



Iron phthalocyanine supported on amidoximated PAN fiber as effective catalyst for controllable hydrogen peroxide activation in oxidizing organic dyes



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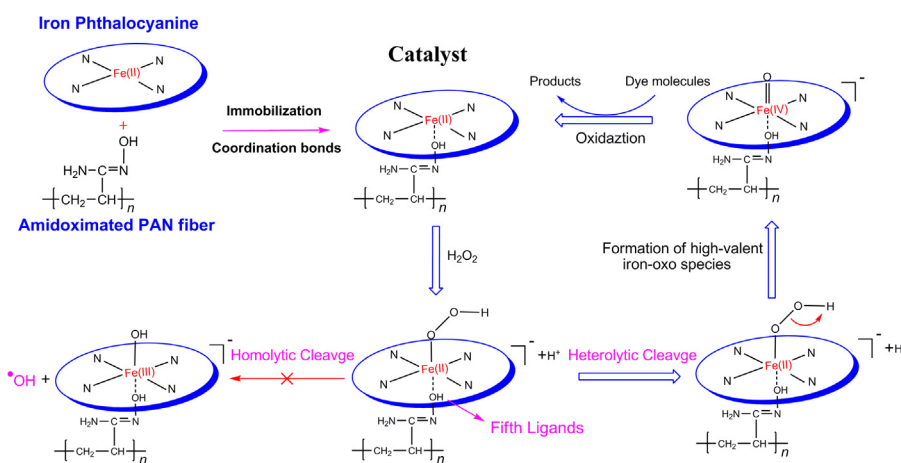
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HIGHLIGHTS

- Amidoximated PAN fiber supported FePc as a bioinspired catalyst.
- The coordination of amidoxime group with FePc as the axial fifth ligand.
- Selective H_2O_2 decomposition via heterolytic cleavage of peroxide O–O bond.
- Dye degradation by high-valent iron-oxo species in this catalytic process.

GRAPHICAL ABSTRACT



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ABSTRACT

Iron(II) phthalocyanine was immobilized onto amidoximated polyacrylonitrile fiber to construct a bioinspired catalytic system for oxidizing organic dyes by H_2O_2 activation. The amidoxime groups greatly helped to anchor Iron(II) phthalocyanine molecules onto the fiber through coordination interaction, which has been confirmed by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and UV–vis diffuse reflectance spectroscopy analyses. Electron spin resonance studies indicate that the catalytic process of physically anchored Iron(II) phthalocyanine performed via a hydroxyl radical pathway, while the catalyst bonded Iron(II) phthalocyanine through coordination effect could selectively catalyze the H_2O_2 decomposition to generate high-valent iron-oxo species. This may result from the amidoxime groups functioning as the axial fifth ligands to favor the heterolytic cleavage of the peroxide O–O bond. This feature also enables the catalyst to only degrade the dyes adjacent to the catalytic active centers and enhances the efficient utilization of H_2O_2 . In addition, this catalyst could effectively catalyze the mineralization of organic dyes and can be easily recycled without any loss of activity.

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1. Introduction

Recently, metallophthalocyanine (MPc) complexes have been extensively studied as mimic enzyme catalysts for activating H_2O_2 , O_2 or other peroxides [1–4], which are widely employed in the elimination of organic contaminants, such as dyes [5,6], phenols [7,8] and sulfides [9]. As an analogue to porphyrin, phthalocyanine compounds are a kind of N_4 -macrocycles with high stability, diverse coordination properties, excellent spectroscopic characteristics and reversible redox chemistry [10]. Nevertheless, the catalytic performance of homogeneous MPc catalyst is limited by the aggregation tendency of phthalocyanine molecules, which would negatively produce catalytically inactive dimers [10]. What is more, the catalyst may also be deactivated by the oxidative self-destruction of MPc molecules during the catalytic oxidation [2]. To solve these problems, numerous support materials have been employed to immobilize MPc molecules to prepare the heterogeneous catalysts, such as zeolites [11], grapheme [12], carbon nanotube [13,14], chitosan [15] and fibrous materials including silk [16,17] and cellulosic [18]. Among these materials, the fibers have the potential to be the ideal candidates because of their unique advantages [16,19,20]: (i) suitable mechanical stability, chemical resistance and excellent flexibility to meet the demands of different reactor geometries; (ii) high affinity towards the organic molecules, and the capability of providing a large contacting surface for the pollutants. In addition, the cellulose fiber support was found to play a pivotal role for enhanced removal of dye pollutants in the MPc activated H_2O_2 system [18]. However, the modification of MPc introducing nitroxyl or sulphonate groups is necessary to immobilize MPc molecules onto the cellulose or silk fiber covalently [16–18], which would increase the treatment cost and cause the catalyst preparation to be more complicated.

