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Article

One-step preparation of $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$ heterojunctions as a peroxymonosulfate activator for relatively highly-efficient methylene blue degradation

Xin Zhao ^a, Qing-Da An ^{a,*}, Zuo-Yi Xiao ^a, Shang-Ru Zhai ^{a,#}, Zhan Shi ^b^a Faculty of Light Industry and Chemical Engineering, Dalian Polytechnic University, Dalian 116034, Liaoning, China^b State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, Jilin, China

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ABSTRACT

Persulfate decontamination technologies utilizing radical-driven processes are powerful tools for the treatment of a broad range of impurities. However, the design of high-performance catalytic activators with multi-functionality remains a great challenge. Therefore, in this study, three-dimensional multifunctional $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$ (N-GN: nitrogen-doped graphene, CNTs: carbon nanotubes) heterojunctions, which can be employed as microwave absorbers and catalysts, were synthesized via a solvothermal method and applied to activate peroxymonosulfate for the degradation of methylene blue (MB). X-ray diffraction (XRD), Fourier transform infrared spectrometer (FTIR), scanning electron microscope (SEM), and X-ray photoelectron microscopy (XPS) analyses revealed that the Fe_xO_y were anchored in-situ onto the N-GN network. Using MB as the model organic dye, various factors, such as degradation systems, PMS loading, initial organic pollutant concentration, and catalyst dosage were optimized. The results revealed that the remarkable efficiency was attributable to the synergistic effects of carbon, nitrogen, and iron-based species. The oxidation system corresponded to the pseudo-first-order kinetic with a k value of $\sim 0.33 \text{ min}^{-1}$. It was demonstrated that both $\text{SO}_4^{\cdot-}$ and $\text{OH}^{\cdot}$ were the predominant reactive species through quenching experiments. Because these heterojunctions were employed as microwave absorbers and have a semiconductor-like texture, the Fe/N co-rich hierarchical porous carbon skeleton favored electron transport and storage. These heterojunctions increase the options for transitional metal catalysts and highlights the importance of designing other heterojunctions for specific applications, such as supercapacitors, energy storage, CO_2 capture, and oxygen reduction electrocatalysts.

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1. Introduction

There have been rapid and constant developments in science and technology; however, environmental problems have become a concern [1]. Among these, water pollution and food contamination are extremely detrimental [5], as well as appli-

cations of poorer biocompatibility and higher toxicity organic dyes [2], e.g., phenolic compounds and antibiotics [3,4]. To solve these issues, several technologies, including photocatalysis [6], catalytic degradation, biodegradation [7], and adsorption [8,9] have been widely employed [10]. Nevertheless, there are still some associated drawbacks, e.g., low efficiency, high

* Corresponding author. E-mail: anqingdachem@163.com

Corresponding author. E-mail: zhairschem@163.com

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cost, and serious secondary pollution [11].

In consideration of these issues, much attention has been given to advanced oxidation process (AOPs) [12,13] to solve the problems, mainly because it can generate high oxidative radicals in these reactions [14]. With the aid of substitution, electron transfer, and addition reactions between radicals and organic compounds, refractory toxic organic macromolecules can be converted into low- or non-toxic small molecules, and can even be directly degraded to carbon dioxide and water [15–17]. Given this, in the past Fenton's reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) has been widely exploited [18,19] because it can generate hydroxyl radicals ($\text{OH}^\bullet$) [20]. However, it is restricted to the harsh conditions of hydroxyl radicals. For instance, the pH value range is only ~ 2.5 – 3.5 . Hydroxyl radicals are also extremely unstable in water, and can easily decompose into hydroxyls [21]. Additionally, metal ion leakage [22] is also a serious issue, resulting in secondary pollution and wastage. Consequently, some available methods had been used to enhance its utilization, such as screening the catalyst types and tailoring the surface properties. In particular, using organic ligands to ameliorate hydroxyl radical acid and alkali resistance is an alternative solution. For instance, Gupta et al. [23] introduced Fe-TAML (tetra-amido macrocyclic ligand) in the typical Fenton systems. In addition, Lente and co-workers [24] investigated the removal manifestation of various nitrogen-doped iron matrix catalysts. Undoubtedly, these are valid ways for elevating the operation conditions.

