



## Fabrication and application of magnetic nanoreactor with multiple ultrasmall cores and mesoporous shell in Fenton-like oxidation



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### ABSTRACT

A new and facile method has been developed in this study for the fabrication of multicore–shell type nanoreactor. On the basis of the characterization results from X-ray diffraction, scanning and transmission electron microscopy, Raman and X-ray photoelectron spectroscopy, and N<sub>2</sub> adsorption/desorption analysis, it has been proved that ultrasmall iron oxide particles (~10 nm) were firstly encapsulated in the matrix of polystyrene spheres via a microemulsion-polymerization-assisted approach, and then were introduced as movable cores inside mesoporous SiO<sub>2</sub> shell. The size of iron oxide particles retained almost unchanged even during the calcination procedure in air, indicating high thermal stability, due to the protection of polystyrene matrix. The obtained nanoreactor was applied as an effective heterogeneous catalyst for total oxidation of methylene blue with aqueous hydrogen peroxide and the ultrasmall iron oxide particles within the hollow interior proved to be active sites for such reaction. Mesoporous SiO<sub>2</sub> shell not only protects the nanometer-sized iron oxide particles against leaching from the nanoreactor into reaction solution, but also enriches the reactant molecules around multiple ultrasmall iron oxide cores and thus enhances the catalytic activity and reaction rate. Importantly, the nanoreactor can be easily recovered by external magnetic field and reused in successive catalytic cycles without significant loss of activity.

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### 1. Introduction

Iron oxide nanoparticles have drawn tremendous interest because of their potential applications in biomedical imaging, drug delivery, energy storage, wastewater cleaning and heterogeneous catalysis [1–6]. Various wet chemical processes, up to now, have been used to synthesize iron oxide nanoparticles including precipitation, thermolysis by organic metallic composition and carbonyl composition [7–15]. Among their catalytic applications, Fenton-like reactions on iron oxide nanoparticles are increasingly replacing iron salt-based homogeneous Fenton reactions because of the advantages associated with avoiding the precipitation of soluble iron salts and the difficulties in recycling [16,17]. However, most iron oxide-based nanoparticles (<50 nm) reported have tended to agglomerate during operation, resulting in a significant

deterioration of the catalytic activity [18,19], although “free” nano-Fe<sub>2</sub>O<sub>3</sub> particles have been shown in one case to be an active and stable catalyst for oxidations [5]. Another issue of concern is that the catalytic sites are contaminated readily when directly exposed in bulk reaction solution [20]. Accordingly, several strategies have been utilized to design iron-based catalysts with stabilized iron oxide nanoparticles for the reactions. It has been extensively reported that iron oxide nanoparticles could be supported on (encapsulated in) porous silicas, polymers and carbon-based materials [2,3,21–23], which could not only favor to stabilize the nanoparticles, but also help in binding various biological ligands to the nanoparticle surface. For examples, Gu et al. have synthesized Fe<sub>2</sub>O<sub>3</sub>/polymer composites consisting of sub-10 nm Fe<sub>2</sub>O<sub>3</sub> nanoparticles and porous polymer by a novel one-pot surfactant-free hydrothermal approach and the composite exhibited high catalytic activity in the reduction of nitroarenes [2]. Geng et al. have reported that iron oxide particles with diameters of 5–10 nm can be highly dispersed on the surface of mesoporous carbon [22].

Besides, constructing nanoreactors with confined core–shell structure is considered to be other ideal ways to address the above

