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Enhanced decomposition of dyes by hemin-ACF with significant improvement in pH tolerance and stability

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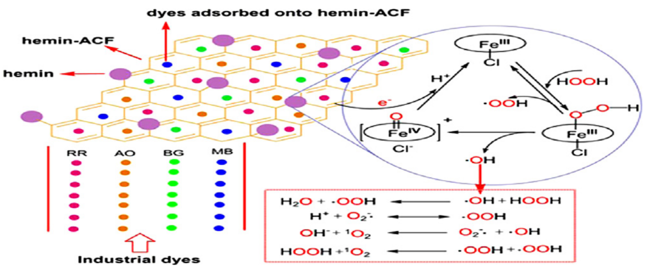
HIGHLIGHTS

- ACF-supported hemin allowed enhanced decomposition of dyes compared with bare hemin.
- Hemin-ACF exhibited excellent pH tolerance over a wide pH range from acidic to alkaline.
- The introduction of ACF accelerated the generation of reactive species by electron transfer from ACF to hemin.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we evaluated a novel heterogeneous catalytic system (hemin-ACF/H_2O_2) based on activated carbon fiber supported hemin for the rapid removal of dyes. Contrast experiments, effects of pH and temperature, and sustained catalytic stability of hemin-ACF for the catalytic decomposition of azo dye RR195 used as a model pollutant were investigated. Surprisingly, the introduction of ACF significantly enhanced the decomposition of dyes by hemin with an obvious improvement in pH tolerance and stability. Inhibition and probe studies combined with electron paramagnetic resonance (EPR) were conducted to ascertain the role of several radicals ($^{\bullet}OH$, $O_2^{\bullet -}/HO_2^{\bullet}$, $^1O_2$ and $Fe^{IV}=O$) on dye degradation. ACF are rich in free electrons, and the π-conjugated macrocyclic structure of hemin may present convenient channels for the transfer of free electrons from the ACF, promoting the generation of hydroxyl radicals and high-valence iron species. These results are promising because they offer new insight for the application of hemin as a catalyzer upon treatment of organic pollutants and contribute to identification of the interaction between support material and catalyzer from a new perspective.

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1. Introduction

Biomimetic catalytic decomposition of organic pollutants has attracted increasing attention over the past few decades [1–4]. Among the various strategies used, metalloporphyrin-based materials have been shown to be the most promising candidates for biomimetic catalytic decontamination [5–7]. Hemin, a biologically active iron-porphyrin compound, is currently considered a potential biomimetic catalyst for the purification of water [8]. However, the direct application of hemin as an oxidation catalyst in aqueous solution is usually challenging due to its molecular aggregation which results in catalytically inactive dimers and its oxidative self-destruction in the oxidizing reaction system [9]. One potential approach to overcome these problems is to synthetically modify the porphyrin structure to achieve a variety of iron porphyrin derivatives for improved catalytic activity and stability [10]. An alternative approach is to immobilize hemin on various supports, such as titanium dioxide [11], montmorillonite [12], β-cyclodextrin [13], hydrogel [14], or graphene [15] to achieve improved stability

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and activity in oxidation reactions in aqueous solutions. Unfortunately, some of these catalysts such as tin porphyrin/TiO_2 [11] showed low efficient activity, while others such as FeP-K10 [12] exhibited unsatisfactory pH tolerance and stability. Moreover, β-cyclodextrin (β-CD)-hemin [13] and hemin-graphene [15] were difficult or inconvenient to separate from the reaction system, which is likely to produce a secondary pollutant. Therefore, the development of novel materials as supports to obtain biomimetic catalysts with improved activity, pH tolerance, stability and separability is highly desired.

Compared to other supports, fibers possess characteristics such as a high specific surface area and a high natural affinity to dyes which occur via physical and chemical interactions. We previously reported that cellulosic fiber-supported metallophthalocyanine allowed enhanced catalytic decomposition of organic pollutants [16]. However, this phase-transfer advanced oxidation process (AOPs) system, Co-TDTAPc-F/H_2O_2, was less efficient for the removal of phenols and dyes under neutral or alkaline conditions. To address these problems, we investigated the use of alternative materials as supports to improve the pH tolerance of the catalyst. Activated carbon fiber (ACF), a turbostratic disordered graphite-like structure, has the potential to further promote the catalytic activity of supported molecular systems such as porphyrin and porphyrin-like species through cation-π or π-π interactions [17,18]. Moreover, it has been intensively used to remove organic pollutants due to its extremely high adsorption capacity and unusual chemical stability [19]. Based on the above considerations, we reported a novel heterogeneous porphyrin-like catalyst, Co-TDTAPc-ACF, which was developed using ACF as a support for metallophthalocyanines [20]. This catalyst exhibited excellent catalytic activity in the oxidative degradation of 4-nitrophenol at neutral pH, thus greatly expanding the adaptable pH range for this metallophthalocyanine catalyst. Nevertheless, this system was almost completely ineffective for the removal of dyes. Therefore, it is essential that highly efficient catalysts are developed to treat dye and phenol pollutants.

