2 \) was externally added. For Fenton degradation, the externally added \( \text{H}_2\text{O}_2 \) could not react with Fenton reagent in time, thus leading to low utilization efficiency of \( \text{H}_2\text{O}_2 \) due to useless decomposition. In comparison, despite the generation amount of \( \text{H}_2\text{O}_2 \) over photocatalysis-self-Fenton system was relatively low, high-fluent degradation ability for 2,4-DCP was demonstrated since highly effective utilization of \( \text{H}_2\text{O}_2 \) facilitated the sustainable generation of ·OH radicals. Meanwhile, as shown in Fig. 3d, the TOC removal rate reached 42.7% for photocatalysis-self-Fenton system, almost 3.8 times higher than Fenton technology (11.1%). Therefore, in comparison with Fenton technology, the photocatalysis-self-Fenton system still demonstrated significantly improved degradation and mineralization ability. Meanwhile, various photocatalysis-self-Fenton system based on three kinds of photocatalyst beside P-g-C3N4, including g-C3N4 nanosheet, PDI and RE resin, all demonstrated high degradation activity for 2,4-DCP (Fig. S6), highlighting the effect of the photocatalysis-self-Fenton system.

Photocatalysis-self-Fenton degradation and mineralization performance for other organic pollutants with various function groups were further investigated. Three kinds of organic pollutants, i.e. 2-methylimidazole-containing compounds (sulfamethoxazole, metronidazole), 2-methylimidazole-containing compounds (sulfamethoxazole, metronidazole), chlorine-containing organics (p-chlorophenol, 2,4,6-trichlorophenol) and antibiotics (ciprofloxacin), were purposely selected as the degradation target. Excitingly, highly efficient degradation and mineralization performance for all the three organic pollutants were demonstrated, as shown in Fig. 4. The degradation activity increased by nearly 2.0-fold compared with photocatalysis, illustrating that the photocatalysis-self-Fenton system could be widely applied in treating various organic pollutants. The wide applicability was speculated to be also ascribed to the sustainable generation of ·OH radicals with strong redox ability.

Finally, the reusability of photocatalysis-self-Fenton system was further evaluated. As shown in Fig. 5a, only 5.7% of activity was decreased after successive degradation for 4 times. The degradation
activity loss may originate from the weight loss of P component in g-C3N4, which leads to 7.0% of activity decrease for H2O2 generation, as shown in Fig. S7. Meanwhile, no obvious structural changes were observed for XPS curve (Fig. 5b) as well as TEM, UV–vis and FTIR characteristic (Fig. S7 b–d) for P-g-C3N4-10 catalyst that was successively utilized for 4 times, further displaying the excellent stability of the photocatalysis-self-Fenton system.

3.3. Mechanism for the photocatalysis-self-Fenton system

To discover clearly the reason for the promoted degradation and mineralization performance of photocatalysis-self-Fenton system, control experiments were carried out, and utilization efficiency of H2O2 in various degradation system was compared as well.

Firstly, the degradation activity under controlled experiment conditions were shown in Fig. 6a and Fig. S8. Negligible degradation activity for 2,4-DCP was observed when P-g-C3N4-10 catalyst was absent. Under N2 atmosphere, slightly enhanced degradation efficiency was exhibited in the presence of P-g-C3N4-10 catalyst, with a degradation rate constant (k) of 0.18 h⁻¹, which should be ascribed to the limited photocatalytic degradation activity [29]. Then the k value increased to be 0.22 h⁻¹ under O2-pumping in the absence of Fe(II) atmosphere, which may be ascribed to the enhanced photocatalytic degradation performance since separation efficiency of photo-generated charge carriers was enhanced through adsorbing electron by O2 [30]. The k value continued to increase to be 0.32 h⁻¹ in the presence of P-g-C3N4-10 and Fe(II) without O2-pumping, owning to the generation of H2O2 through reducing the dissolved oxygen followed by Fenton reaction [31]. Finally, the k value was significantly elevated to be 0.82 h⁻¹ when O2-pumping throughout the reaction in the presence of P-g-C3N4-10 and Fe2+. Under such condition, *OH radicals were continuously produced, leading to the significantly enhanced degradation performance.

