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Preparation of metallophthalocyanine functionalized magnetic silica nanotubes and its application in ultrasound-assisted oxidative desulfurization of benzothiophene

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ABSTRACT

In this study, the preparation and catalytic application of tetra-substituted carboxyl iron phthalocyanine (FeC_4Pc)-loading magnetic silica nanotubes (MSNTs) in oxidative desulfurization (ODS) of benzothiophene was investigated. The resulting materials FeC_4Pc-MSNTs integrate the advantages of silica nanotubes and superparamagnetic characteristics, which exhibited excellent catalytic activity and reusability. Under the best operating condition for the catalytic oxidative desulfurization, the sulfur content in model oil was reduced from 600 ppm to 35 ppm with 94% of total sulfur. Our work herein reveals that the surface functionalized MSNTs will be a promising platform as catalyst carriers.

1. Introduction

Nowadays, increasing attention has been paid to the environment issue caused by sulfur compounds in transportation fuels which is the main source of SO_x in air [1]. Oxidative desulfurization (ODS), an alternative or complementary technology to hydrodesulfurization for deep desulfurization, has been widely studied in recent years [2]. Different supported catalysts compound with H_2O_2 have been used in the oxidation of the organosulfur compounds, such as $H_2O_2/Mo/\gamma\text{-}Al_2O_3$ [3], H_2O_2/Ti-HMS [4], and H_2O_2/Fe/activated carbon [5]. Due to the bulky size of some refractory sulfur compounds (eg.: benzothiophene, dibenzothiophene and their alkyl-derivatives), materials with relatively lager porous structure as supports are thought to be best suited for ODS than conventional microporous solids. With the development of nanotechnology, nanomaterials as promising supported materials have found increasing applications in modern industry applications. Among them, silica nanotubes (SNTs) are attracting a great deal of attention due to their fundamental significance and potential applications in various areas.

SNTs have attracted special interest because of their easy surface functionalization, colloidal suspension formation, and hydrophilic nature [6]. The unique, hollow inner voids of nanotubes allow for filling with species ranging from large polymers to small molecules to meet different requirement [7,8]. And by combining the attractive tubular structure of silica nanotubes with magnetic properties, magnetic silica nanotubes (MSNTs) not only have all the advantages of silica nanotubes, but also have the potential to be separated from solution by external magnetic field [9,10]. It is well known that metallophthalocyanines have been used as an efficient biomimetic catalysts for the oxidation, reduction and other reactions because of their chemical and thermal stabilities and also their rather cheap and facile preparation in large scale [11–14]. According to our previous work [15], the multifunctional nanotubes supported metallophthalocyanine material was expected to be a useful catalyst for ODS process. However, the reports on the applications of these MSNTs in catalytic chemistry are rare.

In this work, the direct preparation of surface amino-functionalized MSNTs, the covalent attachment of FeC_4Pc on the surface of amino-functionalized MSNTs and its application as a new catalyst for the ultrasound-assisted ODS with the viewpoint of green chemistry is reported. The physicochemical properties, catalytic performance and reusability of FeC_4Pc-MSNTs were studied. It reveals that FeC_4Pc supported on MSNTs

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exhibits a high ODS activity because the unique silica surface chemistry of MSNTs provided a benign microenvironment for catalytic reaction.

2. Experimental

2.1. Materials

A commercially available AAO membrane with a diameter of 47 mm and a quoted pore diameter of 200 nm was purchased from Whatman. Tetraethoxysilane (TEOS), 3-aminopropyltriethoxysilane (APTEOS) and ethyl-[3-(dimethylamino) propyl]–carbodiimide hydrochloride(EDC) were purchased from Aldrich. *N*-hydroxysuccinimide (NHS) was purchased from Sigma. FeC_4Pc were obtained from Sigma. Hydrogen peroxide solution was prepared by dilution of 30% aqueous solution and standardized by titration with the standard solution of potassium permanganate. All other chemicals were of analytical-reagent grade and used without further purification.