More recently, compared with unfavorable $\text{OH}^\bullet$, and because of a high redox potential, superior oxidizability, and broader scope of the acid and alkali applications [25], $\text{SO}_4^{\bullet-}$ has been suggested to challenge organic compound pollution. As we demonstrated, Gong et al. [26] found that peroxymonosulfate (PMS) was heterogeneously catalyzed by Fe@ACFs (activated carbon fibers) and displayed almost many times higher rates than the H_2O_2 system. Generally, in order to obtain sulfate radicals, PMS or persulfate are adopted because both have a lower cost and low-toxicity, and are easily available [27]. Unfortunately, neither can decompose abundant radicals without any treatments. Considering these factors, ultrasonic methods, metal ions, thermal radiation, and catalysts have been applied to activate PMS [28,29]. In the first three of these options, the equipment demand and experimental conditions are relatively harsh, and the leakage of homogeneous process leads to metal ions losses. Accordingly, most research has been primarily focused on designing high-performance catalysts [30–32].

Among these, on account of their remarkable properties, many studies have paid particular attention to cobalt metal-based composites. As previously illustrated, Huang et al. [33] demonstrated that high-valent cobalt-oxo intermediates play a great role in CFs-CoPc/PMS/ HCO_3^- systems. Shukla and co-workers combined Co with SiO_2 that exhibited a strong Co and support interaction by forming Co_2SiO_4 and cobalt oxide [34]. However, cobalt itself is a source of pollution [35] due to its poorer biocompatibility and higher toxicity [36,37]. Consequently, in order to overcome this issue, Karthikeyan et al. [38] employed Fe oxides instead of Co_3O_4 for the degradation of *N,N'*-diethyl-*p*-phenyl diamine. Noticeably, this step represents

tremendous progress because iron is inexpensive, environmentally safe, and has a high-authority. More importantly, Ji and co-workers [39] used Fe_2O_3 to activate PMS for Rhodamine B (RhB) decolorization, which showed a high activity. However, active sites of uneven dispersion and agglomeration possibly attenuated its superiority [40]. Fortunately, the appearance of graphite oxide solves this problem as it possesses abundant oxygen functional groups and delocalized π -electron systems; the graphite oxide fixes and anchors metal ions via both physical and chemical forces, as well as π - π stacking interactions [41]. Moreover, due to its excellent electronic conductivity and outstanding layered structure, graphene zigzag edges are active catalytic sites [42]. More amazingly, the structure and properties of graphite would be vastly improved by the addition of carbon nanotubes (CNTs) as they have many superior virtues, such as an outstanding electrochemical performance, a perfect hexagonal structure connection, and excellent flexibility [11]. In regards to the catalyst, after utilizing mixed carbon nanotubes, an interpenetrating polymer network (IPN)-like texture is created with two-dimensional graphite and one-dimensional CNTs, resulting in a three-dimensional material with elevated electron transfer conductivity, propitious to the proceeding catalytic reaction.

Beyond these, the design of a catalytic activator with multi-functionality remains a great challenge. There is consequently a pressing demand to obtain a novel material, which is simultaneously multifunctional and relatively highly-efficient. In view of this, we present a single-step solvothermal method to synthesize $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$ heterojunctions using inexpensive and environmentally-friendly graphene oxide, urea, and ferric salt as the raw materials. These had many virtues that conformed to the mentioned demands. First, the graphene surface had some meteorite-like sunken craters where the iron ions were anchored, which is beneficial for increasing the stability. Moreover, by virtue of the distance between these craters, Fe_xO_y did not agglomerate or aggregate. Conversely, in the case of graphene, the electronic structure was altered around the iron oxides particles [43,44], thus giving rise to an increase in the original spin and density distribution of the electrons [45]. More importantly, this type of material has previously been investigated for microwave absorption [46]. Hence, within this context, the heterojunctions of the semiconductor-like textures were tested for methylene blue (MB) degradation, and the degradation mechanism is discussed in detail on the basis of electron transfer and multi-functionality.