It is well known that remaining a relatively high concentration of Fe (II) is vital for Fenton technology. Therefore, the concentration of Fe(II) in photocatalysis-self-Fenton system was investigated, as shown in Fig. 6b. Interestingly, up to 0.8 mM of Fe(II) concentration was remained after reaction for 3 h in photocatalysis-self-Fenton system. As comparison, only 0.2 mM of Fe(II) was remained for Fenton technology, only one quarter of photocatalysis-self-Fenton system. The higher concentration of Fe(II) originated from the effective reduction of Fe(III) by photo-generated electron was favorable for the improved utilization efficiency of H2O2, thereby producing more *OH radicals [32].

Radial scavenger experiment and EPR measure result (Fig. S9) exhibited that *OH radicals were the predominant active radial in photocatalysis-self-Fenton system. To discover clearly the reason for the high degradation and mineralization ability, the concentration of *OH radicals with prolonged reaction time were measured and illustrated as Figs. 6c and S10. Concentration of *OH radial was determined via measuring PL signal intensity of 7-hydroxycoumarin, which originated from the reaction of *OH radical and coumarin [33]. Little amount of *OH radicals were generated via photocatalysis, which was responsible for its low activity. In comparison, for Fenton technology, *OH radicals with maximum concentration of 26.1 μM were rapidly generated after 0.5 h but stopped generating with time. Interestingly, *OH radicals were sustainably produced in photocatalysis-self-Fenton system, reaching a maximum concentration of 57.7 μM after 3 h, almost 2.2-fold higher than Fenton technology. Sustainably produced *OH radicals were originated from the continual generation and consumption of H2O2, which should be the intrinsic reason for the high-fluent degradation and high mineralization ability. The utilization efficiency of H2O2 over photocatalysis-self-Fenton and Fenton technology was thereby compared and

![Fig. 4. Wide applicability for various organic pollutants over photocatalysis-self-Fenton system. (a) Degradation activity. (b) mineralization degree.](image)

![Fig. 5. Reusability of photocatalysis-self-Fenton system. (a) Degradation activity loss after successive utilization for 4 times. (b) N1S XPS comparison of initial and after 4 cycle for P-g-C3N4-10.](image)
shown in Figs. 6d and S10. The utilization efficiency of H2O2 was only ca. 7.8% for Fenton technology. In comparison, the efficiency increased up to 80% for photocatalysis-self-Fenton system, nearly 10.5 times higher than Fenton technology. Clearly, the high-fluent degradation and high mineralization ability in photocatalysis-self-Fenton system was ascribed to the effective utilization of H2O2 generated in-situ, despite its low yield of H2O2 over P-g-C3N4-10 compared with other semiconductors.

Consequently, based on the results above, the speculated mechanism for the photocatalysis-self-Fenton degradation of 2,4-DCP was tentatively presented and depicted in Fig. 6e. Photo-generated electrons participated in both oxygen reduction reaction (ORR) for H2O2 generation and the Fe(III) reduction, thus substantial ‘OH radicals were continuously produced through Fenton technology, thereby contributing to high-fluent degradation and high mineralization ability for 2,4-DCP. The photogenerated holes took part in the direct oxidation of 2,4-DCP.

4. Conclusion

In summary, a photocatalysis-self-Fenton system was constructed, in which visible light and dioxygen were utilized as external driving force and feed stock, respectively. The system exhibited satisfactory degradation and mineralization performance for 2,4-DCP. The degradation activity was enhanced by 20.5 and 3.7 times, compared to bulk-g-C3N4 photocatalysis and Fenton technology, respectively. The corresponding mineralization degree was 22.5 and 3.8 times higher than the latter two. Meanwhile, the system demonstrated wide applicability and stability for other organic pollutants. The highly effective utilization of H2O2 generated in-situ was responsible for the sustainable generation of abundant ‘OH radicals, which facilitated the high-fluent degradation and high mineralization ability.
CRediT authorship contribution statement

Jun Ma: Conceptualization, Writing - review & editing. Kai Wang: Writing - original draft, Validation, Data curation. Chuan Wang: Validation. Xianjie Chen: Conceptualization, Methodology. Wei Zhu: Methodology, Software. Guoxiang Zhu: Data curation, Validation. Wenqing Yao: Supervision. Yongfa Zhu: Project administration, Funding acquisition, Writing - review & editing.

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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