2.2. Synthesis

2.2.1. Preparation of amino modified MSNTs

The surface amino modified MSNTs(NH_2-MSNTs) were prepared according to the literature [16–18]. Firstly, the AAO membrane was immersed in a mixture solution composed of APTEOS, ethanol, sodium acetate and water for 10 min and heated in vacuum at 130 °C for 2 h. After a brief mechanical polishing and rinsing, the membrane was modified with magnetite nanoparticles by coprecipitating Fe^{3+} and Fe^{2+} under an N_2 stream. Finally, the magnetite-modified AAO membrane was immersed in a pre-made hydrolyzed silica solution for 1 min at 4 °C. This pre-made solution was prepared by mixing TEOS, APTEOS, ethanol, H_2O and HCl and stirred at room temperature. The AAO membrane was then dried at 90 °C under vacuum for 2 h. After dissolving completely the alumina membrane in NaOH (0.1 M), the resulting NH_2-MSNTs were collected by centrifugation, washed with deionized water and ethanol several times.

2.2.2. Preparation of FeC_4Pc-MSNTs

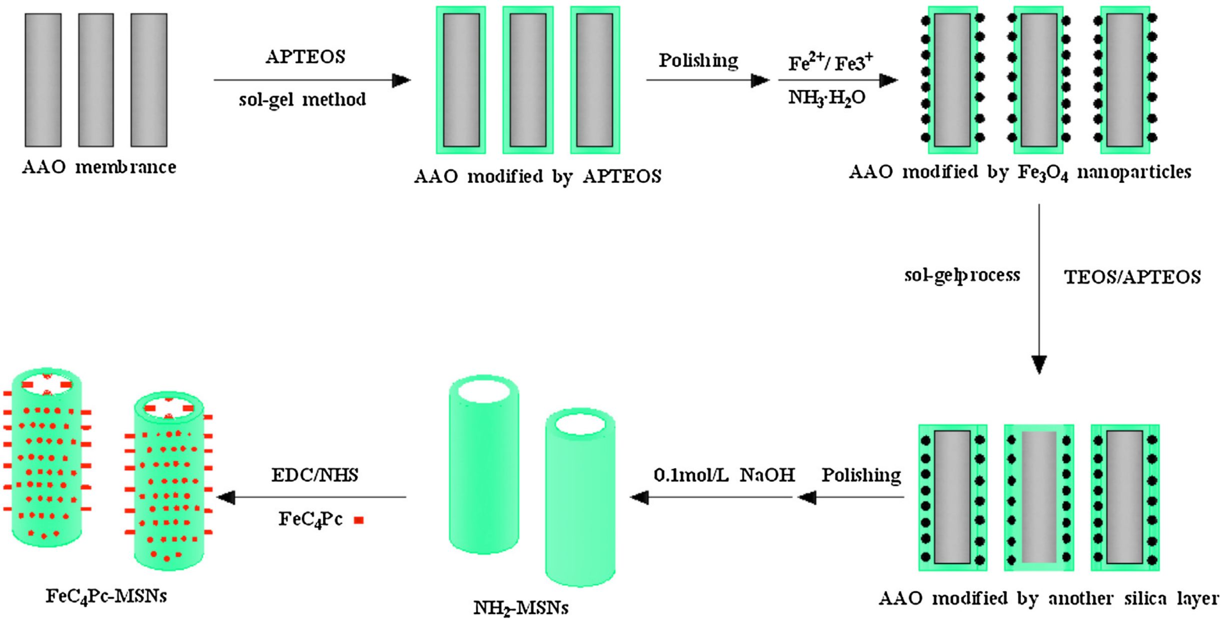
To covalently bind FeC_4Pc to the NH_2-MSNTs, 3 mg FeC_4Pc was firstly added to 2 mL anhydrous dimethylformamide by stirring for 10 min. After appropriate amount of EDC and NHS were added into the FeC_4Pc solution, stirring was continued for another 20 min. 0.2 g NH_2-MSNTs was then added. The sample solution was stirred at room temperature for 2 h to allow the immobilization equilibrium. Thereafter, the immobilized FeC_4Pc was separated from the solution by centrifugation and washing with water several times to remove the desorbed FeC_4Pc completely.

