Facile preparation and high performance of magnetically separable metalloporphyrin

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Jieying Jing [a], Yang Zhang [a], Jie Feng [a], Wenying Li [a,*], William W. Yu [a,b,*]

[a] Key Laboratory of Coal Science and Technology and Training Base of State Key Laboratory of Coal Science and Technology, Taiyuan University of Technology, Taiyuan 030024, China
[b] Department of Chemistry and Physics, Louisiana State University Shreveport, LA 71115, USA

HIGHLIGHTS

- Magnetically separable metalloporphyrin (M-FeTCP) was prepared via covalent conjugation.
- M-FeTCP exhibited high capability in dye decoloration comparing to free FeTCP.
- M-FeTCP could be easily recovered using a permanent magnetic bar.
- M-FeTCP possesses stable recycle performance due to the covalent bond linkage.

GRAPHICAL ABSTRACT
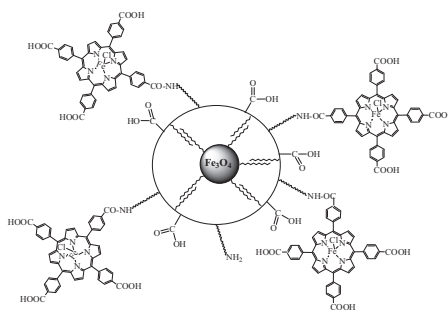
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ABSTRACT

Metalloporphyrins possess promising prospect in the oxidative electron-transfer systems. We report here the controllable synthesis of magnetically separable metalloporphyrin via a covalent bonding between Fe(III) meso-Tetra (4-carboxyphenyl) porphine chloride and magnetic nanoparticles. The as-synthesized magnetically separable metalloporphyrin showed 69.02% decoloration efficiency for Acid orange 7. It could be readily recovered from the reaction solution by using a permanent magnetic bar and its decoloration activity remained 95.64% after three cycles of repetitive uses. The stable recycle performance was ascribed to the covalent bond linkage between the metalloporphyrin molecules and the small sized, non-aggregation, and freely dispersed nanoparticles.

1. Introduction

Degradation of dye wastewater has attracted scientific attention for decades because dyes are widely used in many fields such as textile, paper production, hair coloring, food technology, and the effluents impact the existing treatment plants and water quality [1–3]. Due to its hydrolytic stability, acidic pH and high molecular weight, the environmental persistence and fate of azo dyes are of particular interest because their toxicity, potential carcinogenic nature and non-biodegradation constitute a major threat to the ecosystem. Therefore, it is a challenge to achieve an effective removal of azo dyes from wastewater to minimize their risk and meet the rapidly growing water demand.

Considering that a majority of azo dyes contain oxidizable groups, different methods for azo dye treatment have been investigated such as traditional oxidation [4] and photocatalysis [5–8]. But there is complementary interest in developing other techniques for azo dye degradation. Currently, much effort has

* Corresponding authors at: Key Laboratory of Coal Science and Technology, Training Base of State Key laboratory of Coal Science and Technology, Taiyuan 030024, China. Tel./fax: +86 351 6018453 (W. Li). Department of Chemistry and Physics, Louisiana State University Shreveport, LA 71115, USA. Tel:. +1 318 797 5087; fax: +1 318 797 5090 (W.W. Yu).
E-mail addresses: goatwing2010@gmail.com (W. Li), wyu6000@gmail.com (W.W. Yu).

been devoted to develop new homogeneous photocatalyst based on porphyrin or metalloporphyrin because of their significant roles in oxidative electron-transfer systems [9–13]. Moreover, due to its simulation of cytochrome P-450, metalloporphyrin usage might lead to more selective and "cleaner" processes.

However, the practical application of the homogeneous metalloporphyrin photocatalysts was restricted by its poor stability and limited reuse. The poor stability mainly derived from the self-destruction of metalloporphyrin, and the limited reuse was due to the difficulty in recovering metalloporphyrin from the reaction media. To overcome this problem, various physical and chemical approaches including ion exchange, encapsulation, inorganic support post-modification have been developed to immobilize metalloporphyrins on solid materials such as silica [14], organic polymers [15], zeolites [16], and clays [17], and the obtained supported metalloporphyrins were widely investigated as catalysts. By utilizing the immobilization, the recovery of the metalloporphyrin catalysts from reaction media is easier, but the recovered catalysts often accompany the loss of reactivity, mainly due to the loss of the metalloporphyrin catalysts and the support effects, which are related to the specific surface area of the supports and the physical or chemical interaction between metalloporphyrins and supports.

Magnetic separation is an attractive method for recycling [18–22]. Some investigations have been conducted on synthesizing magnetically separable metalloporphyrin [23–27]. Poursaberi et al. synthesized zirconium-metalloporphyrin grafted Fe_3O_4 nanoparticles for fluoride removal [23]. Fu et al. copolymerized styrene with metalloporphyrins in the presence of Fe_3O_4 magnetic fluid to form magnetic polymer microspheres and applied the catalyst to hydroxylate cyclohexane with molecular oxygen [24,25]. Liu et al. prepared a magnetic nanocomposite-bonded metalloporphyrin by silanation, and demonstrated its catalytic activity and recyclability in the cyclohexane oxidation with iodosylbenzene [26,27]. However, these studies mainly focus on the activity evaluation and the optimization of reaction operational conditions. Limited information is available on the controllable conjugation synthesis of magnetically separable metalloporphyrin, which determine the strength of bonding force between metalloporphyrin and magnetic nanoparticles, affecting the stability and reuse of the obtained metalloporphyrin.

