



Enhanced generation of reactive oxygen species for efficient pollutant elimination catalyzed by hemin based on persistent free radicals



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ABSTRACT

Porphyrin has received increasing interest in the catalysis field due to their excellent catalytic performance, nevertheless, the development of highly efficient porphyrin catalysts is still a significant challenge. In this work, a representative of persistent free radicals (PFRs), multiwalled carbon nanotubes (MWCNTs), was innovatively employed to construct an outstanding catalytic system, hemin-MWCNTs/H₂O₂. The introduction of MWCNTs greatly enhanced the catalytic activity of hemin, representing about 61 times higher reaction rate constant with the dye of methylene blue (MB) as probe compound, which was attributed to more reactive oxygen species (ROS) (*OH and hemin (Fe^{IV}=O)) generation. When MWCNTs were introduced to hemin/H₂O₂ system, the decrease of PFRs concentration in MWCNTs were observed with larger number of trapped electrons, indicating that PFRs might transfer electrons to hemin, thus speeding up the reaction rate-determining step of hemin (Fe^{III}) to hemin (Fe^{II}), resulting in enhanced production of *OH and hemin (Fe^{IV}=O). This study initiates an up-to-date research domain of PFRs-enhanced catalysis, paving the avenue toward developing robust processes for the efficient generation of ROS for applications in catalysis field.

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1. Introduction

Hemin is a biologically active iron-porphyrin compound with peroxidase-like activity and high catalytic performance, which has attracted considerable attention in the catalysis field [1–4]. However, direct application of hemin as molecular catalysts is still of significant challenge due to its molecular aggregation in aqueous solution to form catalytic inactive dimers, which causes passivation of its catalytic activity [5–7]. To overcome these problems, two alternative strategies have been formulated. One strategy is to decorate the porphyrin macrocycle with bulky functional groups to protect the iron porphyrin centers [8]. This strategy, however, is limited by the difficulty of synthesizing these porphyrins [9]. Another alternative strategy is to use high surface area materials, such as titanium dioxide [10], montmorillonite [11], β-cyclodextrin [12], hydrogel [13] to support hemin to achieve improved stability and activity [14]. Although these hemin-based catalysts have

shown better catalytic activity than free hemin in aqueous solutions, which is, however, still not high enough.

It is noteworthy that the catalytic activity of hemin mainly depends on the behavior of electron donation and acceptance between central iron and reactants. Therefore, changing the rate of electron transfer during the oxidation process might influence the catalytic performance of hemin. Recently, it has been reported that some resonance-stabilized radicals, also referred as persistent free radicals (PFRs) could act as electron donor, which can sustainably provide electrons to other electron-acceptors such as various oxidants and higher valent metals [15,16]. This excellent property might feature the capability to accelerate some important catalytic redox processes such as iron-mediated cycle involved the intrinsic drawback of slow iron reduction rate to generate ROS. Therefore, PFRs may find promising application in enhancing the catalytic activity of hemin.

Some studies have suggested that carbonaceous materials contain PFRs, which gradually received attention in catalysis field [17,18]. Therefore, the introduction of carbonaceous materials to hemin system may accelerate electron transfer to hemin to promote the catalytic efficiency due to the role of PFRs. Among carbonaceous materials, carbon nanotubes (CNTs) pos-

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sess outstanding physical properties, excellent chemical stability, mechanical strength and high surface area [19–21]. Moreover, unsaturated π -system of CNTs could enhance the efficiency of electron transfer between CNTs and hemin due to π -stacking interactions [22]. Herein, multiwalled carbon nanotubes (MWCNTs), a representative of PFRs, were used to support hemin covalently to obtain a heterogeneous catalyst (hemin-MWCNTs). To our best of knowledge, reports about hemin-MWCNTs directly as oxidation catalysts and a detail understanding of the role of PFRs in MWCNTs is lacking.

The aim of this study was to investigate the catalytic activity of hemin-MWCNTs, and to reveal the role of PFRs during the catalytic oxidation process. Methylene blue (MB) was selected as a probe compound to evaluate the catalytic activities of hemin-MWCNTs with H_2O_2 as oxidant. Electron paramagnetic resonance (EPR) technology combined with different scavengers, such as radical scavenger, electron capture agents were employed to investigate the mechanism of the positive effect of PFRs in MWCNTs. The findings of this study provide a new insight into the PFRs-enhanced catalytic performance and initiates an inspiring research domain of PFRs in catalysis field.

