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Enhanced Fenton, photo-Fenton and peroxidase-like activity and stability over $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocompositesShafaq 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 $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ 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 $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites. This improvement was attributed to efficient charge transfer between Fe_3O_4 and $\text{g-C}_3\text{N}_4$ at the heterojunctions, inhibition of electron-hole recombination, a high surface area, and stabilization of Fe_3O_4 against leaching by the hydrophobic $\text{g-C}_3\text{N}_4$. The obtained NPs showed a higher degradation potential for rhodamine B (RhB) dye than those of Fe_3O_4 and $\text{g-C}_3\text{N}_4$. 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 $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ 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 $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ 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.

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1. Introduction

Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) has been extensively investigated for its photocatalytic water splitting and catalytic abilities among its properties [1]. The structure of $\text{g-C}_3\text{N}_4$ 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, $\text{g-C}_3\text{N}_4$ can be easily-prepared via a thermal treatment of melamine in an

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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-C₃N₄ contributes to the formation of a lone pair (LP) valence band, which is responsible for the electronic structure and properties of g-C₃N₄ [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-C₃N₄ 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-C₃N₄ 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-C₃N₄ nanocomposites through the immobilization of Fe₃O₄ and achieved increased photocatalytic performance. Our group reported g-C₃N₄/ZnO Z-scheme heterojunctions with enhanced photocatalytic activity [24]. Huang et al. [25] developed CoFe₂O₄/g-C₃N₄ composites with relatively fast g-C₃N₄ photocatalytic activity. All these studies indicate that metal oxide composites of g-C₃N₄ enhance its photocatalytic performance.

Magnetite (Fe₃O₄) is a well-known material with extensive applications, particularly in the field of photocatalysis, and Fenton/photo-Fenton reactions. Fe₃O₄ 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 (H₂O₂) 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'-tetramethylbenzidine dihydrochloride (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 Cu²⁺-modified GO NPs in oxidation reactions of various substrates including do-

pamine, luminol, and NADH.

In this study we propose that iron oxide nanocomposites with g-C₃N₄ when used with H₂O₂ in a Fenton/photo-Fenton system could substantially increase the degradation efficiency of organic pollutants at neutral pH and room temperature. We prepared Fe₃O₄/g-C₃N₄ 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 Fe₃O₄/g-C₃N₄ NPs

Melamine, FeCl₃·6H₂O, sodium acetate trihydrate (C₂H₉NaO₅·3H₂O), MgCl₂, KCl, rhodamine B (RhB), hydrogen peroxide (H₂O₂, 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-C₃N₄ 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 FeCl₃·6H₂O and 3.2 g of C₂H₉NaO₅·3H₂O 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 Fe₃O₄/g-C₃N₄ nanocomposites [23]. 97 mg of the prepared g-C₃N₄ was dispersed in 50 ml deionized water by ultrasonication for 30 min and separately 3 mg of Fe₃O₄ in 10 ml of deionized water was dispersed through ultrasonication for 15 min. Then, Fe₃O₄ suspension was added dropwise into g-C₃N₄ 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 ($\lambda = 0.154178$ 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 Fe₃O₄/g-C₃N₄ nanocomposites was measured by RhB degradation under visible light irradiation in

a neutral pH solution at room temperature. The reaction was performed in a reaction vessel with a water jacket outside to control the reaction temperature. Xe lamp was used as a light source with a UV cut-off filter ($\lambda > 400$ nm). The catalyst at a concentration of 0.5 g L^{-1} was added into 10 ppm of RhB solution together with 11.4 mmol L^{-1} of H_2O_2 . The RhB solution together with the catalyst was allowed to stir for 1 h before the addition of H_2O_2 and irradiation to establish the adsorption-desorption equilibrium between the catalyst and RhB molecules. At 15-min intervals 2 ml samples were withdrawn from the reaction and filtered prior to analysis with a UV 1800PC spectrophotometer (Shanghai Mapada Instruments).