2.3. Characterization

Scanning electron microscope (SEM) and X-ray energy dispersion spectroscope (EDS) images of the MSNTs were taken on a LEO 1530 SEM equipped with ISIS 300 INCA energy and INCA crystal system (Oxford Instrumental Pte. Ltd.). A Tecnai F30 transmission electron microscope (TEM) was used to obtain TEM micrographs of MSNTs. Magnetic characterization of MSNTs was performed by a superconducting quantum interference device (Magnetic Property Measurement System XL-7, Quantum Design). A Hitachi F-4500 fluorescence spectrofluorimeter was adopted to record the steady-state fluorescence spectra and make the fluorescence measurements. A Beckman DU-7400 UV–vis diode array spectrophotometer was used to record absorption spectra.

2.4. Catalytic activities

The catalytic oxidative desulfurization experiments were conducted in a flask using a model oil(MO) consisting benzothiophene (BT) and octane with initial sulfur contents of 600 mg/L. A typical experiment was performed as follows: In a round bottom flask with a heated circulating bath, 10 mL of MO was mixed with FeC_4Pc-MSNTs (or FeC_4Pc), and hydrogen peroxide. The mixture was irradiated using ultrasound for a specific time at a given temperature. After the reaction, the oxidized MO was extracted by extraction solvent and the oil layers were collected and analyzed for sulfur content by gas chromatography with flame photometric.



Scheme 1. Schematic illustration of the synthesis of FeC_4Pc-MSNTs.

3. Results and discussions

3.1. Synthesis of FeC_4Pc-MSNTs and characterization

Template synthesis within the pores of nanoporous alumina membrane is a common method for the preparation of nanotubes and nanowires [7,19], which provides a particularly easy route to accomplish various functionalization. The synthetic procedure for $FePcC_4$-MSNTs was shown in Scheme 1. Usually, the surface functionalization was made after liberating the nanotubes from the template; however, it might cause the inner surface functionalized simultaneously or plugs up both ends opening. In this study, as an alternative, we directly carried out the surface functionalization on the AAO membrane. This is to show that the AAO membrane was first silanized with 3-aminopropyltriethoxysilane, then the inner surface of aminopropyl group modified AAO membrane was coated with a layer of magnetite and another amino silica layer one after the other, while nanotubes were still embedded in the pore of AAO template. After releasing the MSNTs from the AAO membrane, some amino groups were directly exposed on the surface of MSNTs, which can then be conjugated with the free carboxyl of FeC_4Pc via EDC/NHS conjugate chemistry.

Fig. 1(a) shows the TEM images of the prepared MSNTs in the AAO membrane. It can be seen clearly that the magnetite layer on the inner surface of the nanotube (the inner tube wall gets black and thick), and the nanotube has an outside diameter of about 200 nm which was similar to the diameter of the membrane pores. The SEM image from Fig. 1(b) indicates that the nanostructures are really hollow nanotubes. EDS results obtained from Fig. 2(a) reveal these MSNTs consist mainly of Fe and Si, which further confirm that the magnetite distributed in the tubes. According to the room temperature magnetization curves (Fig. 2(b)), the MSNTs are superparamagnetic with the saturation magnetization of ~1.0 emu/g, comparable to reported superparamagnetic silica nanotubes [9,10].