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difficulties of iron oxide nanoparticles, in which the shell part would help to stabilize and defend the active core of iron oxide nanoparticle. Although iron oxide encapsulated core–shell nanoreactors have been successfully prepared [24–26], most of them are commonly used for either convenient separation or redox catalysts. Up to now, little work has been reported in the respect of Fenton-like catalysis [17,19], which might be due to the lack of sufficient Fenton-like catalytically active sites within the iron-based nanosized catalysts based on the strategies applied. In the both cases, either yolk-shell structured  $\text{Fe}_2\text{O}_3$ @mesoporous  $\text{SiO}_2$  nanoreactor or hierarchical yolk-shell structured nanoreactor with  $\text{Fe}_3\text{O}_4$  cores and  $\text{Fe}_3\text{O}_4$ /C shells contains one big single core with diameter larger than 200 nm. As known, multiple small nanometer-sized magnetic particles inside the shell are more advantageous than one relatively big nanometer-sized one; in this way the magnetic intensity of the sample can be easily tuned by varying the amount of magnetic cores [26]. Although yolk-shell type nanocatalyst composed of multiple nanosized  $\text{Fe}_3\text{O}_4$  cores (~16 nm) and mesoporous carbon shell has been fabricated [26], the content of  $\text{Fe}_3\text{O}_4$  nanoparticles in such yolk-shell material is limited to some extent (~3.4 wt.%). To the best of our knowledge, no effective multicore–shell type nanoreactor has been reported for Fenton-like oxidations. Therefore, it is of great interest to develop new method for synthesizing multicore–shell nanoreactors with stable and sufficient iron oxide nanoparticles.

Herein, we developed a new and facile method for the fabrication of multicore–shell type nanoreactor, by introducing movable and multiple cores of ultrasmall iron oxide particles via a microemulsion-polymerization-assisted approach and constructing mesopores in the  $\text{SiO}_2$  shell via template-involved strategy. The nanoreactor was then applied as a heterogeneous catalyst for total oxidation of methylene blue with aqueous  $\text{H}_2\text{O}_2$  and proved to show high catalytic activity, reusability and good magnetic separation property. The magnetic multiple cores of iron oxide nanoparticles not only facilitate the separation of nanoreactor from the reaction solution, but also serve as active sites for Fenton-like reaction.

## 2. Experimental

### 2.1. Preparation of magnetite nanoparticles (nano- $\text{Fe}_3\text{O}_4$ )

The magnetite nanoparticles were prepared according to Masart's method [27]. Typically, 5.6 mM  $\text{FeCl}_2$  and 11.2 mM  $\text{FeCl}_3$  were dissolved into 150 mL of  $\text{H}_2\text{O}$  and heated to 50 °C under nitrogen atmosphere, then 15 mL of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  was added to induce the coprecipitation reaction, and 0.5 mL of oleic acid (OA) was added to improve the monodispersity of the nano- $\text{Fe}_3\text{O}_4$ , finally, the product was collected by a magnet and washed with ethanol and cyclohexane for three times.

### 2.2. Preparation of $\text{Fe}_3\text{O}_4$ /PS nanoparticles

The  $\text{Fe}_3\text{O}_4$ /PS nanoparticles were prepared according to Yan et al.'s route [28]. The monodispersed nano- $\text{Fe}_3\text{O}_4$  were dispersed into the mixture of styrene (St; 2.8 mL), 3-trimethoxysilyl propyl methacrylate (MPS; 1.2 mL) and cyclohexane (1.0 mL) with the aid of ultrasound to form the oil phase. Meanwhile, 0.32 g of sodium dodecyl sulfate (SDS), 0.15 g of  $\text{Na}_2\text{HPO}_4$  and 0.096 g of  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  were dissolved in 120 mL of deionized water to form an aqueous solution with a pH value at 7. The above-mentioned oil phase and aqueous solution were mixed and ultrasonicated for 15 min to yield miniemulsion and then transferred to a three-necked flask. 0.06 g of potassium persulfate (KPS) was dissolved in 1.0 mL of deionized water, and then added into the

flask to initiate the polymerization. After it was kept for 12 h at 70 °C under continuous stirring and protection of  $\text{N}_2$ , the prepared  $\text{Fe}_3\text{O}_4$  nanoparticles encapsulated in the matrix of polystyrene spheres were centrifuged at 2000 rpm, washed three times with deionized water, and dried under vacuum, yielding the nanoparticles of  $\text{Fe}_3\text{O}_4$ /PS in size of 200–800 nm. The particle of  $\text{Fe}_3\text{O}_4$ /PS in size of 100–200 nm was obtained under centrifugation at 4000 rpm, which denoted as  $\text{Fe}_3\text{O}_4$ /PS-sm.