2.4. GC-MS analysis of the reaction intermediates

To determine whether any intermediates remained at the end of the above reaction, gas chromatography–mass spectroscopy (GC-MS, Trio-2000, Micromass, U.K.) analysis was performed. A Quartz chromatographic column BPX 70: size $28 \text{ m} \times 0.25 \text{ mm}$, was used with the following operating conditions: sampling inlet temperature, 260°C ; programming temperatures, 60 – 260°C at a rate of 6°C min^{-1} ; ion source temperature, 180°C ; electron energy, 70 eV .

2.5. Oxidation reactions over $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$

For a typical TMB oxidation reaction, $30 \mu\text{L}$ of H_2O_2 (final concentration of $2.6 \mu\text{mol L}^{-1}$), $300 \mu\text{L}$ of sodium acetate buffer ($\text{pH} = 4.5$), and $40 \mu\text{L}$ of TMB (with final concentrations of 0.2 , 0.4 , 0.8 , 1.6 , and 3.2 mmol L^{-1}) were mixed together at room temperature. Then, $100 \mu\text{L}$ of an aqueous solution of $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ (30 mg mL^{-1}) catalyst was added into the above solutions. A colour change was observed after a few seconds. The catalytic oxidation activity of TMB was measured by taking aliquots at 2 min intervals and recording the absorbance at 650 nm with a UV 1800PC spectrophotometer (Shanghai Mapada Instruments). Kinetic studies were performed using the Michaelis–Menten equation and double-reciprocal or Lineweaver–Burk plots.

For a typical dopamine oxidation reaction, $200 \mu\text{L}$ of MES buffer solution ($\text{pH} = 5.5$, 50 mmol L^{-1} , $2 \text{ mmol L}^{-1} \text{ MgCl}_2$, and $10 \text{ mmol L}^{-1} \text{ KCl}$) and $40 \mu\text{L}$ of $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ catalyst (30 mg mL^{-1}) were mixed. Dopamine solutions with a variety of concentrations (final concentrations of 0 , 1 , 2 , and 4 mmol L^{-1}) were added to the above solutions along with H_2O_2 ($3.5 \mu\text{mol L}^{-1}$). Catalytic oxidation of dopamine and the formation of the aminochrome product was monitored spectroscopically at $\lambda = 480 \text{ nm}$ with the use of a UV 1800PC spectrophotometer (Shanghai Mapada Instruments).

3. Results and discussion

3.1. Characterization results

XRD pattern of the obtained $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites (NC) are shown in Fig. 1. Characteristic peaks of $\text{g-C}_3\text{N}_4$ are clearly visible. The strongest peak for $\text{g-C}_3\text{N}_4$ was observed at

Fig. 1. XRD pattern of the $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite.

27° . This peak corresponds to the (002) plane that represents the aromatic ring layer spacing or inter-layer spacing in $\text{g-C}_3\text{N}_4$ [33], and confirms the graphitic nature of $\text{g-C}_3\text{N}_4$ with a d-spacing of 0.326 nm . The other characteristic peak of $\text{g-C}_3\text{N}_4$ appeared at 13° at a relatively low intensity. This peak corresponds to the (100) plane with a d-spacing of 0.68 nm , and could be assigned to the organized stacking layers of the chains of tri-s-triazine units in the $\text{g-C}_3\text{N}_4$ structure [33]. The characteristic peaks of Fe_3O_4 , had low intensities in the XRD pattern and could be assigned to the (220), (311), (400), (511), and (440) planes. This result indicates that magnetite is present in the nanocomposites, which have a cubic spinel structure. The weak intensity of the peaks was attributed to the low content of Fe_3O_4 in the sample. The XRD results confirmed that the obtained material was a nanocomposite in which both $\text{g-C}_3\text{N}_4$ and Fe_3O_4 retained their original structure in the composite.