The presence of amino groups on the inner/outer surface of MSNTs and the efficiency of FeC_4Pc immobilized can be identified by fluorescamine method [20]. Fluorescamine itself is a colorless, non-fluorescent reagent that reacts readily under mild conditions with primary amines to form stable, highly fluorescent compounds. Fig. 3(a) shows the fluorescence excitation and emission spectra of the NH_2-MSNTs/fluorescamine and FeC_4Pc-MSNTs/fluorescamine systems. It can be seen that before FeC_4Pc reacting with the aminos of NH_2-MSNTs, the fluorescence of the system was very high with the fluorescence emission maximum at 475 nm (1, 1′). In contrast, after the conjugation reaction, the fluorescence signal of the system decreased markedly (2, 2′). The results demonstrated the presence of amino groups on the surface of MSNTs and a high coupling efficiency between FeC_4Pc and the NH_2-MSNTs. Moreover, according to the absorption values of the NH_2-MSNTs, FeC_4Pc-MSNTs (Fig. 3(b)), and series of free FeC_4Pc in which the calibration curve was made, the amount of bound FeC_4Pc on the MSNTs can be roughly determined, and the results show that the amount of FeC_4Pc conjugated into the magnetic silica nanotubes was about 1.1 wt%. The high loading of FeC_4Pc on the MSNTs can be attributed to the large surface area offered by the nanostructure and sufficient amino groups on the surface of MSNTs. The high-capacity FeC_4Pc immobilization ability of MSNTs together with the attractive magnetic properties provided by the Fe_3O_4 nanoparticles makes them promising for applications in various fields.

3.2. Optimization conditions for the ODS based on the catalysis of FeC_4Pc

It is well known that metallophthalocyanines have been used as an efficient biomimetic catalysts for the oxidation [11,13]. In this work, the sulfur removal of MO was used as probe reaction to study the catalytic activity of FeC_4Pc. In order to optimally utilize the catalytic characterization of FeC_4Pc in ODS process, we first tested the effect of reaction temperature, ultrasound reaction time and H_2O_2/S mole ratio on sulfur removal. Fig. 4 shows the efficiency of desulfurization at different temperatures. The sulfur removal increased at first then decreased with increasing reaction temperature in the range of 40–80 °C. Oxidation at higher temperature was unfavorable due to the decomposition of hydrogen peroxide to undesirable side products (H_2O and O_2) other than hydroxyl radicals, which decreases the efficiency of the desulfurization process and affects the quality of oil [21]. Moreover, reaction at temperature higher than 80 °C may lead to the oxidation of useful components in the fuel. In view of these reasons, the reaction temperature was set at 60 °C.

Sulfur reduction of BT under varying ultrasonication times (10–60 min) is shown in Fig. 5. Assisted by ultrasound, emulsions produced by sonication are finer and more stable, which further enhances the interfacial area available for reaction. Application of ultrasonic irradiation in the system causes an increase in sulfur reduction rate, which is due to an increase in effective local concentration of reactive species and an improvement in mass transfer in the interfacial region. Hence, high sulfur removal rate was achieved at ultrasonication time of 30 min. On the other hand, further increasing ultrasonication time from 30 to 60 min, no

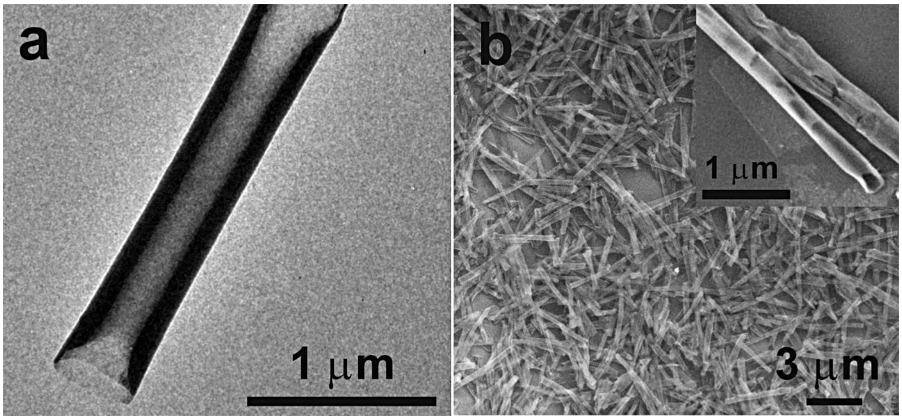


Fig. 1. TEM image (a) and SEM image (b) of the MSNTs.