2. Experimental

2.1. Materials

Peroxymonosulfate ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$, 42%–46% KHSO_5) were purchased from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China). Tert-butanol (TBA), MB ($\geq 82\%$) was obtained from Sinopharm Chemical Reagent Co., China. The potassium permanganate, urea, hydrogen peroxide (30 wt%), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, sodium nitrate, sulfuric acid (98 wt%), and ethanol were supplied by Tianjin Kermel Chemical Reagent Co., Ltd.

The graphite oxide (GO) was synthesized via a modified Hummers' method [43]. The CNTs were obtained from Shenzhen Nanoport Co., Ltd. All the above-mentioned chemicals were of analytical grade and used directly without any further purification.

2.2. Fabrication of $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$

Firstly, 35 mg of GO was dispersed into de-ionized water (40 mL) with ultrasonic treatment (53 kHz) for ~1 h under room temperature. As the mixture turned brown, 5 mg of CNTs was dissolved into the above solution, which also supported by ultrasonic treatment. Then, 10 mmol/L of urea and 4.6 mmol/L of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were simultaneously added into the solution followed by 30 min of continuous magnetic stirring. In the solvothermal process, the mixture was transferred and sealed into a 60 mL Teflon-lined stainless autoclave at 180 °C for 6 h. After reactor cooling, the final product was transferred into a beaker and washed by deionized water (60 mL) and ethanol (60 mL) three times and through magnetic filtration. Meanwhile, $\text{Fe}_x\text{O}_y/\text{GN}/\text{CNTs}$, N-GN were also fabricated via the same method by adding different raw materials. For example, in the preparation of $\text{Fe}_x\text{O}_y/\text{GN}/\text{CNTs}$, urea was not used, unlike in the preparation of $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$. For another instance, in the preparation of N-GN, urea and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were not used.

2.3. Characterization

The morphology and structure of samples were investigated by transmission electron microscopy (TEM, Hitachi H9000NAR) and scanning electron microscope (SEM, JEM JEOL 2100). The X-ray diffraction (XRD) patterns were observed using a Rigaku model D/max-2700 diffractometer. The surface compositions were captured by X-ray photoelectron spectroscopy (XPS, PHI 5000). Fourier transform infrared (FTIR) spectroscopy (Perkin-Elmer 400 spectrometer, Llantrisant, UK) over the wavenumber range of 400–4000 cm^{-1} was applied. The structural deformation was determined by Raman spectra (RM2000, Renishaw, UK). The magnetic properties were tested by a vibrating sample magnetometer (VSM). A UV-vis spectrophotometer (Agilent Cary 60 spectrophotometer, Germany) was utilized to quantify the MB concentrations at the maximum absorption wavelength (664 nm).

2.4. Evaluation of catalytic activity

The MB degradation tests were explored. Firstly, a known amount of as-prepared catalysts (0.1–0.8 g/L) and a certain concentration of MB solution (30–500 mg/L) prepared adequately in advance were added into a beaker flask. A magnet was then placed under the bottom of the beaker flask to separate the catalysts from the MB solution, and 4 mL of the solution was loaded into a quartz cuvette for UV-vis spectrophotometer analysis. Subsequently, a predetermined concentration of PMS solution (0.5–5 mmol/L) was added. After a certain period of reaction time intervals, 4 mL of the solution was extracted for UV-vis spectrophotometer analysis, as above. After

completion of each degradation process, the catalysts were recycled through magnetic filtration and washed with ethanol and water three times, and used for the reusability test. Radical quenching experiments were also studied. The experimental procedure was similar as that described above; however, various dosages of ethanol or TBA were added.

