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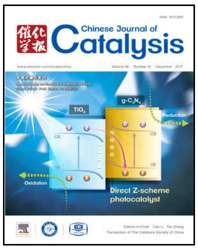

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Enhanced Fenton, photo-Fenton and peroxidase-like activity and stability over Fe_3O_4/g-C_3N_4 nanocomposites

Shafaq Sahar [a], Akif Zeb [a,b], Yanan Liu [a], Naseeb Ullah [a], Anwu Xu [a,*]

[a] Division of Nanomaterials and Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, Anhui, China

[b] Institute of Environmental Sciences and Engineering (IESE), School of Civil and Environmental Engineering (SCEE), National University of Sciences and Technology (NUST), Sector H-12, Islamabad, Pakistan

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ABSTRACT

We prepared the Fe_3O_4/g-C_3N_4 nanoparticles (NPs) through a simple electrostatic self-assembly method with a 3:97 weight ratio to investigate their Fenton, photo-Fenton and oxidative functionalities besides photocatalytic functionality. We observed an improvement of the Fenton and photo-Fenton activities of the Fe_3O_4/g-C_3N_4 nanocomposites. This improvement was attributed to efficient charge transfer between Fe_3O_4 and g-C_3N_4 at the heterojunctions, inhibition of electron-hole recombination, a high surface area, and stabilization of Fe_3O_4 against leaching by the hydrophobic g-C_3N_4. The obtained NPs showed a higher degradation potential for rhodamine B (RhB) dye than those of Fe_3O_4 and g-C_3N_4. As compared to photocatalysis, the efficiency of RhB degradation in the Fenton and photo-Fenton reactions was increased by 20% and 90%, respectively. Additionally, the horseradish peroxidase (HRP) activity of the prepared nanomaterials was studied with 3,3,5,5-tetramethylbenzidinedihydrochloride (TMB) as a substrate. Dopamine oxidation was also examined. Results indicate that Fe_3O_4/g-C_3N_4 nanocomposites offers more efficient degradation of RhB dye in a photo-Fenton system compared with regular photocatalytic degradation, which requires a long time. Our study also confirmed that Fe_3O_4/g-C_3N_4 nanocomposites can be used as a potential material for mimicking HRP owing to its high affinity for TMB. These findings suggest good potential for applications in biosensing and as a catalyst in oxidation reactions.

1. Introduction

Graphitic carbon nitride (g-C_3N_4) has been extensively investigated for its photocatalytic water splitting and catalytic abilities among its properties [1]. The structure of g-C_3N_4 resembles that of graphite and consists of multiple parallel layers of stacked tri-s-triazine units held together by van der Waals forces [2,3]. This stacking of tri-s-triazine units is responsible for the nanoflake-like structure of carbon nitride and its large surface area. This material shows no solubility in most solvents such as water, alcohol, tetrahydrofuran (THF), diethyl ether, or toluene, which makes it an attractive photocatalyst material for degrading organic pollutants in the environment [4]. In comparison with other photocatalytic materials, carbon nitride is cheap, stable, and has low toxicity. Furthermore, g-C_3N_4 can be easily-prepared via a thermal treatment of melamine in an in-

* Corresponding author. Tel/Fax: +86-551-63602346; E-mail: anwuxu@ustc.edu.cn

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ert atmosphere [5,6], and has a mid-wide band gap of 2.7 eV [1]. Notably, nitrogen present in the structure of g-C_3N_4 contributes to the formation of a lone pair (LP) valence band, which is responsible for the electronic structure and properties of g-C_3N_4 [7]. Many studies have been conducted on the photocatalytic properties of carbon nitride; however, investigations of the degradation of organic pollutants by this material are somewhat limited owing to the fast electron-hole recombination [8–10]. As reported in previous studies, the band gap of g-C_3N_4 can be tuned by reshaping the morphology of the material, surface modifications or the separation of the holes and electrons [11]. The latter effect can be achieved by doping of g-C_3N_4 with either metallic or non-metallic ions and through the formation of composites with other nanomaterials that are photocatalytically active [12–22]. Liu et al. [23] prepared g-C_3N_4 nanocomposites through the immobilization of Fe_3O_4 and achieved increased photocatalytic performance. Our group reported g-C_3N_4/ZnO Z-scheme heterojunctions with enhanced photocatalytic activity [24]. Huang et al. [25] developed $CoFe_2O_4$/g-C_3N_4 composites with relatively fast g-C_3N_4 photocatalytic activity. All these studies indicate that metal oxide composites of g-C_3N_4 enhance its photocatalytic performance.