To characterize the morphology and structure of the nanocomposites, SEM and TEM analyses were performed. Fig. 2(a) shows an SEM image of the $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ sample. The sheets of $\text{g-C}_3\text{N}_4$ could be identified easily from the SEM images. The bright features represent NPs of Fe_3O_4 , having an average size of 60 nm . The SEM image shows that the Fe_3O_4 NPs are firmly attached to the surface of the $\text{g-C}_3\text{N}_4$ sheets. Fig. 2(b) shows a TEM image of a thin graphene-like $\text{g-C}_3\text{N}_4$ nanosheet with darker regions indicating overlap of the sheets, having a lateral size of the order of micrometres. Fe_3O_4 (NPs) could be seen dispersed on the $\text{g-C}_3\text{N}_4$ surface and show some agglomeration. Fig. 2(c) and (d), respectively, show an STEM image and elemental mapping of the distribution of the four elements in the $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite.

To analyse the composition and valence states of the $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites, XPS analysis was performed (Fig. 3). Fig. 3(a) shows a survey spectrum of the nanocomposites, indicating the presence of the four elements present in the material including carbon, nitrogen, iron and oxygen and their respective atomic ratios. Fig. 3(b) shows peak fitting of the C 1s spectra. The peaks appearing at 284.8 , 288.3 , and 286 eV could be ascribed to the C-N-C coordination, C-(N)₃ group and adventitious carbon, respectively [5]. The N 1s region of the spectrum, shown in Fig. 3(c), consists of three peaks that could be attributed to the C-C group at 398.8 eV , N-(C)₃ group at 399.5 eV and the C-N-H group at 401 eV [5].

Fig. 2. SEM (a), TEM (b), STEM (c) image and elemental mapping (d) of the $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite.

Fig. 3. XPS survey spectrum of $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites (a), high resolution XPS spectra of C 1s (b), N 1s (c) and Fe 2p (d).

Fig. 3(d) shows the region of Fe 2p spectrum. Two prominent peaks are visible at approximately 725 and 711 eV. These two peaks were attributed to $\text{Fe } 2p_{1/2}$ and $\text{Fe } 2p_{3/2}$, respectively. Appeared satellite peaks indicate that the Fe element is present in the form of Fe_3O_4 in the $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites. Both oxidation states of Fe (II) and Fe (III) exist [34]. No signals for Fe-C or Fe-N were detected, suggesting that no chemical bond formed between the Fe_3O_4 and $\text{g-C}_3\text{N}_4$ [23].

3.2. Optical property measurements

The absorption range of light is of considerable importance for photodegradation of pollutants. For this purpose, UV-visible diffuse reflectance spectra (UV-Vis DRS) were measured. Fig. 4 shows that $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ had a broad absorption in the UV-visible region confirming the light absorption properties of the NC. A red shift was found for the $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ composite, which could be attributed to a charge transfer transition between the Fe_3O_4 and $\text{g-C}_3\text{N}_4$ that is responsible for its higher photocatalytic ability and redox behaviour [23]. The pure $\text{g-C}_3\text{N}_4$ showed an absorption edge at approximately 450 nm

Fig. 4. UV-Vis diffuse reflectance spectra of pure g-C₃N₄ and g-C₃N₄/Fe₃O₄ nanocomposite.

corresponding to a band gap of 2.76 eV [35]. This edge increased in Fe₃O₄/g-C₃N₄ nanocomposite with a red shift of about 600 nm as compared to the pure g-C₃N₄.

3.3. Fenton activity evaluation of Fe₃O₄/g-C₃N₄

The Fenton activity of the Fe₃O₄/g-C₃N₄ nanocomposites was examined with the model recalcitrant, RhB dye in the dark and under visible light irradiation. It has been reported in previous studies that the H₂O₂ degradation follows the Haber–Weiss mechanism in presence of metal oxides [36]. The proposed reaction mechanism in the photo-Fenton dye degradation involves the formation of superoxide radicals as a result of the reaction between H₂O₂ and •OH.

