



One-pot synthesis of Fe₂O₃ loaded SiO₂ hollow particles as effective visible light photo-Fenton catalyst



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ABSTRACT

Amorphous Fe₂O₃ loaded SiO₂ hollow particles were obtained via a one-pot two-step solution synthesis followed by calcination. With the help of citrate ions, the iron containing resorcinol formaldehyde resin nanoparticles (Fe-RF NPs) were first synthesized through the extended Stöber method. Then silica coating is further conducted in a one-pot manner. It was found that the silica layer can effectively prevent the inner Fe₂O₃ nanoparticles from becoming large during heat treatment, endowing them with small size and amorphous structure. The final product exhibits good catalytic performance in photo-Fenton degradation of methylene blue with visible light.

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1. Introduction

Fenton process can be used effectively for organic waste water treatment [1]. However, for the homogeneous Fenton process, the main drawback is the formation of large quantity of ferric hydroxide sludge, which adversely affects the environment and brings waste disposal issues [1,2]. These limitations can be overcome to some extent by application of heterogeneous catalysts [2]. It has been proven that both UV and visible light irradiation can enhance the Fenton process by accelerating regeneration of the active Fe²⁺ species [2–4]. Since visible light carries much more energy than UV in the sunlight spectrum, the visible light photo-Fenton process should be more promising for large scale application [5]. Fe₂O₃ is a cost effective, environment benign and relative stable compound. Up to now, both α - and γ -Fe₂O₃ have been widely used as catalysts for Fenton process [6–12]. However, nanosized Fe₂O₃ particles always suffer from severe aggregation in solutions, so it is necessary to load them into some carries to warrant their dispersion and allow pollutants to easily reach the vicinity of the Fe₂O₃ surface [13–18].

Among the commonly used catalyst supports, silica has

attracted much attention due to its high stability and easiness of preparation [19]. To date, a lot of methods have been developed to synthesize Fe₂O₃/silica composites [20–30]. For example, Tadic' group prepared α -Fe₂O₃ nanoparticles embedded in amorphous silica matrix by a sol-gel combustion method [21] and also synthesized core-shell type γ -Fe₂O₃@SiO₂ nanostructures by directly coating the magnetic core with silica layer [22]. Ferroudj et al. synthesized γ -Fe₂O₃/SiO₂ nanocomposite microspheres through a water-in-oil emulsion reaction method, which served as heterogeneous photo Fenton catalysts for degradation of pollutants in water [20]. Although these methods are highly effective, the silica supports with porous structures and large surface area are preferred for the Fenton reaction due to high exposure of the catalysts and good accessibility of the reactant toward the active centers [19,24]. Coelho et al. synthesized hematite and maghemite loaded mesoporous silica, which degraded methylene blue dye effectively through the Fenton reaction [15]. Sirotnin's group reported the synthesis of α - and γ -Fe₂O₃ loaded MCM-41 with different Fe content (1–11 wt%) [24]. They found that at room temperature, the Fe³⁺ ions leached out from the silica matrix and catalyzed the oxidation of phenol following a homogeneous mechanism, but at 80 °C the oxidation of phenol occurred via a heterogeneous mechanism.

In addition to the above mentioned solid porous silica, hollow silica materials with large interior void and porous wall (shell) have

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recently gained much attention as catalyst supports, in which the porous shell can prevent the inner catalyst from aggregation, and the interior void provides large space for enriching the reactants [25–32]. For instance, Song and co-workers synthesized yolk-shell structured α -Fe₂O₃@mesoporous SiO₂ through a polymeric carbon assisted method. In their Fenton reactions to degrade methylene blue, the activity increased with increasing the void space [28]. They attributed this phenomenon to the better reactant enrichment of the larger void space. Chen et al. fabricated magnetic nanoreactor with multiple ultrasmall (10 nm) γ -Fe₂O₃ cores and mesoporous SiO₂ shells, which showed improved catalytic performance compared with the γ -Fe₂O₃ nanoparticles for methylene blue degradation [30].

Recently, Miao et al. reported synthesis of γ -Fe₂O₃ loaded hierarchical porous silica by impregnation method. They found that in the photo-Fenton reaction, the sample produced at lower calcination temperature (150 °C) degraded Orange II much faster than those obtained at higher calcination temperatures [33]. This phenomenon is due to the fact that the iron oxide produced at lower temperature has a low degree of crystallinity and the surface iron can take part in the Fenton reaction more easily. In addition, it is generally accepted that Fe₂O₃ particles with small size can provide large number of active sites which can enhance their catalytic performance [30,34].

Based on the above studies, the porous hollow silica structures loaded with small Fe₂O₃ nanoparticles of low crystallinity can be a suitable catalyst for photo-Fenton reactions. To date, there are two strategies commonly used to incorporate catalyst into hollow silica particles. For the first one, hollow silica particles are prepared first, followed by catalyst loading. In the second one, catalyst is prepared first, and then, silica shell is outward constructed [25,26]. However, these two preparations are very tedious to proceed, which hampers their wide application.

