

## Regular Article

# Coordinative integration of copper (II) and iron (II) phthalocyanine into amidoximated PAN fiber for enhanced photocatalytic activity under visible light irradiation

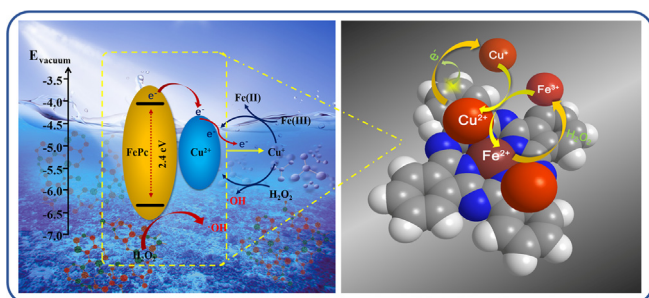


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## GRAPHICAL ABSTRACT



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## ABSTRACT

Metal phthalocyanine (MPC) complexes hold great promise for photocatalysis applications because of their high visible light harvesting efficiency and semiconductive properties. However, the effective development requires the suppression of their rapid charge recombination. Transition metal ions can act as electron traps to enhance the charge separation of semiconductors, but challenges still remain for bimetallic co-catalysis of MPC due to the difficulties in the combination between them. Herein, we proposed a new approach to enable the assisted metal ions to interact with MPC through fibrous support, constructing a novel bimetallic photocatalyst via simultaneously immobilizing iron(II) phthalocyanine (FePc) and Cu(II) onto the surface of amidoximated polyacrylonitrile (PAN) fiber. Taking the photodegradation of organic dyes as model reactions, this bimetallic catalyst achieves much higher photoactivity than that of the monometallic FePc catalyst, and effectively converts surface  $H_2O_2$  into hydroxyl radicals rather than superoxide radicals and high-valent metal-oxo species. The Cu(II) not only enables the transfer of photoexcited electrons from FePc, but also promotes the running of Fe(II)/Fe(III) cycle to boost reactive radicals generation through  $H_2O_2$  activation. The strategy of coupling Cu(II) with MPC through fibrous support provides a facile and promising solution for the advancement of MPC-based photocatalysis via visible light energy.

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## 1. Introduction

Many toxic organic materials, including those found in textile dyeing wastewaters [1], organohalides [2] and phenol [3] are recalcitrant pollutants that are highly resistant to natural degradation.

In this respect, artificial intervention is highly necessary to deal with these environment-related issues. In recent years, photocatalytic oxidation technology has gradually become a promising branch in contaminant treatment, with superiorities like mild reaction conditions, environmentally friendly process and high reactivity. Upon light absorption, photocatalyst transforms into the excited state and thus repeatedly interacts with the reaction partners forming reactive intermediates and regenerates itself after each cycle of such interactions [4]. The reactive intermediates, e.g. hydroxyl radicals ( $\cdot\text{OH}$ ) which possess a redox potential as high as 2.8 eV, have the capacity to degrade most of the organics without selectivity, even microorganisms and viruses [5]. Therefore, the exploration of highly reactive photo-oxidative systems is of great interest for the development of green chemistry. To date, semiconductor photocatalysis in aqueous contaminant elimination may be separated mainly in two categories [6]: one is inorganic semiconductor catalysts, e.g. metal oxides or sulfides; and the other is organic semiconductors or metallorganic compounds [7,8]. Inorganic semiconductors with appropriate structures have been widely reported as photo-induced oxidative catalysts, covering the advantages like high oxidizing capacity, non-toxicity and remarkable chemical stability [9,10]. However, they suffer from low catalytic activity under visible light irradiation due to their intrinsic wide band gap [11], and the difficulties in nano-scaled substrate recycling.

Recently, metallophthalocyanine (MPc) complexes have drawn great attention to construct biomimetic catalysts for environmental remediation [12–15]. As a metallorganic semiconductor, MPc often shows broad spectral response in the red/near-infrared and visible-light region, and the relatively low delocalization energy for the macrocyclic electrons enables it to act as both an electron donor and acceptor. In addition, MPc exhibits high stability, diverse coordination properties and reversible redox chemistry due to its highly conjugated  $18\pi$ -electron system [16,17]. These features impart MPc with great potential to prepare high performance photocatalysts. However, few studies have involved the development of MPc based light-driven catalysts, probably due to their fast charge recombination. During the past decade, numerous supports including graphene [18], carbon nanotubes [19] and fibrous materials [20,21] have been employed for MPc immobilization to construct heterogeneous catalysts, as the homogeneous MPc catalysts have always suffered from their aggregation tendency and self-oxidation by catalytic intermediates [22,23]. Among these supports, fibrous materials have been considered as ideal candidates exhibiting particular advantages, such as suitable mechanical and chemical stability, low cost and flexibility in modeling different shapes [24–26]. In our previous report, amidoximated polyacrylonitrile (PAN) fiber has been used to synthesize biomimetic catalysts by anchoring iron phthalocyanine (FePc) through axial coordination bonds [27], due to its high affinity for metal ions and excellent chemical/physical stability [28,29]. More importantly, the amidoximated PAN fiber can induce strong absorbance in the visible region by coordinating with the metal ions, imparting the catalysts with high potential to utilize visible light [30,31]. Previous studies have found that visible light irradiation significantly enhanced the catalytic activity of amidoximated PAN fiber supported Fe(III) catalyst in organic dyes degradation [32–34]. Moreover, we have also designed a visible light-driven catalyst by immobilizing Fe(II) 2,2'-bipyridine onto amidoximated PAN fiber [35]. However, FePc, with a bandgap of 2.4 eV [36], did not exhibit high efficiency for visible light utilization when supported on amidoximated PAN fiber, where the enhanced catalytic activity mainly originated from the photosensitized dyes [27].