Along with the photo-Fenton activity measurements of Fe₃O₄/g-C₃N₄ NC the photo-Fenton activities of bare g-C₃N₄ and Fe₃O₄ were also evaluated. The C/C₀ time plots (where C is the concentration of dye at a given time and C₀ is the concentration of dye at equilibrium) were drawn for analysis of RhB degrada-

tion over 50 min. Fig. 5(a) shows that the photo-Fenton activity of Fe₃O₄/g-C₃N₄ NC was respectively four and three times as high as those of pure g-C₃N₄ and Fe₃O₄, respectively. Pure g-C₃N₄ has been reported to generate reactive hydroxyl species from H₂O₂ under visible light irradiation [37]. A low degradation RhB rate was observed in the case of g-C₃N₄, owing to rapid electron-hole recombination and a low affinity for H₂O₂ adsorption on the g-C₃N₄ surface. Fe₃O₄ has good Fenton activity; however, several factors hinder its degradation of organic pollutants. These include inhibition of the reaction due to the formation of [Fe(II)(H₂O)₆]²⁺ at neutral or alkaline pH, which in turn leads to formation of a [Fe(II)(OH)(H₂O)₅]⁺ complex with H₂O₂, thus blocking Fe(II) ions in the magnetite that are essential for an active heterogeneous Fenton reaction, leaching of Fe ions and low surface area of magnetite which decreases the availability of H₂O₂ to adsorb on the surface of Fe₃O₄ for generating •OH radicals [38,39]. In the Fe₃O₄/g-C₃N₄ nanocomposite, we presume that all the above-mentioned limitations could be overcome through the enhanced charge transfer between Fe(III) in Fe₃O₄ and the LUMO of g-C₃N₄ [23], together with the higher surface area for H₂O₂ adsorption and good stability of Fe₃O₄ protected by hydrophobic g-C₃N₄ sheets. The synergistic effect from the combination of Fe₃O₄ and g-C₃N₄ contributes to the enhanced redox and Fenton activity of the Fe₃O₄/g-C₃N₄ hybrid compared with the performances of Fe₃O₄ or g-C₃N₄ alone.

The degradation rate of RhB dye in the Fenton reaction was compared with the rate of photocatalytic degradation. We found that the photo-Fenton process was five times as fast as photocatalytic degradation, as shown in Fig. 5(b). This was attributed to the generation of •OH radicals by Fe₃O₄ in the presence of H₂O₂ even in the dark, which supports the redox reaction. The reaction was further enhanced when exposed to light irradiation. Complete degradation of RhB dye was observed within 60 min for the photo-Fenton reaction compared with approximately 120 min for the case of photocatalytic degradation, as reported by Liu et al. [23].

3.4. RhB degradation kinetics and reusability of Fe₃O₄/g-C₃N₄

Fig. S1(a) shows the time dependant degradation of RhB dye

Fig. 5. (a) C/C₀ vs time plot for the photo-Fenton degradation of RhB in comparison with g-C₃N₄ and Fe₃O₄; (b) Degradation of RhB in photocatalysis, Fenton and photo-Fenton reaction over Fe₃O₄/g-C₃N₄ nanocomposites.

Fig. 6. Reusability of the $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ NC for visible light degradation of RhB.

at neutral pH and room temperature under visible light irradiation, resulting in the degradation of more than 90% of the RhB in 60 min. The kinetics of this reaction were examined to determine the reaction rate and regression coefficient R^2 . From the kinetic plot in Fig. S1(b), we found the reaction rate to be 0.02 min^{-1} . A high R^2 value implies that the reaction follows first-order kinetics. Fig. S1(c) shows the RhB dye degradation process and the reaction solution before and after degradation; a colourless solution formed after the 60 min photo-Fenton reaction.