In this present work, we employed carbodiimide activation approach to controllably prepare magnetically separable metalloporphyrin by forming a strong covalent bond. Fe(III) meso-Tetra (4-carboxyphenyl) porphine chloride ($C_{48}H_{28}ClFeN_4O_8$, FeTCP) was chosen as a model catalyst to verify the feasibility of this approach. Coupling agent dosage and magnetite nanoparticles concentration was investigated to adjust the conjugation efficiency and Acid orange 7 (a typical model of azo dye) decoloration reaction was used to evaluate the activity of the as-synthesized magnetically separable metalloporphyrin. The magnetic material used in this work was nanosized magnetite (Fe_3O_4) particles. These magnetically responsible super small carriers were different from traditional solid supports and other magnetic particles, because they were free-standing and no aggregation in solution. Thus the conjugated metalloporphyrins were minimally affected by these nanoparticles and they preserved their original performance even after multiple recycling.

2. Experimental

2.1. Materials

Metalloporphyrin Fe(III) meso-Tetra (4-carboxyphenyl) porphine chloride (FeTCP) was purchased from Frontier Scientific. 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC), N-hydroxysulfosuccinimide sodium salt (Sulfo-NHS), hydro-

gen peroxide solution (H_2O_2, 35%), tris(hydroxymethyl)aminomethane, and Acid orange 7 were purchased from Sigma–Aldrich. FeO(OH), oleic acid, 1-octadecene, poly(maleic anhydride-alt-1-octadecene) (PMAO, Mn = 30,000–50,000), and chloroform ($CHCl_3$) were purchased from Aldrich. NH_2-PEG-NH_2 (Mw = 6000) was purchased from RAPP Polymere. pH 6.8 buffer powder (the main components were NaCl, KCl, Na_2HPO_4, KH_2PO_4) was purchased from Fisher Scientific and the buffer solution was made to contain $0.10\ mol\ L^{-1}$ total salts. Ultrapure water with resistivity of $18.20\ M\Omega\ cm$ from Milli-Q Plus (Millipore) was used for the preparation of all aqueous solutions. All chemicals were used as received.

2.2. Synthesis of amino-functionalized magnetite nanoparticles

Monodisperse magnetite (Fe_3O_4) nanoparticles were synthesized via organic thermal decomposition reported by Yu et al. [28,29], Typically, a mixture of 0.180 g FeO(OH) fine powder (2 mmol), 2.820 g oleic acid (8 mmol) and 5.000 g 1-octadecene was heated under stirring to 320 °C and kept at this temperature for 60 min, obtaining the Fe_3O_4 nanoparticles dispersed in organic solution (Fig. 1A). PMAO reacted with NH_2-PEG-NH_2 through the anhydride and NH_2 groups to form PMAO-PEG-NH_2 (Fig. 1B). Then the purified Fe_3O_4 nanoparticles in $CHCl_3$ were mixed with the predetermined amount of PMAO-PEG-NH_2 and the resultant solution kept stirring at room temperature for 60 min. Next, 50 mL water was added to the mixture and rotavap was employed to slowly evaporate $CHCl_3$ at room temperature, resulting in a clear black solution. The obtained black solution was purified to remove excess polymer by ultracentrifugation (41,000 rpm, 20 °C for 2 h). Ultrapure water was used to redisperse the Fe_3O_4 nanoparticles again and the ultracentrifugation process was repeated twice to get purified aqueous Fe_3O_4 nanoparticles with amino functional groups (Fe_3O_4–NH_2, Fig. 1C).

2.3. Synthesis of magnetically separable metalloporphyrin

Magnetically separable metalloporphyrin was synthesized by covalently bonding FeTCP to the surface of Fe_3O_4–NH_2 nanoparticles through an EDC-mediated reaction in the presence of sulfo-NHS in pH 6.8 buffer solution (the conjugation process for FeTCP bonding to Fe_3O_4–NH_2 nanoparticles is shown in Fig. 2). Typically, a certain amount of EDC and sulfo-NHS was added to FeTCP solution, and the obtained mixture was continually stirred for 20 min to activate the carboxylic group of FeTCP at room temperature. Then Fe_3O_4–NH_2 solution with certain concentration was added. Mix the solution well and allow it to proceed for 2 h at room temperature. Finally the resultant solution was purified via centrifugation (6000 rpm, 25 min). The final product was dispersed in 2 mL pH 6.8 buffer solution. Fig. 1D illustrates the formed magnetically separable metalloporphyrin (M-FeTCP).

2.4. Characterization

Transmission electron microscopy (TEM) images were taken by a JEOL 2100 field emission TEM operating at 200 kV. A Rigaku Geigerflex X-ray diffractometer (XRD) with Cu Kα radiation (λ = 0.154 nm) was used to characterize the crystallographic structure of the as-synthesized Fe_3O_4 nanoparticles. A scan rate of 0.034 °/s was applied to record the pattern in the 2θ range of 20°–80°, and the accelerating voltage and current were 40 kV and 40 mA, respectively. Infrared spectra were collected on a Nicolet Fourier transform infrared spectrometer (FTIR) using KBr pellets in the wavenumber range of 4000–650 cm^{-1}. The concentration of Fe_3O_4–NH_2 nanoparticles was determined by inductively coupled plasma mass spectrometer (ICP-MS, Perkin Elmer Nexion 300).