On the other hand, transition metal ions adsorbed on the surface of semiconductors have exhibited a certain ability to trap the photo-induced electrons [37–39], which may greatly enhance

the photocatalytic activity of FePc by hindering the charge recombination. Unfortunately, due to difficulties in achieving combination between FePc and other transition metal ions, there are very few studies reported on the bimetallic co-catalysis with FePc. Herein, we proposed a new approach to enable the assisted metal ions to interact with FePc through the fibrous support, constructing a novel bimetallic photocatalyst via simultaneously immobilizing FePc and Cu(II) on the amidoximated PAN fiber. The as-prepared photocatalyst exhibits highly efficient and universal activity for photodegradation of several organic dyes by  $\text{H}_2\text{O}_2$  activation under visible light irradiation. More importantly, compared to the monometallic FePc supported PAN fibrous catalyst, the dye degradation rate via this bimetallic photocatalytic system was greatly improved, which corresponds to a high utilization of visible light. In addition, the Cu(II) also significantly changed the photocatalytic mechanism of this bimetallic catalytic system, whereby the main active species generated is  $\cdot\text{OH}$ , in contrast to high-valent iron-oxo species that are generally involved. The significant photoactivity enhancement could be attributed to a synergistic effect between FePc and Cu(II) to produce reactive radicals as following: (1) Cu(II) traps the photo-induced electrons from the photoactivated FePc to enhance the charge separation, and the formed cationic radical  $^*\text{FePc}$  can react with surface  $\text{H}_2\text{O}_2$  to produce  $\cdot\text{OH}$ . (2) the generated Cu(I) reacts with Fe(III) to accelerate the regeneration of Fe(II), which can activate  $\text{H}_2\text{O}_2$  to provide  $\cdot\text{OH}$  through the Fenton reaction. (3) the generated Cu(I) directly reacts with  $\text{H}_2\text{O}_2$  to generate  $\cdot\text{OH}$  through a Fenton-like reaction. The proposed Cu(II) assisted FePc photocatalytic system may open a new route for the design of higher efficiency MPc-based visible light induced photocatalysts.

## 2. Experimental section

### 2.1. Materials and reagents

The commercial PAN knitting bulky yarns that consisted of twisted PAN fibers (the content of acrylonitrile monomer: 86.96%) were obtained from Shanghai Shilin Spinning Corporation. FePc (95%) was purchased from Beijing Bailingwei Technology Co. Ltd. Hydroxylamine hydrochloride, sodium hydroxide, copper sulfate, hydrogen peroxide (30%, w/w), 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO), dimethyl sulfoxide (DMSO), Rhodamine B (RhB) and methylene blue (MB) were of analytical grade. C.I. Basic Red 29 (BR29), Reactive Red 195 (RR195) and Acid Black 234 (AB234) were purchased as commercial dyes and used after purification by the re-precipitation method. The structures of these dyes are shown in Fig. S1.

### 2.2. Preparation and characterization of the catalysts

PAN fibers were chemically modified with hydroxylamine hydrochloride (Eq. (1)) to obtain the amidoximated PAN fibers (AO-PAN) using method as our previous report [27], and the conversion degree of nitrile groups to amidoxime groups was controlled at  $60 \pm 0.5\%$  in all samples [34]. To synthesize the bimetallic catalyst, typically, FePc was placed into 100 ml of copper sulfate aqueous solution, the mixed suspension vigorously stirred for 20 min and then transferred into a Teflon-lined stainless steel container. Subsequently, 1.0 g of AO-PAN was immersed into the above container, and the mixture was treated at  $80^\circ\text{C}$  for 60 min under continuous agitation using an Ahiba Nuance dyeing machine (Datacolor International). Then the fibrous materials were filtered, washed and dried under vacuum to obtain the Cu/Fe bimetallic supported PAN fibrous catalyst (CuFePc-PAN). For comparison, the reaction of copper sulfate solution and FePc suspension with

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