Reusability and stability of the catalytic material is also of a great importance for Fenton/photo-Fenton reactions. To study the durability and stability of $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ NC, we performed recycling tests by recovering the nanoparticles used in the first

reaction through centrifuging the reaction mixtures, and washing and drying the nanoparticles before reusing them in further reactions. Fig. 6 shows that there was no notable decrease in the activity of the catalyst even after three degradation reaction cycles. These results indicate that the catalyst has high stability and could be reused again.

3.5. GC results

To confirm the complete degradation of RhB by the nanocomposites and to ensure that no reaction intermediates remained, we performed GC-MS analysis of the colourless solution obtained after the 60-min reaction. The GC-MS results in Fig. 7 show a characteristic peak of the RhB dye (10 ppm) which disappeared on completion of the reaction. This result confirms that $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ degraded all the aromatic rings present in the dye and no intermediates formed as a result of catalytic reaction over the short reaction time.

3.6. Horseradish peroxidase like activity of $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$

Oxidation experiments were also performed to evaluate the HRP catalytic activity of $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$. HRP mimicking catalysts are considered to be interesting materials owing to their possible applications as a substitute for natural enzymes. Previous studies have reported that TMB is oxidized in the presence of HRP mimicking catalysts and hydrogen peroxide and the reaction completion is indicated by the appearance of a blue colour indicating formation of an oxidation product of TMB with strong absorbance at 650 nm [40,41]. For oxidation experi-

Fig. 7. GC-MS analysis of the RhB solutions before and after 60-min photo-Fenton degradation over $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ catalyst.

Fig. 8. (a) UV-visible absorption spectra for TMB oxidation in different conditions of the catalytic reaction; (b) Dependence of the HRP activity on the catalyst concentration; (c) Dependence of the peroxidase-like activity on TMB concentration; (d) TMB oxidation reaction process and oxidized TMB (inset).

ments we selected TMB as substrate at a mild acidic pH of 4.5, which is considered to be optimal for peroxidase activity [41]. Fig. 8(a) shows the considerable oxidation activity of TMB indicating that the Fe₃O₄/g-C₃N₄ NC could be considered to be a potential HRP mimicking catalyst. Furthermore, no oxidation of TMB occurred in the absence of Fe₃O₄/g-C₃N₄ or H₂O₂. To optimize the activity of the TMB oxidation reaction, the optimal amount of catalyst and different concentrations of TMB were also evaluated. The optimal amount of catalyst for TMB oxidation was found to be approximately 30 mg ml⁻¹ (Fig. 8(b)). The effect of TMB concentrations on the oxidation was explored (Fig. 8(c)). These results indicated that there was gradual increase in the peroxidase like activity as the TMB concentration increased.

Kinetic parameters such as the Michaelis constant (K_m) and maximum reaction rate (V_{max}) were calculated based on the Michaelis–Menten equation, $1/V_0 = K_m/V_{max} [1/[S] + 1/K_m]$. Here, V_0 is the initial velocity of the reaction, V_{max} is the maxi-

um velocity, $[S]$ represents the substrate concentration and K_m is the Michaelis constant. Table 1 shows a comparison of K_m and V_{max} values for different catalysts. The K_m value of our nanocomposites was markedly lower than that of HRP but comparable to that of previously reported catalysts. The low K_m value (0.162) of our material indicated a higher affinity of TMB towards Fe₃O₄/g-C₃N₄ NC than towards HRP.