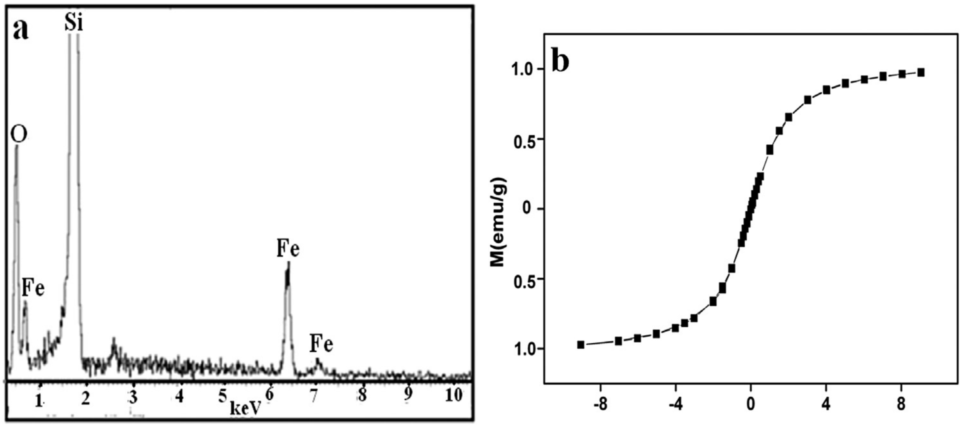


Fig. 2. EDS spectrum (a), and magnetization curve (b) of the MSNTs at room temperature.

obvious changes in desulfurization rate was observed. It is well known that application of ultrasound causes cavitation where extreme local conditions of high temperature and pressure are created [22]. So we deduced that the decrease in oxidation activity maybe due to the low thermal stability of H_2O_2 and FeC_4Pc caused by prolonging ultrasonication time. And perhaps another reason for this phenomenon is that longer reaction duration will yield more complete oxidation of organosulfur compounds to their corresponding sulfones.

Under reaction temperature 60 °C, ultrasonication time 30 min, effect of H_2O_2/S molar ratios on sulfur removal was investigated (Fig. 6). It can be seen from Fig. 6 that the sulfur removal rate increased from 39% at $H_2O_2/S = 5$ to 76% at $H_2O_2/S = 15$. With the further increase of the H_2O_2/S ratio, the sulfur removal rate was reduced. This decrease could be explained probably by the excessive nonproductive decomposition of hydrogen peroxide to oxygen and water when H_2O_2 concentration was higher than a certain value. This is in agreement with the results of Duarte previous study [23], who reported that higher values of molar proportion led to the reduction of sulfur removal rate. Therefore, $H_2O_2/S = 15$ was chosen as the best molar ratio.

3.3. Catalytic performance of FeC_4Pc-MSNTs for BT removal

The catalytic performance of FeC_4Pc-MSNTs as a function of reaction time is depicted in Fig 7, and the catalytic performance of free FeC_4Pc is also shown in Fig 7 for comparison. It can be seen from Fig 7 that the bound FeC_4Pc exhibits higher catalytic activity than the free FeC_4Pc which showed the relative lower sulfur removal of 76% after 0.5 h. Under the same conditions, the catalyst FeC_4Pc-MSNTs showed the highest sulfur removal of 94%, being higher than that of the free FeC_4Pc by about 21%, and being roughly equal to some latest research results [24,25]. According to our previous experiment results [15], we think that the enhanced catalytic activity can be attributed to the benign surrounding microenvironment provided by the silica matrix, which can protect FeC_4Pc molecules from aggregation and increase the accessibilities of active sites to BT. It has been reported that the amino-functionalized carrier structures have important effects on the dynamics, stability, especially activity of the immobilized catalysts [26]. Furthermore, the strong interaction between FeC_4Pc and amino groups on MSNTs would likely lead to the even immobilization of FeC_4Pc on the surface of MSNTs and therefore allows FeC_4Pc to adopt conformations effective for BT molecules to access the active sites.