It is well known that the Stöber method is facile for synthesizing silica particles via hydrolysis and condensation of silicon alkoxides in alcohol solution in the presence of water and base catalyst [35]. Recently, the Stöber method has also been successfully extended to synthesize resorcinol formaldehyde resin (RF) particles, due to their convenience and flexibility [36]. Based on the similarities in synthesis between silica and RF particles, some novel approaches have been established to construct a series of core-shell and hollow materials [37–42].

Herein, a one-pot two-step Stöber process is developed to synthesize silica coated Fe-RF nanoparticles (Fe-RF/SiO₂ NPs) (Scheme 1). Citrate acid is used to form stable complexes with iron in ammonia solution and to facilitate iron incorporation into RF particles. The as-prepared Fe-RF/SiO₂ NPs are subsequently calcined in air to form the final Fe₂O₃/SiO₂ HPs. In our method, removing of the RF template and forming of the iron oxide inside silica shell are both achieved during calcination. It is also worth

noting that the silica shell can effectively prevent the inner Fe₂O₃ nanoparticles from becoming large and crystallizing during calcination. The samples obtained after calcining at 550 °C (Fe₂O₃/SiO₂ HPs-550) have a large surface area of 278.8 m² g⁻¹. The size of the occluded Fe₂O₃ nanoparticles is found to be 3–5 nm and the structure of them is amorphous. The material exhibits superior activity in the visible light photo-Fenton process for degradation of methylene blue.

2. Experimental

2.1. Chemicals

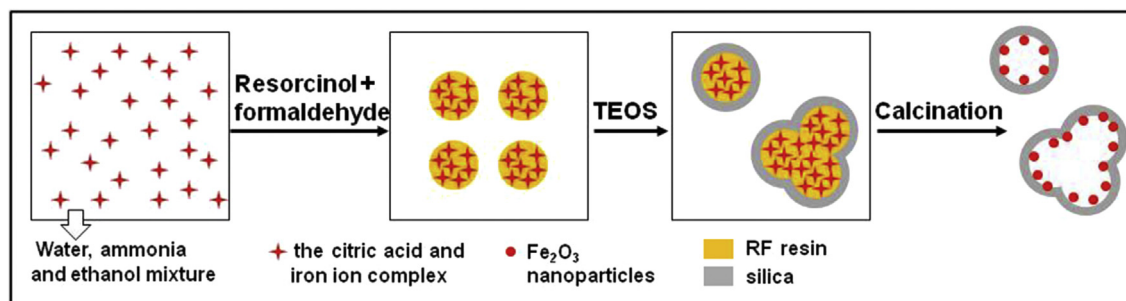
Ferric chloride hexahydrate (FeCl₃·6H₂O), citric acid monohydrate (C₆H₈O₇·H₂O), tetraethyl orthosilicate (TEOS), hydrogen peroxide (H₂O₂, 30%), ammonia solution (25%), resorcinol, formaldehyde, terephthalic acid (TA) and ethanol are purchased from Sinopharm Chemical Reagent Company. All the reagents are analytical grades and used without purification.

2.2. Synthesis of Fe₂O₃/SiO₂ HPs

270.0 mg ferric chloride hexahydrate (FeCl₃·6H₂O) and 71.4 mg citric acid monohydrate (C₆H₈O₇·H₂O) were dissolved in a mixed solution of 15 ml deionized water and 12 ml ethanol under magnetic stirring. After that, 0.8 ml ammonia solution (25%) was dropped into the above mixture, which turned the color of the solution from yellow to brown, without precipitate. To synthesize Fe-RF nanoparticles (Fe-RF NPs), 0.2 g resorcinol and 0.28 ml formaldehyde were added into the above mixture and stirred for 10 h. Again, 40 ml ethanol, 0.8 mL ammonia and 0.75 mL tetraethyl orthosilicate (TEOS) were added into the mixture to achieve the silica coating. The mixture was further stirred overnight. The solid products formed in the solution were collected by centrifugation and finally calcined in air for 4 h. The samples obtained at 550 °C and 800 °C were denoted as Fe₂O₃/SiO₂ HPs-550 and Fe₂O₃/SiO₂ HPs-800, respectively. For comparison purpose, pure Fe₂O₃ nanoparticles were also prepared by direct calcining Fe-RF NPs at 550 °C.

2.3. Characterization

The samples were characterized by X-ray diffraction (XRD, Bruker D8), X-ray photoelectron spectroscopy (XPS, Axis Ultra), transmission electron microscope (TEM, JEM-3010), thermogravimetric analysis (TGA, DTG-60AH), and Fourier transform infrared spectroscopy (FTIR, Nicolet Avatar 360). The particle size was measured by dynamic light scattering (DLS) on a Zetasizer NanoZS (Malvern Instruments). The specific surface area was measured by a ASAP 2020 system (Micromeritics). UV–Vis spectra were recorded on a 7600 MC UV–Vis spectrophotometer (BILON). The photo



Scheme 1. Schematic illustration of the preparation of Fe₂O₃/SiO₂ HPs.

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