3.7. Dopamine oxidation by Fe₃O₄/g-C₃N₄

Dopamine is a neurotransmitter present in the central nervous system (CNS) of mammals and plays a vital role in the cardiovascular, renal, CNS, hormonal function as well as in the control of emotions, attention, arousal, movement, and perception [46]. Dopamine imbalances in the body can lead to disorders such as Parkinson's disease, schizophrenia, depression, and hormonal imbalances [46]. Catalytic oxidation of dopamine is utilized for the quantitative analysis of the dopamine levels in the human body. Dopamine oxidation is indicated by the formation of an aminochrome product (480 nm) as reported in previous studies [32]. Fig. 9(a) shows the oxidation of dopamine (4 mmol L⁻¹) over Fe₃O₄/g-C₃N₄ for 30 min. Fig. 9(b) shows the oxidation of different concentrations of dopamine monitoring at 480 nm with respect to time. Fig. 9(b) shows that as the dopamine concentration increased, the absorbance also increased, indicating that the aminochrome product formation depends on the concentration of dopamine. To estimate the rate of dopamine oxidation, kinetics were also examined as shown in Fig. 9(c), the rate constant of the oxidation of dopa-

Table 1

Comparison of Michaelis–Menten constant (K_m) and maximum reaction rate (V_{max}) of reported materials with Fe₃O₄/g-C₃N₄ NC and HRP for TMB oxidation.

Catalyst	K_m (mmol L ⁻¹)	V_{max} ($\times 10^{-8}$ mol L ⁻¹ s ⁻¹)	Ref.
HRP enzyme	0.434	10	[42]
Fe ₃ O ₄ MNPs	0.098	3.44	[43]
Co-g-C ₃ N ₄	0.113	8.46	[44]
Cu NPs/g-C ₃ N ₄	0.389	58.4	[45]
Fe ₃ O ₄ /g-C ₃ N ₄ NC	0.162	53.6	This study

Fig. 9. (a) UV-visible absorbance at 480 nm measured over time to show the oxidation of dopamine in the presence of the $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites; (b) dependence of aminochrome product formation on the concentration of dopamine; (c) kinetics of the same reaction; (d) reaction process of the oxidation of dopamine over $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites.

mine was found to be 1.21 min^{-1} . The linear regression coefficient was calculated to be $R^2 = 0.973$. This high value suggests that the oxidation of dopamine follows first-order kinetics.

4. Conclusions

This research provides insight into the potential applications of the $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites, prepared through an electrostatic self-assembly method. The resulting nanocomposite shows good potential for degrading RhB dye in a short time through a photo-Fenton reaction due to efficient charge transfer between Fe_3O_4 and $\text{g-C}_3\text{N}_4$, prevention of electron-hole recombination, and improved stability of Fe_3O_4 over $\text{g-C}_3\text{N}_4$ nanosheets. High photo-Fenton activity of $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ NC could be used in natural environments for remediation of recalcitrant. Furthermore, the high affinity of the NC for TMB makes it an excellent candidate for mimicking HRP. The oxidation potential of the catalyst for dopamine enables determination of dopamine concentration, indicating that the material could also be used as a catalyst for various biological based oxidation reactions with potential applications in the fields of biosensing, biocatalysis, and biomedicine.

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Graphical Abstract

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Enhanced Fenton, photo-Fenton and peroxidase-like activity and stability over Fe₃O₄/g-C₃N₄ nanocomposites

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Fe₃O₄/g-C₃N₄ nanocomposite efficiently degraded Rhodamine B via Fenton and photo-Fenton reactions, mimicked horseradish peroxidase-like activity for TMB oxidation, and oxidized dopamine showing potential for use in biocatalysis.

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Fe₃O₄/g-C₃N₄复合催化剂增强芬顿/光-芬顿和类过氧化物酶反应的活性及稳定性

