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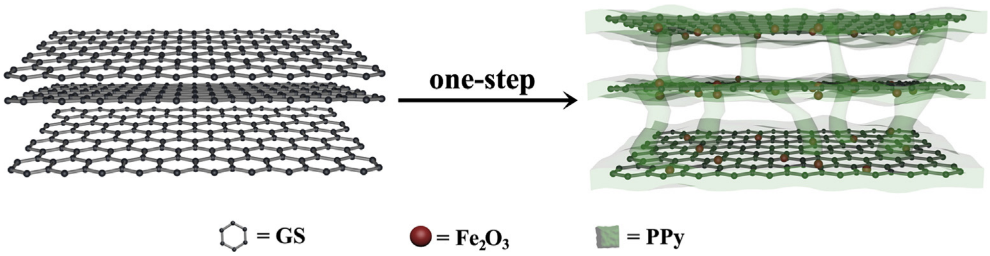
One-pot preparation of ternary reduced graphene oxide nanosheets/Fe_2O_3/polypyrrole hydrogels as efficient Fenton catalysts

Junshuai Zhang [a], Tongjie Yao [a,*], Chenchen Guan [a], Nanxi Zhang [c], Hui Zhang [b], Xiao Zhang [a], Jie Wu [b,*]

[a] MIIT Key Lab of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, China
[b] Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, School of Chemistry and Materials Science, Heilongjiang University, Harbin, China
[c] School of Life Science and Technology, Harbin Institute of Technology, Harbin, China

GRAPHICAL ABSTRACT

Ternary reduced graphene oxide nanosheets/Fe_2O_3/polypyrrole hydrogels were prepared in one-step. They showed superior removal efficiency towards methylene blue *via* heterogeneous Fenton reaction.



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ABSTRACT

Ternary reduced graphene oxide nanosheets (rGSs)/Fe_2O_3/polypyrrole (PPy) hydrogels with Fe_2O_3 nanoparticles (NPs) embedded between rGSs and PPy layer were prepared in one-pot. The ternary hydrogels exhibited an interconnected and porous three-dimensional network with *co*-existence of macropores and mesopores. Fe_2O_3 NPs uniformly dispersed on rGS surface with the diameter of 8.8 nm. Control experiments were carried out to investigate the roles of components in formation of ternary hydrogels. During heterogeneous Fenton degradation of methylene blue (MB) dyes, the ternary hydrogels exhibited much better removal efficiency than the reference samples, not only because rGSs and PPy layer altered the adsorption, dispersity and diameter of Fe_2O_3 NPs; but also owing to the structural merits of ternary hydrogels. The effects of operating conditions, such as initial MB concentrations, dosages of catalysts and H_2O_2, were carefully investigated. With the help of Fe_2O_3 NPs, ternary rGSs/Fe_2O_3/PPy hydrogels could be easily separated *via* a magnet. In recycling experiments, they showed superior reusability.

1. Introduction

In recent decades, the water pollution caused by persistent organic substances, such as fertilizers, pesticides and dyes, has become a worldwide environmental problem, and its effective remediation is an ongoing subject. Advanced oxidation processes (AOPs) are powerful technologies, and accepted as promising alternative approaches for organic water contamination. Fenton reaction, as one of the most important AOPs, owns its unparalleled advantages, including benign process, superior removal efficiency, no selectivity and easy operation and maintaining [1–3].

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* Corresponding authors.
E-mail addresses: yaotj@hit.edu.cn (T. Yao), wujie@hlju.edu.cn (J. Wu).

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Unfortunately, the applications of homogeneous Fenton system (Fe^{2+}/H_2O_2) are greatly limited by expensive and complex process for disposal of iron sludge, as well as difficult reusability of catalysts. To overcome these drawbacks, heterogeneous Fenton catalysts have been developed to replace traditional homogeneous Fenton system. Among them, magnetic materials, such as Fe_3O_4, Fe_2O_3 and FeOOH, are deeply studied [4–7], not only because of being abundant and inexpensive, but also due to high activity. More importantly, they can be quickly separated by external magnetic field, which dramatically improves the reusability.

In heterogeneous Fenton reaction, H_2O_2 converts to $^{\cdot}OH$ on the catalyst surface to initiate the decomposition of organic pollutants. Obviously, the surface area is a crucial factor to determine the reaction rate. Compared with bulk-phase materials, nanoparticles (NPs) process larger surface area and supply more active sites for conversion of H_2O_2; therefore, they are more suitable candidates for heterogeneous Fenton catalysts. Nevertheless, once the size decreases to nanoscale, magnetic NPs are prone to aggregate because of strong anisotropic dipolar interactions, which inevitably results in loss of high dispersity and activity. To improve their stability and activity, a support is usually required to load magnetic NPs [8,9].

