



# Visible-light-assisted peroxydisulfate activation and mechanism for the degradation of pharmaceuticals over pyridyl-functionalized graphitic carbon nitride coordinated with iron phthalocyanine



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## ARTICLE INFO

### Article history:

Received 23 March 2017

Received in revised form 30 May 2017

Accepted 19 June 2017

Available online 20 June 2017

### Keywords:

g-C<sub>3</sub>N<sub>4</sub>

Excited-state FePcCl<sub>16</sub>

Visible light

Mechanism

Degradation pathway

## ABSTRACT

Recently, peroxydisulfate (PMS)-based advanced oxidation processes (AOPs) have received increasing attention because of their capability and adaptability in decontamination. The couple of solar light and PMS activation is an environmentally friendly and efficient strategy for environmental remediation. Herein, the iron hexadecachlorophthalocyanine (FePcCl<sub>16</sub>) was used to coordinate with graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), which was functionalized by pyridine-based ligand isonicotinic acid (INA) to prepare a distinctive catalyst, g-C<sub>3</sub>N<sub>4</sub>-INA-FePcCl<sub>16</sub>. The experimental results revealed that g-C<sub>3</sub>N<sub>4</sub>-INA-FePcCl<sub>16</sub> can activate PMS efficiently for the elimination of carbamazepine (CBZ) under visible light irradiation over a wide pH range. Upon irradiation with visible light, CBZ was destroyed by the solid g-C<sub>3</sub>N<sub>4</sub> with generated sulfate (SO<sub>4</sub><sup>•-</sup>) and hydroxyl (\*OH) radicals, on the other hand, high-valent iron (Fe(IV)=O) species accompanied by SO<sub>4</sub><sup>•-</sup> and \*OH radicals were produced by excited-state FePcCl<sub>16</sub> (\*FePcCl<sub>16</sub>) during oxidation, which is different from a traditional PMS activation system. The axial pyridine-based ligand was protected under the FePcCl<sub>16</sub> macrocyclic structure shield. Noteworthy, in the absence of visible light, g-C<sub>3</sub>N<sub>4</sub>-INA-FePcCl<sub>16</sub> showed a higher catalytic performance than pure g-C<sub>3</sub>N<sub>4</sub>, FePcCl<sub>16</sub> and a mechanical mixture of the two. This study allows for the construction of an effective and environmental catalytic system, which can be applied to purify water that contains refractory pollutants.

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## 1. Introduction

The occurrence of pharmaceutically active compounds (PhACs) in environments has received increasing attention because of their potential threat to human health and aquatic ecosystems [1,2]. As emerging persistent contaminants, PhACs are believed to be toxic to living organisms even though the concentration is very low [3]. Therefore, it is necessary to develop efficient technologies to eliminate PhACs. Advanced oxidation processes (AOPs) that use reactive species have been applied extensively in rapid degradation and complete mineralization of the recalcitrant organic pollutants [4–6]. Among various AOPs, peroxydisulfate (PMS, 2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>, oxone), as a favorable alternative to hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), has received attention because of its ability to generate both hydroxyl (\*OH) and sulfate (SO<sub>4</sub><sup>•-</sup>) radicals, as well as its improved flexibility over a broad pH range [7,8]. Numerous methods for PMS activation have been proposed including transi-

tion metals [9–12], ultraviolet (UV) [13], ultrasound [14], carbon catalysts [15,16] and so on. The most common catalysts are transition metals, with Co<sup>2+</sup>/PMS system gives the best results of SO<sub>4</sub><sup>•-</sup> generation. However, the application of Co<sup>2+</sup> is limited because of its potential carcinogenic effects [17].

In contrast with cobalt, iron is more environmentally friendly, which makes it a potentially fascinating catalyst. Recently, some investigations have reported the use of Fe<sup>2+</sup> in PMS activation to form active radical species [18,19]. However, the Fe<sup>2+</sup>/PMS system can only be operated under acidic conditions because of the hydrolysis and precipitation of Fe<sup>2+</sup> [20], and the transformation rate from Fe<sup>3+</sup> to Fe<sup>2+</sup> is slow [21,22]. Iron phthalocyanine (FePc) is a potential material that could overcome these drawbacks. FePc as an efficient and stable Fenton-like catalyst could improve the pH tolerance for a higher catalytic performance [23]. It may be also applicable to PMS-related conditions. Second, the unique electron-rich characteristic of FePc could accelerate the transformation rate from Fe<sup>3+</sup> to Fe<sup>2+</sup> [24]. Simultaneously, FePc is a member of the metallophthalocyanines (MPcs) family, which is well-known for an intrinsic broad spectral response in the red/near-infrared (IR) and visible-light region, and has been applied widely in the photocatalytic field