Magnetite (Fe_3O_4) is a well-known material with extensive applications, particularly in the field of photocatalysis, and Fenton/photo-Fenton reactions. Fe_3O_4 nanoparticles (NPs) have a well-defined cubic spinel structure in which both valence states, i.e., ferrous Fe (II) and ferric Fe (III), are present [26,27]. Studies have indicated that magnetite operates efficiently in acidic media. However, this material has a low surface area and Fe ions can leach into the solution during the reaction process, which hinders its application to degradation of pollutants in the natural environment [28,29]. Therefore, many studies have focused on its composites with other materials that enhance its stability and catalytic activity.

Fenton, photo-Fenton reaction processes are a type of an advanced oxidation process (AOP), which are considered to be effective for the degradation of organic pollutants in the environment, particularly for recalcitrants. These pollutants cannot degrade naturally and their degradation by photocatalysts is slow, requiring a long time for their complete remediation from the environment. Fenton processes involve the use of hydrogen peroxide (H_2O_2) as an external source to generate hydroxyl radicals in the presence of metallic species such as Fe(II) and Cu(II), and sometimes, in the presence of visible light [30]. Hydroxyl radicals can efficiently degrade pollutants in a short time.

Metal oxide NPs and noble metal NPs with graphene oxide (GO) have also been investigated for their horseradish peroxidase (HRP) mimicking activity in the case of 3,3,5,5 tetramethylbenzidinedihydrochloride (TMB) oxidation and for their applications in oxidation of glucose, dopamine, and NADH, through both heterogeneous and homogeneous catalysis [31,22,32]. These metal oxides are of considerable interest owing to their applications as an alternative to natural enzymes present in mammalian bodies and their possible uses in biological sensors. Shan et al. [32] successfully used Cu^{2+}-modified GO NPs in oxidation reactions of various substrates including dopamine, luminol, and NADH.

In this study we propose that iron oxide nanocomposites with g-C_3N_4 when used with H_2O_2 in a Fenton/photo-Fenton system could substantially increase the degradation efficiency of organic pollutants at neutral pH and room temperature. We prepared Fe_3O_4/g-C_3N_4 NPs through a simple electrostatic self-assembly method, investigated its catalytic properties and TMB as well as dopamine oxidation activity.

2. Experimental

2.1. Preparation of Fe_3O_4/g-C_3N_4 NPs

Melamine, $FeCl_3\cdot 6H_2O$, sodium acetate trihydrate ($C_2H_9NaO_5\cdot 3H_2O$), $MgCl_2$, KCl, rhodamine B (RhB), hydrogen peroxide (H_2O_2, 30%), and TMB were purchased from Aladdin Ltd. (Shanghai, China). Dopamine hydrochloride and 2-(*N*-morpholino)ethanesulfonic acid were purchased from Sigma-Aldrich. All chemicals were of analytical grade and used without further purification.

Melamine was used for the preparation of g-C_3N_4 via solid state synthesis. 5 g of melamine powder was placed in an alumina crucible and heated at 530 °C in a tube furnace for 2 h at a heating rate of 5 °C min^{-1} under nitrogen atmosphere.

1.09 g of $FeCl_3\cdot 6H_2O$ and 3.2 g of $C_2H_9NaO_5\cdot 3H_2O$ were dissolved in 40 ml ethanol, and added to an autoclave. The mixture was hydrothermally treated at 180 °C for 12 h. The autoclave was allowed to cool down to room temperature after reaction. The obtained product was washed several times with deionized water and ethanol, and dried at 80 °C overnight in a drying oven.

An electrostatic self-assembly method was used to prepare the Fe_3O_4/g-C_3N_4 nanocomposites [23]. 97 mg of the prepared g-C_3N_4 was dispersed in 50 ml deionized water by ultrasonication for 30 min and separately 3 mg of Fe_3O_4 in 10 ml of deionized water was dispersed through ultrasonication for 15 min. Then, Fe_3O_4 suspension was added dropwise into g-C_3N_4 suspension under vigorous stirring and further stirred for 24 h. The obtained product was centrifuged, washed, and dried at 60 °C overnight. Finally, the product was dried in a vacuum oven at 80 °C for 3 h.

2.2. Characterization

Sample characterization was performed through X-ray diffraction (XRD) on a Rigaku (Japan) D/max-γA X-ray diffractometer with a Cu target radiation source (λ = 0.154178 nm), X-ray photoelectron spectroscopy (XPS) for the elemental composition of the material was performed on a PerkinElmer RBD upgraded PHI-5000C ESCA system and a scanning electron microscope (SEM, JSM 6700F, JEOL) was used for surface characterization of the material.

2.3. Fenton activity measurements

Fenton activity of the Fe_3O_4/g-C_3N_4 nanocomposites was measured by RhB degradation under visible light irradiation in