3.4. Stability of FeC_4Pc-MSNTs

In order to investigate the stability of FeC_4Pc-MSNTs, the sulfur removal of MO over the fresh and regenerated FeC_4Pc-MSNTs are shown in Fig. 8. The reusability was examined by conducting the activity measurements of the FeC_4Pc-MSNTs for three cycles. After

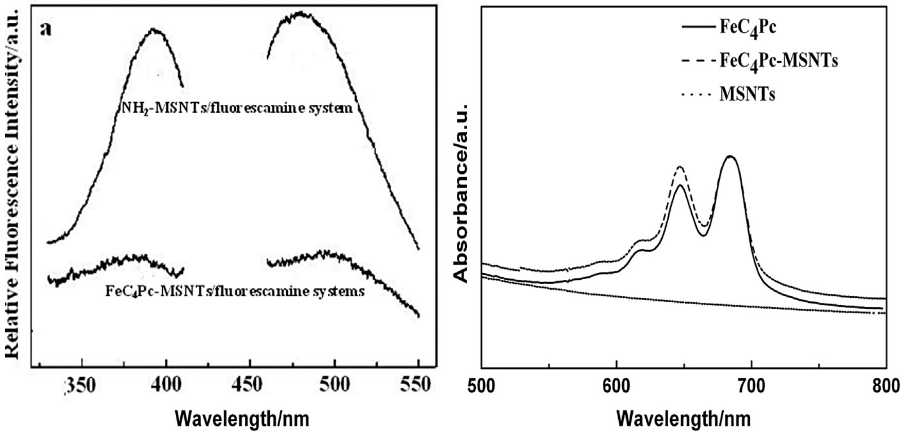


Fig. 3. (a) Fluorescence after reacting with fluorescamine. (b) UV–vis absorption spectra of MSNTs, FeC_4Pc-MSNTs and FeC_4Pc.

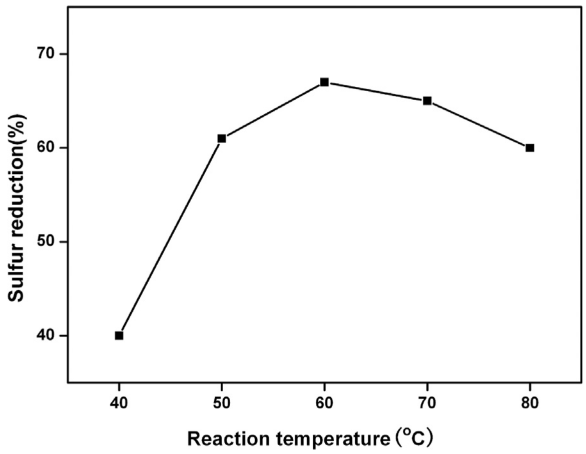


Fig. 4. Effect of temperatures on the sulfur reduction of BT. Reaction conditions: $n(H_2O_2)/n(S) = 10$, Time = 20 min.

each experiment the FeC_4Pc-MSNTs were recovered, regenerated by solvent extraction in order to remove the adsorbed species, and then fresh MO, hydrogen peroxide were added for the next run. For comparison, the repeated use performance using catalysts without any treating was also conducted. As can be seen from Fig. 8, sulfur removal decreased from 94% to 79% after triple use of catalysts without solvent treatment, and sulfur removal still reached 88% using the catalysts regenerated by methanol. The results show that deactivation of catalysts can be inhibited by methanol extraction to remove the adsorbed species (BT/BTO_2) on the catalyst surface, suggesting that the catalysts regenerated by methanol have a better repeated use performance. Moreover, the catalysts FeC_4Pc-MSNTs can be easily recovered after completion of the reaction by means of physical centrifugation or magnetic separation, which provides a good precondition for the repeated use of immobilized FeC_4Pc.