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[25–27]. Accompanied by light-harvesting, MPCs can be excited to their excited state with unique photochemical and photophysical behaviors, many studies related to excited-state MPCs have been reported [28–30]. So far, numerous derivatives of FePc have been synthesized with various substituent groups [24,31–33]. Among them, iron hexadecachlorophthalocyanine (FePcCl<sub>16</sub>) is considered more stable because the strong electron-withdrawing chlorinated substituents at the periphery can protect its macrocyclic structure. However, the use of FePcCl<sub>16</sub> is limited because of its aggregation, which can be overcome by introducing appropriate support materials.

In recent years, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) as a visible-light photocatalyst has been used widely because of its unique planar structure, photocatalysis, low cost, and thermal stability [34–37]. More recently, g-C<sub>3</sub>N<sub>4</sub> has been found to be a feasible candidate for the catalytic activation of PMS towards the degradation of organic contaminants [38–40]. However, the rapid charge recombination, low surface and poor absorption of visible light have restricted its application. Many strategies have been explored to enhance its photocatalytic activity, such as heteroatom doping [41,42], heterojunctions construction [43,44] and dye sensitizing [45]. We noted that the immobilization of MPCs onto g-C<sub>3</sub>N<sub>4</sub> could extend the spectral response region of g-C<sub>3</sub>N<sub>4</sub>, improve the MPCs dispersion and provide them with specific photoelectronic properties [25,46,47]. In our previous study, we prepared g-C<sub>3</sub>N<sub>4</sub>/ZnTcPc catalyst using g-C<sub>3</sub>N<sub>4</sub> coupled with zinc tetracarboxyphthalocyanine (ZnTcPc), and the product showed a higher photocatalytic activity [48]. But the preparation method for this catalyst is only suitable for MPCs with carboxyl, which are difficult to obtain. Inspired by MPCs can be linked covalently or noncovalently to other ligands, such as porphyrin, pyridine, and indole, which can also be fixed to g-C<sub>3</sub>N<sub>4</sub>. So, an appropriate ligand was proposed as a “bridge” to connect various MPCs and g-C<sub>3</sub>N<sub>4</sub>.

In this work, we used pyridine-based ligand isonicotinic acid (INA) to act as a “bridge”, and designed a facile approach to synthesize a distinctive catalyst, g-C<sub>3</sub>N<sub>4</sub>-INA-FePcCl<sub>16</sub>, using FePcCl<sub>16</sub> that is axially coordinated with INA-modified g-C<sub>3</sub>N<sub>4</sub>. Carbamazepine (CBZ), is one of the most frequently detected PhACs in the aquatic environment, and was selected as probe compound to evaluate the catalytic performance of the as-prepared catalysts. The constructed g-C<sub>3</sub>N<sub>4</sub>-INA-FePcCl<sub>16</sub>/PMS/visible light system shows strong catalytic activity for CBZ decomposition, which is attributed to the efficient generation of Fe(IV)=O, SO<sub>4</sub><sup>•-</sup> and •OH. And visible-light-induced \*FePcCl<sub>16</sub> was identified as the major factor that is responsible for the formation of Fe(IV)=O species, which could not be detected in the dark. A possible pathway for the degradation of CBZ was proposed using high-definition mass spectrometry (HDMS) coupled with gas chromatography/mass spectrometry (GC-MS).

## 2. Experimental

### 2.1. Materials and reagents

CBZ, benzotriazol-1-yl-oxotripyrrolidinophosphonium hexafluorophosphate (PyBOP), PMS, diisopropylethylamine (DIEA) and dimethyl sulfone (DMSO<sub>2</sub>) were from Aladdin Chemical Co. Ltd. Tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) were from the Tianjin Wing Tai Chemical Co. Ltd. 5, 5-Dimethyl-pyrroline N-oxide (DMPO) was obtained from the Tokyo Chemical Industry Co. Ltd. Methanol and acetonitrile (Merck, Germany) for UPLC were of chromatographic grade. All chemicals were of analytical grade and were used as received without further purification.

