

Supplementary Information

The coupling of hemin with persistent free radicals induces nonradical mechanism for oxidation of pollutant

Bin Jiang, Dejun Dai, Yuyuan Yao,* Tiefeng Xu, Renhong Li, Renjie Xie, Likun Chen, Wenxing Chen

National Engineering Lab of Textile Fiber Materials & Processing Technology (Zhejiang),
Zhejiang Sci-Tech University, Hangzhou 310018, China

*Corresponding author: Email: yyy0571@126.com Tel.: +86-571-86843810; Fax: +86-571-86843255.

Experimental Section

Materials. 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 sulf-oxide (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. 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. All other chemicals were analytical reagents.

Catalyst preparation

Preparation of o-MWCNTs. Raw MWCNTs were immersed in a 37% (v/v) HCl and sonicated for 30 min to remove any metal catalyst particles. The purified MWCNTs were oxidized at room temperature with 6 M HNO₃ under sonication for 12 h, and washed with deionized water until the pH value was close to 7, obtaining carboxylic acid-functionalized MWCNTs (o-MWCNTs).

Preparation of SOCl₂-modified MWCNTs. The carboxyl-terminated MWCNTs were then refluxed in excess SOCl₂ at 80 °C for 12 h. The excess SOCl₂ was washed by distillation, and SOCl₂-modified MWCNTs was obtained by drying the resulted product under vacuum.

Preparation of p-MWCNTs. The solid reacted with p-phenylenediamine in dry degassed DMF mixed with several drops of pyridine at 130 °C for 8 h. The excess p-phenylenediamine was removed completely by washing with DMF, anhydrous ethanol, distilled water for several times.

Drying this remaining product in vacuum, resulting in the p-phenylenediamine-functionalized MWCNTs (p-MWCNTs).

Preparation of SOCl₂-modified hemin. The hemin was refluxed in excess thionyl chloride at 75 °C for 24 h. The remaining black solid after filtration was washed by distillation, obtaining SOCl₂-modified hemin.

Preparation of hemin-MWCNTs. The p-MWCNTs reacted with SOCl₂-modified hemin in dry degassed DMF mixed with several drops of pyridine at 100 °C for 24 h. The excess SOCl₂-modified hemin was removed completely by washing with DMF, distilled water for several times until the pH value was close to 7. The hemin-MWCNTs was obtained by drying the remaining product at ambient temperature. The content of hemin in hemin-MWCNTs was calculated to be 61 μmol/g, using the iron content in hemin-MWCNTs measured by atomic absorption spectrometer.

Experimental procedure. The catalytic oxidation of various contaminants were carried out in a 40-mL glass beaker while controlling the temperature at 25 °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 (50 μM, 20 mL); (b) supported catalyst hemin-MWCNTs (0.7 g/L, containing 84.5 μM hemin) or hemin-ACF (0.5 g/L, containing 84.5 μM hemin) with or without AA (15 mM); (c) oxidant H₂O₂ (25 mM). 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 were recorded at ambient temperature using a Bruker A300 spectrometer (Germany). 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. Before the EPR test, the solid samples (hemin-MWCNTs, hemin-ACF) were collected and dried under vacuum.

Decomposition rate

The decomposition rate can be represented as follows:

$$\text{The residual of dyes} = C_t/C_0 * 100\% = A_t/A_0 * 100\%;$$

where C_0 is the initial concentration of target dyes and C_t is the actual concentration of target dyes after reaction time t , and A_0 is the initial absorbance of target dyes and A_t is the absorbance of target dyes after reaction time t .

Discussion

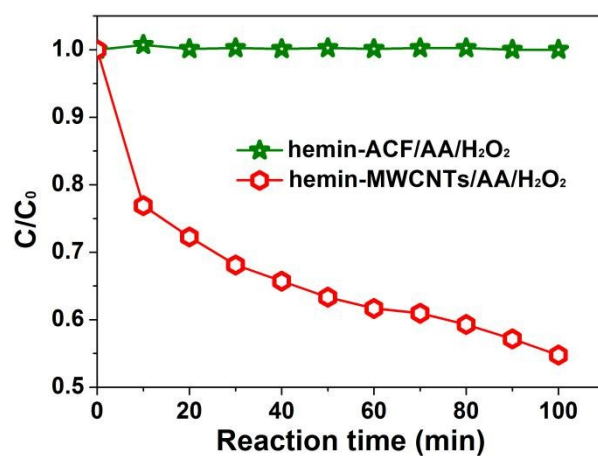
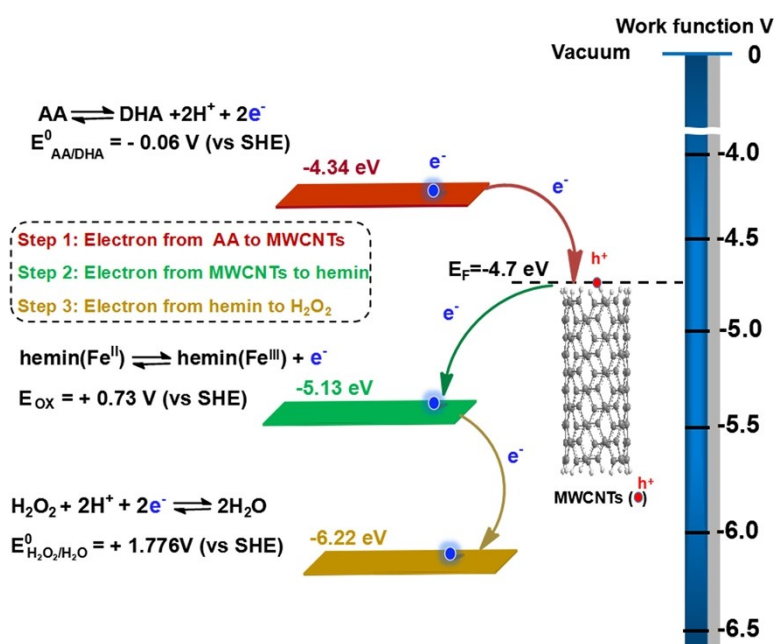


Fig. S1. The concentration change of RR M-3BE in ethanol solution in two systems.



Scheme S1. Schematic illustration of the hemin-MWCNTs/AA/H₂O₂ catalytic system involving electron transfer from low to high electrochemical potential.

The work function of MWCNTs has been determined to be approximately -4.7 eV, which is related to the Fermi energy (E_F) of metallic MWCNTs or is defined as the HOMO energy of semiconducting MWCNTs.¹ The oxidation potential of hemin(E_{ox}) was +0.97 V.² In addition, the

HOMO level of hemin (E_{HOMO} (hemin)) was -5.13 eV based on the empirical formula $E_{\text{HOMO}} = -e$ ($E_{\text{ox}} + 4.4$) (eV).³ In the hemin-MWCNTs/AA/H₂O₂ system, the high reduction potential (+1.8 V vs. SHE)⁴ enabled H₂O₂ to oxidize hemin(Fe^{II}) to hemin(Fe^{III}) via axial coordination between H₂O₂ and the central iron ion.⁵ The MWCNTs could be rapidly reduced by AA (oxidation potential: 0.06 V),⁶ resulting in the generation of •Asc-. Finally, MWCNTs could also provide electrons for the reduction of hemin(Fe^{III}) to hemin(Fe^{II}), resulting in hole generation.

References:

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