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Visible-light-assisted generation of high-valent iron-oxo species anchored axially on g-C_3N_4 for efficient degradation of organic pollutants

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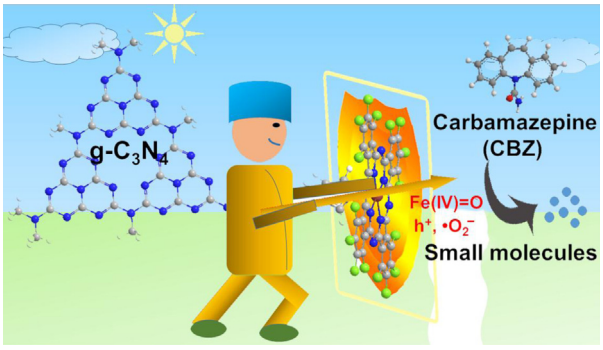
HIGHLIGHTS

- g-C_3N_4-IMD-$FePcCl_{16}$ were prepared by axial coordination between g-C_3N_4 and $FePcCl_{16}$.
- The generation of anchored species under visible-light irradiation.
- The fabrication converts the mechanism based on ·OH into anchored species.
- Transformation products of CBZ were finally transformed to small molecules.

GRAPHICAL ABSTRACT



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ABSTRACT

As highly active species, in theory, hydroxyl radicals (·OH) can move freely and destroy almost all organic compounds, including catalysts with a conjugate structure. Therefore, a system that can generate oxidative species with a high activity, but where the active species is anchored to avoid autooxidation, is urgently required. In this work, we fabricated a novel visible-light-assisted advanced oxidation process based on high-valent iron species (Fe(IV)═O) over graphitic carbon nitride (g-C_3N_4) that was coordinated to iron hexadecachlorophthalocyanine ($FePcCl_{16}$) through imidazole ligands (IMD). Under visible-light excitation, the phthalocyanine ring of the g-C_3N_4-IMD-$FePcCl_{16}$/hydrogen peroxide (H_2O_2) can be motivated to an excited state $FePcCl_{16}^*$, in which active H_2O_2 and the generation of anchored Fe(IV)═O species are used for the degradation of carbamazepine (CBZ). Because the molecular movement of transient Fe(IV)═O species is restricted, the possibility of oxidative collision is minimized, which provides good stability. An analysis of the electron paramagnetic resonance, gas chromatography/mass spectrometry, photoluminescence spectra, periodic on/off photocurrent density response and the photo-assisted catalytic active experiments, indicates that the rapid generation of Fe(IV)═O species occurs as the catalyst contacts the H_2O_2, which inhibits the conduction-band electrons of the g-C_3N_4 from reacting with H_2O_2 and generating ·OH. This study provides insight into the construction of suitable structures that will enhance visible-light-assisted catalytic oxidation activity and allow for the fabrication of an anchored highly active species.

1. Introduction

The pervasive global problems of emerging, recalcitrant and toxic contaminants has garnered great concern regarding aquatic environments and human health [1,2]. These micropollutants are

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present at low levels in high backgrounds, but yield associated problems, such as detrimental ecological effects and long-term threats to the human body [3,4]. The micropollutants include pharmaceuticals, pesticides, personal-care products and industrial chemicals, with mostly conjugated structures that lead to a high persistence and no degradation by traditional treatment [5,6]. A series of oxidation methods has been explored to remove these micropollutants, with the most common technology being advanced oxidation processes (AOPs) [7–9]. AOPs are considered to be efficient methods for sewage treatment with the generation of highly reactive species, which include electrochemical oxidation based on the electro-Fenton process [10], ozonation process with ozone [11] and photocatalytic degradation technology equipped with photo-Fenton treatment [12–14]. Among various AOPs, the photo-assisted catalytic degradation of micropollutants with environmental H_2O_2 has attracted extensive attention because of its promising potential for the use of visible light and the efficient removal of pollutants [15,16]. As a photocatalyst, graphitic carbon nitride (g-C_3N_4), which is composed of elements that are abundant on earth, is of great application value. However, its performance has been restricted to the low catalytic activity of H_2O_2 decomposition [17]. Several methods have been devoted to improving its capacity to activate H_2O_2, which is accompanied mainly by the generation of hydroxyl radicals (·OH) [18,19]. The non-selectivity of ·OH may destroy the catalyst during contaminant degradation. Therefore, the development of a technology with an excellent performance and the selective elimination of recalcitrant pollutants is of utmost urgency.

Metallophthalocyanines (MPcs) and metalloporphyrins (MPs) usually serve as coordination complex catalysts and have been used extensively to mimic enzyme catalysts that are responsible for H_2O_2, O_2 or other peroxide activation to improve catalytic performance [20–22]. A bio-inspired strategy to eliminate pollutants with H_2O_2 addition has been reported based on an axial coordination between g-C_3N_4 and hemin through imidazole ligands (IMD), which shows a high efficiency for contaminant degradation, a good stability in the catalytic oxidation system and a wide pH utilization range [23]. Access to hemin is difficult and the system presented above yields a low visible-light utilization efficiency. The exploration of an alternative for the good application of visible light used in AOPs is a common target among researchers. MPcs are attractive catalysts for analogous structures with MPs and accessibility with respect to cost and simple preparation [24]. Their central metal element and extended delocalized π-electron conjugated macrocyclic structure offers MPcs a strong absorption in the visible-light region, and therefore they are used extensively as catalytic oxidants or photosensitizers [25].