Compared with metallophthalocyanine, metalloporphyrin has analogous π-conjugated structures, but exhibits higher activity, and may have potential in the construction of a novel ACF-supported catalyst with higher catalytic activity. Conversely, hemin which is a principal porphyrin, has shown very good efficiency for the activation of hydrogen peroxide in alkene epoxidations [21,22], however, its use in the decomposition of dyes has not yet been adequately explored due to its poor stability in catalytic reactions. Herein, we report a novel highly efficient hemin-ACF catalyst generated by combining ACF with the bioactive hemin through covalent interactions. Compared with free hemin, hemin-ACF exhibited much higher catalytic activity over a wide pH range. A notable advantage of the hemin-ACF catalyst is its stability against decomposition due to self-catalytic oxidation under experimental conditions. More importantly, in contrast to other reports related to ACF, the roles of ACF on the catalytic decomposition of dyes in the system of hemin-ACF/H_2O_2 were further revealed in our research, which is beneficial to understanding the interaction between support material and catalyzer from a new perspective and to gaining further insight into exploring more efficient heterogeneous supported catalysts for environmental remediation.

2. Experimental

2.1. Materials

ACF was obtained from Jiangsu Sutong Carbon Fibers Co. Ltd. (Jiangsu, China). Hemin (98 wt%) was purchased from Aladdin Reagent (Shanghai, China). Tris buffer (99 wt%) was purchased from Shanghai Boao Biotech Co. Ltd. (Shanghai, China). Thionyl chloride, *N*,*N*-dimethylformamide (DMF), methanol, dimethyl sulfoxide (DMSO), dimethyl sulfone ($DMSO_2$), p-phenylenediamine (p-PDA), o-phenylenediamine (o-PDA), 2,3-diamino phenazine (DAPN), benzoquinone, sodium azide (NaN_3) and hydrogen peroxide (30 wt%, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) were used as analytical reagents. C. I. Reactive Red 195 (RR195) was used as the model dye without further purification. Doubly distilled water was used throughout the dye decomposition process. The spin trapping reagent, 5,5-dimethyl-pyrroline-oxide (DMPO) and 2,2,6,6-tetramethyl-4-piperidone (TEMP) were supplied by Tokyo Chemical Industry Co. Ltd., Tokyo, Japan). All other chemicals were analytical reagents.

2.2. Catalyst preparation

ACF was subjected to oxidizing, amidating, water washing and drying, and hemin-ACF was prepared by immobilizing hemin to p-phenylenediamine-functionalized ACF through covalent bonding (see Supplementary Material for a detailed description of the process). In the preparation process, o-ACF, p-ACF and hemin-ACF represent oxidizing ACF, p-phenylenediamine-functionalized ACF, and p-phenylenediamine-functionalized ACF supported hemin, respectively.

2.3. Experimental procedure

The binding site between ACF and hemin was investigated using X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD, UK) with Al (mono) Kα irradiation ($h\nu = 1486.6$ eV) at a pass energy of 160 eV (wide scan) and 20 eV (narrow scan), respectively. All binding energy peaks of the XPS spectra were calibrated by placing the principal C 1s binding energy peak at 284.7 eV. The catalytic oxidation of RR195 was carried out in a 40 mL glass beaker while controlling the temperature at 50 °C using a constant temperature shaker water bath (SHA-B, Guowang Laboratorial Equipment Factory, China). A typical reaction mixture contained the following initial concentrations: (a) dye RR195 (50 μM, 20 mL); (b) supported catalyst hemin-ACF (10 g/L, containing 169 μM hemin) or hemin (169 μM); and (c) oxidant H_2O_2 (50 mM). We presumed that the catalytic oxidation of RR195 followed pseudo first-order kinetics. The values of apparent rate constant k_{obs} for the catalytic reaction can be obtained from the slope of the plot of $\ln(C_t/C_0)$ versus time. Electron paramagnetic resonance (EPR) signals of radicals trapped by DMPO were recorded at ambient temperature using a Bruker A300 spectrometer. The settings for the EPR spectrometer were as follows: center field, 3518 G; microwave frequency, 9.77 GHz; modulation frequency, 100 kHz; power, 20.00 mW. The Brunauer–Emmet–Teller (BET) specific surface area, pore volume and mean pore size of the samples were determined using a high speed automated area and pore size analyzer (F-Sorb3400, China).

3. Results and discussion

3.1. Characterization of hemin-ACF

XPS experiments were used to demonstrate the formation of covalent bonds during the fabrication of hemin-ACF. As shown in Fig. 1, the XPS spectra from a wide scan showed a significant decrease of oxygen in p-ACF when compared with o-ACF, indicating that a part of hydroxy in the carboxyl group was consumed by the amidation reaction. When the p-phenylenediamine-functionalized ACF reacted with hemin, a new band of iron and a marked increase of oxygen and nitrogen were detected, suggesting that hemin was supported on p-ACF. Furthermore, as shown in Fig. S1B,

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