### 2.3. Preparation of Multi- $n\text{Fe}_2\text{O}_3$ @Meso- $\text{SiO}_2$ nanoreactor

0.2 g of  $\text{Fe}_3\text{O}_4$ /PS nanoparticles were dispersed in the solution containing 120 mL of deionized  $\text{H}_2\text{O}$ , 50 mL of ethanol, 2.6 g of cetyltrimethyl ammonium bromide (CTAB) and 13 mL of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (25%). After ultrasonic for 20 min, 400  $\mu\text{L}$  of tetraethyl orthosilicate (TEOS) was added, and the mixture was vigorously stirred at room temperature for 24 h. The precipitate was harvested after collection by external magnetic field and washed with deionized water and ethanol for three times, and then dried at 80 °C for 6 h. The product was heat-treated at 250 °C for 2 h and then calcined at 550 °C for 8 h to remove the organic components. The final product was denoted as Multi- $n\text{Fe}_2\text{O}_3$ @Meso- $\text{SiO}_2$ . For comparison, bared spherical  $\text{Fe}_2\text{O}_3$  was prepared by calcination of  $\text{Fe}_3\text{O}_4$ /PS nanoparticles and SL- $\text{Fe}_2\text{O}_3$ @Meso- $\text{SiO}_2$  with single large  $\text{Fe}_2\text{O}_3$  core was prepared by the same procedure applied for Multi- $n\text{Fe}_2\text{O}_3$ @Meso- $\text{SiO}_2$ , but using single large  $\text{Fe}_3\text{O}_4$  nanoparticles (155 nm) that were synthesized according to the previous study [29] instead of  $\text{Fe}_3\text{O}_4$ /PS nanoparticles. Also, a catalyst with similar core–shell structure as Multi- $n\text{Fe}_2\text{O}_3$ @Meso- $\text{SiO}_2$  but smaller reactor size (100–400 nm) (Multi- $n\text{Fe}_2\text{O}_3$ @Meso- $\text{SiO}_2$ -sm) was synthesized by the similar procedure applied for Multi- $n\text{Fe}_2\text{O}_3$ @Meso- $\text{SiO}_2$ , but using  $\text{Fe}_3\text{O}_4$ /PS-sm.

### 2.4. Characterization

Powder XRD patterns were measured on a Bruker D8 Advance instrument using  $\text{Cu K}\alpha$  radiation. FT-IR spectra were recorded on a Perkin Elmer 100 spectrometer. The isotherms of nitrogen adsorption/desorption were measured at liquid nitrogen temperature using a Micromeritics ASAP2020 system. The pore-size distribution was calculated using Barrett–Joyner–Halenda (BJH) model. Scanning electron microscopy (SEM) images were taken on a Hitachi S-4300 apparatus. Transmission electron microscopy (TEM) investigation was performed on FEI F30 and Hitachi H-7650. Magnetic properties were measured using a Lake Shore 7410 vibrating sample magnetometer at 298 K. X-ray photoelectron spectroscopy (XPS) measurements were recorded using a PHI 5000C ESCA system with  $\text{Al K}\alpha$  radiation ( $h\nu = 1486.6$  eV). The Raman spectra were determined on a Renishaw in Via micro Raman spectroscopy system, using the TE air-cooled  $576 \times 400$  CCD array in a confocal Raman system (wavelength: 633 nm). The incident laser power was kept at 0.1 mW, and total accumulation times of 5 s were employed.

### 2.5. Catalytic testing

In a typical run, the reaction suspension was prepared by adding a given amount of catalyst with equivalent  $\text{Fe}_2\text{O}_3$  (10.0 mg of  $\text{Fe}_2\text{O}_3$  or 12.0 mg of Multi- $n\text{Fe}_2\text{O}_3$ @Meso- $\text{SiO}_2$ ) to a glass vial containing 20 mL of methylene blue (MB) solution (50 mg/L). Prior to reaction, suspension was sonicated for 5 min and shaken (150 rpm) in the dark for 60 min to establish the adsorption/desorption equilibrium. Fenton-like reaction was initiated by adding a known concentration of  $\text{H}_2\text{O}_2$  (1.3 mL, 30 wt.%) to the solution. Samplings were taken at a given time intervals during the reaction. The catalyst was separated

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