As an environmentally friendly catalyst, iron (II) phthalocyanine (FePc) has been applied extensively in catalytic oxidation reactions with H_2O_2 addition to form anchored high-valent iron (Fe(IV)═O) species that can remove recalcitrant pollutants [26–28]. However, in an acidic oxygen reduction reaction, FePc is unstable compared with its substituted compound, perchlorinated iron (II) phthalocyanine ($FePcCl_{16}$), and pure FePc powders are prone to aggregation in aqueous solution, which may lead to the generation of catalytically inactive dimers [29,30]. We combine g-C_3N_4 with $FePcCl_{16}$ by axial coordination to improve the photo-assisted catalytic oxidation activity with the generation of anchored Fe(IV)═O by H_2O_2 activation. Such a photo-assisted AOPs can generate anchored species with a high visible-light-assisted catalytic oxidative activity and minimize the possibility of autooxidation.

The g-C_3N_4-IMD-$FePcCl_{16}$ photocatalysts have been fabricated by imidazole-functionalized g-C_3N_4 and coordinated with $FePcCl_{16}$, which is an extension of our previous study. Carbamazepine (CBZ) is a prevalent pharmaceutical in effluents worldwide and is resistant to degradation in sewage treatment or in ecological environments. Therefore, CBZ has been selected as a model in this study [31,32]. The g-C_3N_4-IMD-$FePcCl_{16}$ composites can activate H_2O_2, and exhibit enhanced visible-light-assisted catalytic performance over a wide range of contaminants. From this point of view, a reasonable design and construction of a system based on anchored active species is an effective method for the development of visible-light-assisted catalysts with a high efficiency. The possible generation of reactive species was detected by electron paramagnetic resonance (EPR) and gas chromatography/mass spectrometry (GC–MS). High-definition mass spectra (HDMS) analyses were used to explain the CBZ degradation pathway under visible-light irradiation.

2. Experimental

2.1. Materials and reagents

Imidazole was from the Aladdin Industrial Corporation (Shanghai, China). CBZ, 5,5-dimethyipyrroline-oxide (DMPO), 5-bromovaleryl chloride, 4,5-imdidazoledicarboxylic and dry tetrahydrofuran (THF) were from the Macklin Biochemical Technology Co. Ltd (Shanghai, China). Other chemical compounds were of analytical grade and were used without further purification.

2.2. Preparation of g-C_3N_4-IMD-$FePcCl_{16}$

g-C_3N_4 was obtained according to a previous report [33]. Typically, urea was kept in a crucible and heated to 550 °C at 2.5 °C/min for 3 h. The yellow product was collected without further treatment. $FePcCl_{16}$ was synthesized by a reported method [34]. The g-C_3N_4 and $FePcCl_{16}$ structures are presented in Fig. 1. g-C_3N_4-IMD-$FePcCl_{16}$ photocatalyst was prepared by four procedures with the synthetic process as shown in Scheme S1. First, g-C_3N_4 was placed into ultrapure water and sonicated for a week, before being freeze-dried for further use. The second and third procedures were the same as our previous study to obtain g-C_3N_4-Br and g-C_3N_4-IMD precursors [23]. Then, g-C_3N_4-IMD and $FePcCl_{16}$ were mixed in THF and held in the dark for 6 h. The dispersion was treated by THF and ultrapure water accordingly. The g-C_3N_4-IMD-$FePcCl_{16}$ compound was obtained after freeze-drying. As a reference, a suite of g-C_3N_4-IMD-$FePcCl_{16}$ catalysts with different feed ratios between g-C_3N_4 and $FePcCl_{16}$ were obtained under the same conditions and marked 0%, 1.5%, 3.5% and 5.5%. A mechanical mixing composite (feed ratio of g-C_3N_4 and $FePcCl_{16}$ of 3.5%) was obtained by refluxing in THF, centrifugation, washing with ultrapure water and freeze-drying. The amount of $FePcCl_{16}$ in g-C_3N_4-IMD-$FePcCl_{16}$ (3.5%) as determined by X-ray fluorescence was 1.8814%.

2.3. Characterization

Crystal-phase analyses were carried out on a DX-2700 X-ray diffractometer (XRD) (Dandong Fangyuan, China) equipped with Cu-Kα radiation. Ultraviolet (UV)-visible (vis) diffuse reflection spectra (DRS) were obtained on a UV–vis spectrometer (1J1-0015, HITACHI). Fourier-transform infrared spectroscopy (FTIR) spectrograms were collected by using a Thermo Nicolet 5700 FTIR analyzer. Thermogravimetric analysis (TGA) was performed on a TGA 1 (Mettler Toledo, Switzerland) with the heating rate of 10 °C/min. A Thermo Scientific K-Alpha spectrometer (monochromatic Al Kα, 1486.6 eV) was used for X-ray photoelectron spectroscopy (XPS). High-definition ESI-MS were measured on an ultra-performance liquid chromatography (UPLC)/Synapt G2-S HDMS system (Waters Q-TOF, USA).