2. Experimental

2.1. Materials and reagents

MWCNTs (lot no. OEAKE, 40–60 nm diameter) were Tokyo Chemical Industry Co., Ltd. Hemin (98 wt%) was purchased from Aladdin Reagent (Shanghai, China). Thionylchloride, *N,N'*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *p*-phenylenediamine (*p*-PDA), *o*-phenylenediamine (*o*-PDA), 2,3-diamino phenazine (DAPN), hydrogen peroxide (30 wt%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were used as analytical reagents. Methylene Blue (MB), Basic Brilliant Green (BG), Acid Red 1 (AR1), Acid Orange 7 (AO7), Reactive Red X-3B (RR X-3B) and Reactive Brilliant Red 3BF (RR 3BF) were used as the model contaminants without further purification. The spin trapping reagent, 5,5-dimethyl-pyrroline-oxide (DMPO) was supplied by Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. Doubly distilled water was used throughout the contaminants decomposition process.

2.2. Catalyst preparation

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

2.3. Analytical methods

The chemical structures of hemin and hemin-MWCNTs were analyzed with X-ray diffraction (XRD) (see Supplementary material for details). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD analyzer, and the standard Mg K α (1256.6 eV) X-ray source operated at 10 mA and 15 kV. All binding energies were referenced to Au (4f_{7/2}) at 84 eV. Catalytic oxidation of dyes were carried out in a 20 mL glass beaker at 50 °C using H_2O_2 as oxidant under shaking condition. A typical reaction mixture contained the following initial concentrations: (a) dyes (50 μM , 20 mL); (b) supported catalyst hemin-MWCNTs

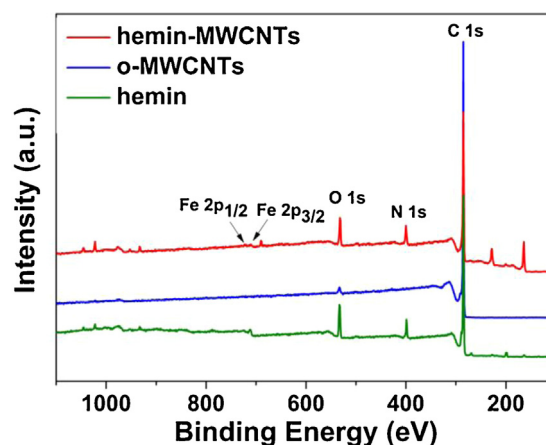


Fig. 1. XPS spectra of hemin, *o*-MWCNTs and hemin-MWCNTs.

(1 g/L, containing 61 μM hemin) or hemin (61 μM); and (c) oxidant H_2O_2 (50 mM). At given time-points, samples were passed through 0.22 μm pore size cellulose filters and analyzed immediately with a UV-vis spectrometer (Hitachi U-3010) by measuring the removal of dyes at the maximal wavelength. EPR signals of radicals trapped by DMPO were recorded at ambient temperature on a Bruker A300 spectrometer. The settings for the EPR spectrometer were as follows: center field, 3520 G; sweep width, 100 G; microwave frequency, 9.77 GHz; modulation frequency, 100 kHz; power, 20.00 mW. The total number of electrons released during the oxidation in the system was detected by the ABTS method.

3. Results and discussion

3.1. Characterization of hemin-MWCNTs

In this work, the bonding forms of hemin-MWCNTs were characterized using X-ray diffraction XRD (for detail, see Supplementary material) and X-ray photoelectron spectroscopy (XPS).

As shown in Fig. 1, compared with the spectrum of *o*-MWCNTs, the new bands of iron and nitrogen in the spectrum of hemin-MWCNTs were detected with a marked increase of oxygen. Moreover, according to full half-widths of the N1s peaks in hemin (Fig. 2A), N1s peaks occurring at 398.4 eV and 400.1 eV were attributed to four chemically equivalent N atoms, which binded to the central iron atom in the porphyrin ring [23]. No N1s signal was detected in *o*-MWCNTs (Fig. 2B); nevertheless, the spectra of N1s presented a different aspect when hemin was immobilized on MWCNTs. Besides the peaks of N1s (398.4 eV) and (400.1 eV) in hemin, the peak at 401.4 eV (Fig. 2C) might be explained by the nitrogen of amide group ($-\text{NH}-\text{CO}-$) being used for bonding between the carboxyl and substituted amino ($-\text{NH}_2$) groups. Furthermore, the O1s peaks gave coincident information about the bonding environment of hemin-MWCNTs (Fig. 3). For *o*-MWCNTs, the 531.7 eV peak and the 533.3 eV peaks were assigned to oxygen in a C=O double bond and a single bond of the hydroxyl group (C–O–H) (Fig. 3A), respectively. However, the proportion of C–O–H peaks was much smaller in hemin-MWCNTs (Fig. 3B), indicating that a part of the C–O–H was consumed by the amidation reaction. These results suggested that hemin was supported on MWCNTs covalently via amide linkage.

3.2. Oxidative removal of MB

Methylene blue (MB), a representative cationic dye, is widely used as a stain by many industries and the chemical structure of MB are shown in Fig. S3. In this study, MB was selected as

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