### 2.2. Catalyst preparation

g-C<sub>3</sub>N<sub>4</sub> synthesis was according to Chen et al. [49]. FePcCl<sub>16</sub> was synthesized according to the literature [50]. The preparation of g-C<sub>3</sub>N<sub>4</sub>-INA-FePcCl<sub>16</sub> is as shown in Scheme 1. An environmental liquid exfoliation route was conducted by exfoliating g-C<sub>3</sub>N<sub>4</sub> into ultrathin nanosheets in ultrapure water for 5 d, before it was freeze-dried for further use [51]. INA, PyBOP and DIEA were dissolved in 200 mL dry DMF, and ultrasonicated for 1.5 h. The ultrasonicated g-C<sub>3</sub>N<sub>4</sub> was dispersed in 100 mL dry DMF and added drop-wise to the above solution at 100 mL/h. After reacting for 6 h at 60 °C, the solution was centrifuged, washed with DMF and ultrapure water, and freeze-dried to obtain g-C<sub>3</sub>N<sub>4</sub>-INA powder. Finally, g-C<sub>3</sub>N<sub>4</sub>-INA and FePcCl<sub>16</sub> were added to 200 mL THF in the dark for 6 h. After reaction, the solution was centrifuged, and washed with THF and ultrapure water. Then g-C<sub>3</sub>N<sub>4</sub>-INA-FePcCl<sub>16</sub> powder was obtained after the sample was freeze-dried. A series of g-C<sub>3</sub>N<sub>4</sub>-INA-FePcCl<sub>16</sub> catalysts with diverse loading of FePcCl<sub>16</sub> were prepared. From the X-ray fluorescence (XRF) test, the as-prepared catalysts were defined as g-C<sub>3</sub>N<sub>4</sub>-INA-FePcCl<sub>16</sub> (0.67%), g-C<sub>3</sub>N<sub>4</sub>-INA-FePcCl<sub>16</sub> (1.70%) and g-C<sub>3</sub>N<sub>4</sub>-INA-FePcCl<sub>16</sub> (3.58%). The mechanical mixture of g-C<sub>3</sub>N<sub>4</sub> and FePcCl<sub>16</sub> was termed g-C<sub>3</sub>N<sub>4</sub>/FePcCl<sub>16</sub> (1.70% FePcCl<sub>16</sub> in the mixture).

### 2.3. Photocatalytic experiments

To evaluate the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub>-INA-FePcCl<sub>16</sub>, a Q-Sun Xe-1 test chamber (USA) (Fig. S1) served as the light source, and a UV cutoff filter (Shanghai Seagull Colored Optical Glass Co., Ltd.) was used to filter the UV light ( $\lambda < 420$  nm) to ensure illumination by visible light only. CBZ was selected as a probe compound. The experiment was conducted in a 40 mL glass beaker at room temperature. Before irradiation, g-C<sub>3</sub>N<sub>4</sub>-INA-FePcCl<sub>16</sub> (0.1 g/L) was dispersed in CBZ aqueous solution (25  $\mu$ M) and ultrasonicated for 2 min. PMS was added as an oxidant. The CBZ concentration was detected by UPLC equipped with the Acquity BEH C18 column (1.7  $\mu$ m, 2.1  $\times$  50 mm, Waters), and a mixture of acetonitrile and water (20:80, v/v) was used as the mobile phase with a flow rate of 0.35 mL/min for the UPLC experiments.

### 2.4. Analytical methods

The catalyst chemical structures were analyzed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). UV–vis spectra and UV–vis diffuse reflectance absorption spectra (DRS) were obtained to explore the optical absorption performance of the samples. Photoluminescence (PL) spectra and the transient photocurrent response were used to investigate the photoelectrochemical properties of the catalysts. Electron paramagnetic resonance (EPR) signals of radicals trapped by DMPO were detected in a Bruker A300 spectrometer at ambient temperature. To detect whether high-valent iron (Fe(IV)=O) species were generated, designed measurements were carried out by gas chromatography/mass spectrometry (GC-MS, GC: Agilent 6890N equipped with an OV1701 capillary column 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m; MS: Agilent 5973i) and UPLC/Synapt G2-S HDMS (Waters Q-TOF, USA) in positive mode. The degradation intermediates of CBZ in the g-C<sub>3</sub>N<sub>4</sub>-INA-FePcCl<sub>16</sub>/PMS/visible light system were identified by UPLC Synapt G2-S HDMS (Waters, USA). The procedures and corresponding parameters are described in the supplementary material.

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