3.5. The mechanism of BT oxidation in the FeC_4Pc-H_2O_2 system

Oxidative desulfurization is considered to be one of the most promising technologies for deep desulfurization of fuel oil. The method is composed of oxidizing the sulfur compounds to form sulfones and/or sulfoxides, which are highly polar and could be easily removed via adsorption, solvent extraction or distillation [27]. As one of the key steps for ODS process, the reactions of iron (II) porphyrin complexes with various oxidants such as peroxyacids and hydroperoxides have been extensively studied [28,29]. It is reported that a monomeric porphyrin complex is catalytically active in the porphyrin-H_2O_2 system [30]. Scheme 2 shows the mechanism of BT oxidation catalyzed by FeC_4Pc-MSNTs. A non-stacked monomeric FeC_4Pc reacts with hydrogen peroxide to generate iron(III) hydroperoxide porphyrin intermediate, then the hydroperoxide O—O bond cleave to form a ferryl-oxo complex

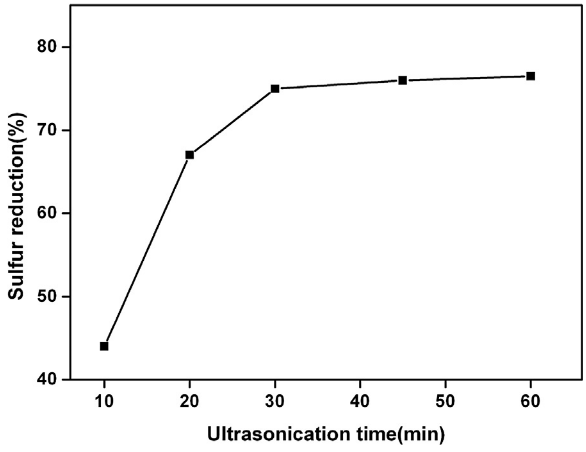


Fig. 5. Effect of ultrasonication time on the sulfur reduction of BT. Reaction conditions: $n(H_2O_2)/n(S) = 10$, Temperature = 60°C.

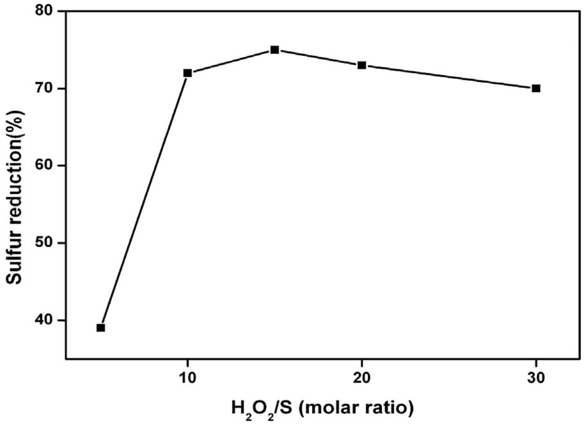


Fig. 6. Effect of different H_2O_2/S molar ratios on the sulfur reduction of BT. Reaction conditions: Temperature = 60 °C, Time = 30 min.