For catalytic reactions that employ H_2O_2 as the oxidant, the competition of hemolytic cleavage and heterolytic cleavage of the peroxide O–O bond has been discussed, corresponding to the production of hydroxyl radicals ($\cdot\text{OH}$) and high-valent metal-oxo species, respectively [21]. Both the $\cdot\text{OH}$ and high-valent metal-oxo species have been proved to be most effective in oxidizing organic contaminants. However, the inefficient decomposition of H_2O_2 into H_2O and $\frac{1}{2}\text{O}_2$ often takes place with the hemolytic cleavage of the peroxide O–O bond, and the generated $\cdot\text{OH}$ has shown no selectivity as it can move freely to oxidize any organic matter in aqueous solution and can even destroy the catalysts [22,23]. In contrast, the high-valent metal-oxo species may exhibit higher selectivity since only the substrates adjacent to the catalysts can be oxidized, and the stability of the supported catalysts is also improved by minimizing the possibility of autodecomposition. Therefore, effective strategies for optimizing the MPc catalytic systems should selectively catalyze H_2O_2 decomposition via the heterolytic cleavage of the peroxide O–O bond [24]. The catalytic processes of native enzymes such as peroxidase provide an effective approach to design the MPc catalysts, where the axial fifth ligand was recognized to be a key factor to control the reaction channels [25,26]. Collins has also pointed out that the binding of electron-releasing ligands to the metal ion favored the formation of high-valent metal-based species [22]. Thus, additional ligands have been employed to control the reaction channel of H_2O_2 decomposition [23,27]. Li and co-workers constructed a bioinspired catalytic system using ordered-mesoporous-carbon-bonded cobalt tetraaminophthalocyanine as a catalyst, and the linear dodecylbenzenesulfonate could act as the fifth ligands to induce the heterolytic cleavage of the peroxide O–O bond [23]. In addition, the cellulosic fiber-bonded cobalt phthalocyanine catalyst was also found to be capable of selectively catalyzing the H_2O_2 decomposition with linear alkylbenzene sulfonate as the fifth ligands [27]. Unfortunately, the additives like the sulfonate compounds were necessary for

these catalytic systems, limiting their practical application for most technologies. Thus, finding materials that have suitable structures to coordinate with MPc themselves is more conducive to facilitate the construction of mimic catalytic systems.

Polyacrylonitrile (PAN) fiber is a low cost synthetic fiber and it can be easily modified with hydroxylamine by partial conversion its nitrile groups into amidoxime groups [28–31]. The amidoximated PAN fibers have been widely studied as excellent supports for Fe ions to prepare heterogeneous Fenton catalysts [19,32–36], as the amidoxime groups have shown great ability to coordinate with the metal ions. This feature enables the amidoximated PAN fiber to immobilize MPc molecules through axial coordination bonds without introducing any functional groups onto the MPc molecules. More importantly, the amidoxime groups may act as the fifth ligands of MPc to control the catalytic reaction channels. However, to the best of our knowledge, there are few studies which use modified PAN fiber as the support material for MPc molecules.

In this study, we synthesized a novel bioinspired MPc catalyst by anchoring iron(II) phthalocyanine (FePc) molecules onto amidoximated PAN fiber by the method of dyeing. FePc was selected as the oxidation catalyst mainly due to its outstanding oxygen transfer ability. FePc molecules were found to be anchored onto amidoximated PAN fiber through coordination bonds, and the coordination interaction of FePc with the amidoxime groups was elucidated using several techniques. A widely used dye, Rhodamine B (RhB) is chosen as the main target pollutant to investigate the catalytic properties of the catalysts by activating H_2O_2 . In addition, the degradation of two commercial dyes including the anionic C.I. Reactive Red 195 (RR195) and cationic C.I. Basic Red 29 (BR29) were also examined using the prepared catalyst. The immobilization modes have shown great influence on the reaction channel of FePc molecules, and the amidoxime groups could act as the fifth ligands to promote the heterolytic cleavage of the peroxide O–O bond. The reaction mechanism for this catalytic process is also proposed and discussed based on the electron spin resonance (ESR) results. This research offers a new strategy for designing MPc catalysts with high selectivity towards H_2O_2 activation to oxidize organic pollutants in water.

2. Experimental

2.1. Materials and reagents

The commercial PAN knitting bulky yarns (PAN yarn) that consisted of twisted PAN fibers (the content of acrylonitrile monomer is 86.96%) were obtained from Shanghai Shilin Spinning Corporation. FePc was purchased from Tokyo Kasei Corporation, and Horseradish peroxidase (POD) was obtained from Shanghai Guoyuan Bio Technology Corporation. Hydroxylamine hydrochloride, hydrogen peroxide (30% w/w), *N,N*-Diethyl-*p*-phenylenediamine (DPD), 5,5-Dimethyl-L-pyrroline-N-oxide (DMPO), dimethyl sulfoxide (DMSO) and RhB were of laboratory grade and used without further purification. RR195 and BR29 were purchased as commercial dyes and used after purification by the re-precipitation method. The structures of RhB, RR195 and BR29 are shown in Fig. 1. Double distilled and deionized water was used throughout this study.

2.2. Preparation and characterization of the catalysts

The amidoximated PAN fibers (AO-PAN) with different conversion degree from nitrile groups to amidoxime groups (CP%) were obtained according to the method reported in our previous study [33], and the synthesis of AO-PAN can be described by reaction (1). Subsequently, 0.50 g of AO-PAN was immersed into 150 ml of an aqueous dispersion of FePc, and the mixture was stored in an air-

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