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摘要: 石墨相的氮化碳(g-C₃N₄)已被广泛用于光催化、水分解、光子检测器、电池、以及光电阴极。与其他光催化材料相比, g-C₃N₄具有价格低廉, 易制备, 无毒无污染等优点。此外, C₃N₄具有适宜的带隙(2.7 eV), 能有效地吸收可见光。有关C₃N₄的光催化研究很多, 但是其降解效率受限于电子空穴对的快速复合。因此, 为了提高C₃N₄光催化反应效率, 需要对其进行改性。磁铁矿(Fe₃O₄)广泛用于光催化和芬顿/光-芬顿反应。Fe₃O₄晶体具有反式尖晶石结构, 其中Fe²⁺和Fe³⁺同时存在。研究表明, 磁铁矿在酸性条件下催化效果显著, 然而, 它的比表面积小, 随着反应时间的推移, 铁离子会溶出, 不利于有机物降解反应。因此, 近来许多研究着重于磁铁矿复合物的制备, 以提高磁铁矿的稳定性及催化性能。

本文通过惰性气氛高温焙烧三聚氰胺制备了g-C₃N₄, 再通过氯化铁和乙酸钠在乙醇中于180 °C溶剂热反应, 制备Fe₃O₄纳米粒子, 最后通过静电自组装过程制备出Fe₃O₄/g-C₃N₄纳米复合材料。利用X射线衍射(XRD), 扫描电子显微镜(SEM)及X射线光电子光谱(XPS)等手段验证其组成和结构。XRD结果表明, Fe₃O₄/g-C₃N₄复合材料中可以清晰看到Fe₃O₄和g-C₃N₄的衍射峰, 说明这两种材料的晶相得以保持。SEM和TEM结果表明, Fe₃O₄纳米颗粒很好地附着在g-C₃N₄薄片上。XPS结果表明, 氮化碳中存在典型的三种N峰; 此外还存在铁的两种价态。光-芬顿活性测试中, 相同条件下, Fe₃O₄/g-C₃N₄在60 min内将罗丹明B(RhB)几乎降解完全, 而单组份的Fe₃O₄或g-C₃N₄对RhB的降解小于50%。可见, 复合后的Fe₃O₄/g-C₃N₄光催化性能得到很大提升。单g-C₃N₄本身由于快速的电子空穴复合以及对双氧水的弱亲和力, 因而对RhB降解效果差。单独的Fe₃O₄由于在中性或者碱性条件下反而会抑制光催化芬顿活性。对于制备的Fe₃O₄/g-C₃N₄复合材料, 具有以下优点: (1)电子在Fe³⁺和g-C₃N₄的LUMO轨道上的转移降低了电子-空穴对的复合; (2) Fe₃O₄均匀分布在g-C₃N₄上, 对于H₂O₂的吸附提供了有利的高比表面积; (3) Fe₃O₄和g-C₃N₄之间的界面相互作用使得Fe₃O₄的稳定性提高。通过降解RhB的动力学研究, 得到反应速率为0.02 min⁻¹, 属准一级反应。分析检测结果表明, 光-芬顿反应后, RhB分子被彻底矿化降解, 没有中间产物生成, 最终降解为CO₂和水。

同时, 通过对辣根过氧化物酶(HRP)模拟催化进行测试, 以3,3',5,5'-四甲基联苯胺盐酸盐(TMB)作为基质, 同时添加双氧水和Fe₃O₄/g-C₃N₄, 在pH值为4.5条件下, TMB可以被有效氧化。实验表明, Fe₃O₄/g-C₃N₄添加量为25 mg/ml时, 对TMB氧化性能最佳。复合催化剂还用于多巴胺的催化氧化反应。结果表明, 多巴胺的氧化反应速率常数为1.21 min⁻¹, 属一级动力学反应。

总之, 复合材料提高了RhB的光催化降解活性和稳定性; 对TMB和HRP亲和性好, 表现出高的类过氧化物酶反应活性; 有效的多巴胺氧化反应表明其有望用于生物基氧化反应中。实验结果表明, 本文发展的Fe₃O₄/g-C₃N₄复合材料为其他类型复合材料的制备与应用提供了新的思路。

关键词: Fe₃O₄/g-C₃N₄纳米复合材料; 芬顿反应; 染料降解; 类辣根过氧化物酶活性; 辣根过氧化物酶模拟反应

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