Graphene, a two-dimensional (2D) nanosheet of sp^2-hybridized carbon, has attracted much attention, owing to large surface area, high ratio of lateral size to thickness, impressive mechanical strength and rich electronic states. Some studies have explored using reduced graphene oxide nanosheets (rGSs) as support for magnetic NPs to perform heterogeneous Fenton reaction [10–12]. The enhanced catalytic activity and stability were attributed to the synergistic effects between rGSs and magnetic NPs. However, due to strong π-π attractions and hydrogen interactions, rGSs tended to restack, which led to an obvious reduction of accessible surface area and stability, and hence loss of the efficacy. At present, assembling 2D rGSs to three-dimensional (3D) hydrogels was a feasible method to solve this problem, since it not only effectively avoided the restacking, but also maximally preserved the outstanding intrinsic properties of rGSs. Additionally, the porous structure was usually generated in 3D hydrogels, which was beneficial for improving the mass diffusion and transport in Fenton reaction. Recently, many approaches have been established to construct graphene-based hydrogels, including hydrothermal method, chemical reduction and electrochemical method [13–15]. Some papers have reported preparation of magnetic NPs/graphene hydrogels. However, it usually required multiple steps to synthesize the target products. For example, Yang and *co*-workers firstly synthesized Fe_3O_4 NPs, and then assembled the rGSs to 3D hydrogels in the presence of Fe_3O_4 NPs [16]. Xiao and *co*-workers have prepared Fe_2O_3/rGSs *via* formation of FeOOH as precursor of Fe_2O_3 under high temperature [17]. Apparently, complex procedure resulted in low efficiency, time-wasting, and suffered from difficulty in scaling up. From this view, the synthesis of magnetic NPs/graphene hydrogels in a simple way, especially in one-pot, still represented a technologically crucial yet challenging problem.

Based on above consideration and our previous work [18,19], herein, we have explored a feasible way to prepare rGSs/Fe_2O_3/polypyrrole (PPy) hydrogels. In hydrogels, rGSs acted as skeletons and PPy acted as "cross-linker" to connect skeletons together, which led to an interconnected and porous structure. The merits of our work were: (i) Reduction and assembly of graphene oxide nanosheets (GSs), polymerization of pyrrole monomer and synthesis of Fe_2O_3 NPs were combined together; therefore, the preparation process was only required one-pot under ambient condition. (ii) 3D porous structure of rGSs/Fe_2O_3/PPy hydrogels not only avoided the restacking of rGSs, but also favored for mass transport and diffusion. (iii) Owing to the isolation of PPy molecular chains and electrostatic force between negatively charged GSs and Fe^{3+}, the average size of highly dispersed Fe_2O_3 NPs was only 8.8 nm, which was beneficial for increasing their surface area; and hence, promoting the degradation efficiency. (iv) The detachment, leaching and aggregation were hindered *via* confining Fe_2O_3 NPs between rGSs and PPy layer, which improved their stability. The morphologies, structures and compositions of ternary hydrogels were characterized in detail, and the roles of components in the formation process were revealed. They were applied as heterogeneous Fenton catalysts towards the degradation of methylene blue (MB) dyes. The removal efficiency and reusability were carefully investigated.

2. Materials and methods

2.1. Materials

The pyrrole monomer was purchased from Alfa-Aesar and was distilled under reduced pressure and stored at −4 °C prior to use. MB dyes, $FeCl_3\cdot 6H_2O$, $NaBH_4$, KNO_3, $KMnO_4$, H_2SO_4, H_2O_2 (30 wt %), $NH_3\cdot H_2O$ (28 wt%) and graphite were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were analytical grade and used as received. The water used was purified through a Millipore system with a resistivity of 18.2 $M\Omega\cdot cm^{-1}$.

2.2. Preparation of rGSs/Fe_2O_3/PPy hydrogels

GSs were synthesized from graphite powder according to the Hummers' method [20], and the concentration was adjusted to 1.7 mg/mL. Typically, 60 μL pyrrole monomer was added into 30 mL as-prepared GSs solution. Subsequently, 0.1 g $FeCl_3\cdot 6H_2O$ was added into above mixture to initiate the oxidation polymerization. The solution color gradually changed from dark-brown (the color of GSs solution) to black (the color of PPy homopolymer). After 6.0 h, 1.0 mL $NH_3\cdot H_2O$ was injected into the system, and the reaction was allowed to proceed for another 1.0 h. Finally, the products were washed by water for 3 times, and then freeze-dried.

2.3. Heterogeneous Fenton degradation of MB dyes

A series of experiments were carried out to measure the activity of samples towards degradation of MB dyes. All experiments were performed at room temperature and pH = 6.5. Typically, rGSs/Fe_2O_3/PPy hydrogels were added into MB solution and mechanically stirred for 10 min to achieve uniform dispersion. Then, H_2O_2 was injected to initiate Fenton reaction, and this time was set to be the start time. At given time intervals, the reaction solution was sampled and removed hydrogels, then measured by UV–vis spectrophotometer. The degradation efficiency was analyzed by C_t/C_0, (C_t and C_0 was the MB concentrations at time t and 0, respectively, which was measured from the intensity of absorbance A_t/A_0). The reaction rate constant k was calculated by a linear plot of $\ln(C_t/C_0)$ *vs.* reaction time t based on the pseudo-first-order kinetic equation.

In recycling study, 100 mg hydrogels were added into 30 mL MB solution with a concentration of 50 mg/L. Then, 10 mL H_2O_2 was immediately injected into above reaction solution to initiate the Fenton reaction. After complete degradation, the hydrogels was fixed at the bottom of flask by a magnet. Finally, the supernatant liquid was carefully removed by a straw. In next cycle, 30 mL MB solution was added, and the hydrogels remained at the bottom of flask were re-dispersed under mechanically stirring. Subsequently, 10 mL H_2O_2 was injected to restart the Fenton reaction. The process was repeated for 4 times.