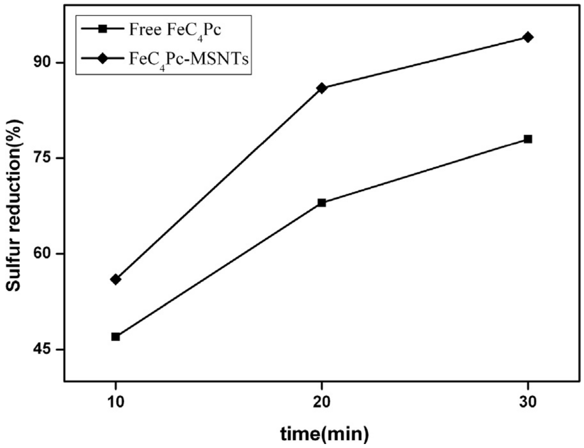


Fig. 7. Catalytic performance of FeC_4Pc and FeC_4Pc-MSNTs as a function of reaction time. Reaction conditions: $n(H_2O_2)/n(S) = 15$, Temperature = 60°C, Time = 30 min.

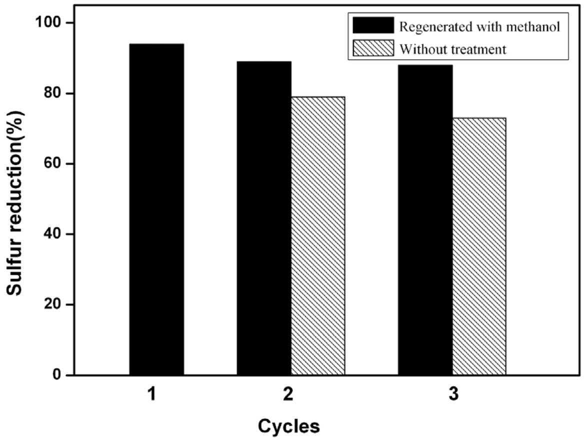
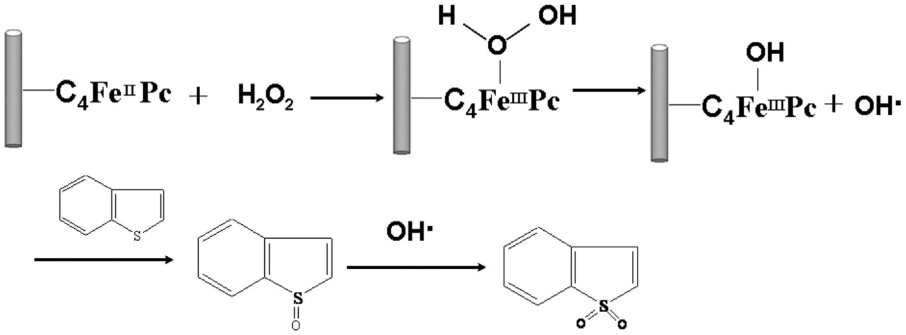


Fig. 8. Reusability of the FeC_4Pc-MSNTs. Reaction conditions: $n(H_2O_2)/n(S) = 15$, Temperature = 60°C, Time = 30 min.



Scheme 2. The mechanism of BT oxidation catalyzed by FeC_4Pc-MSNTs.

and a hydroxyl radical [29]. The hydroxyl radical was proposed as the active species in the oxidative reduction of BT. Bonding FeC_4Pc on MSNTs can suppress the dimerization of FeC_4Pc to a certain extent, which would be favorable for the improvement of the activity and the stability of the catalyst.

4. Conclusion

In this work, we report a facile method to fabricate the multifunctional surface amino-functionalized MSNTs via AAO template membrane method together with modified sol–gel method and FeC_4Pc was immobilized on the surface of MSNTs via EDC/NHS conjugate chemistry. It was found that the immobilized FeC_4Pc exhibited excellent catalytic activity and reusability. The good performance of FeC_4Pc-MSNTs in ODS indicated that the organically functionalized MSNTs provided high immobilization efficiency and a benign microenvironment for catalytic reaction due to the unique silica surface chemistry. The successful application of the FeC_4Pc-MSNTs in ODS confirmed that these MSNTs can act as novel supports for organic molecules, and this will pave a new road for their application in many fields.

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