3. Results and discussion

3.1. The formation mechanism of $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$

The fabrication process is illustrated in Scheme 1. Typically, for the hummers' method of oxidation, the oxygen-containing groups, such as hydroxyl (–OH), epoxy (–CH(O)CH–), and carboxyl (–COOH), were formed and transformed into negative groups under the ionization process. Therefore, after ultrasonic treatment, the urea and Fe^{2+} cations were combined with these groups by chemical force and electrostatic interactions. Additionally, due to their perfect hexagonal structure connection, excellent flexibility, and outstanding reactivity, the CNTs were effectively combined with the GO sheets resulting in a change to the Eigen electronic structure. Furthermore, owing to their one-dimensional structure, they also prevented the GO from collapsing and agglomerating under high temperature carbonization by forming a three-dimensional interpenetrating polymer network (IPN)-like texture. Then, during the hydrothermal process, some Fe^{2+} ions were anchored onto the GO sheets in the form of $\text{Fe}(\text{OH})$, and the rest were oxidized to Fe^{3+} , leading to the formation of $\text{FeO}(\text{OH})$. The structural defects and surface functionalities of the CNTs, similar to the oxygen-containing functional groups of GO, were not only considered to be ideal catalytic components, but acted as active sites to for iron ions and nanoparticles to attach to; they can also can be regarded as matrix materials for the iron oxides. The nitrogen-containing gases, such as ammonia generated from the urea decomposition, also bonded with the negatively charged groups via organic chemical reactions, resulting in the formation of nitrogen-enriched graphene. Finally, at a high pressure and different temperature between the upper and lower parts of the mixture solution, Fe_2O_3 and partly Fe_3O_4 from $\text{Fe}(\text{OH})$ and

Scheme 1. Formation progress diagram of the $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$ heterojunctions.

FeO(OH) were adsorbed and grown on the graphite surface in situ. As a result, both nanocrystals were anchored onto the surface of the N-doped graphene sheets, leading to the formation of a $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$ composite.

3.2. Structural characterization of resultant samples

3.2.1. FTIR

Fig. S1 shows the bonding of the organic functional groups tested through FTIR. For graphite oxide, there is a wide, strong peak near 3436 cm^{-1} , belonging to the stretching vibration of hydroxyl groups and a small amount adsorbed water. The broad peak near 1631 cm^{-1} is ascribed to the $\text{C}=\text{C}$ sp^2 hybrid absorbing vibration. The 1726 cm^{-1} peak is in line with the unsaturated group $\text{C}=\text{O}$. The peak at $\sim 1385\text{ cm}^{-1}$ is likely to be due to $\text{C}-\text{OH}$ bending vibration absorption and that at $\sim 1117\text{ cm}^{-1}$ is consistent with the stretching vibration absorption of $\text{C}-\text{O}/\text{C}-\text{O}-\text{C}$ [47]. Hence, the appearance of the oxygen-containing groups illustrates the successful oxidation of graphite. After the hydrothermal treatment, these groups were distinctly removed, which can be observed for $\text{Fe}_x\text{O}_y/\text{GN}$. In addition, a powerful peak near 565 cm^{-1} is ascribed to the $\text{Fe}-\text{O}$ bond stretching vibration [48]. Moreover, as demonstrated by the $\text{Fe}_x\text{O}_y/\text{N-GN}$ spectrum, although there are some peaks near 3438 , 1632 , and 1385 cm^{-1} , these peaks decreased considerably and some even disappeared, which is because some of the graphite oxide was reduced by nitrogen. However, one weak peak around 1119 cm^{-1} was still observed and is ascribed to the $\text{C}-\text{N}$ stretching vibration [49]. Another near 1419 cm^{-1} is attributed to $\text{C}=\text{N}$. These results suggest that nitrogen was successfully doped into the graphite oxide. As shown in the $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$ FTIR spectrum, there is no sensible variation compared with the other FTIR results. Nonetheless, the dispersion of CNTs led to the change of the physical forming of graphite, preventing it from lumping and aggregating, and therefore, providing a large surface area and inducing a better dispersion of active sites.

3.2.2. XRD

As represented in Fig. S2, the crystalline structure of composites was characterized through XRD analysis. Clearly, there are minor distinctions among the diffraction patterns. All of these emerged as fluctuations near 24.6° , 32.16° , 36.2° , 41.1° , 54.1° , 57.5° , 63.1° , and 66.0° , which are associated with the (012), (104), (110), (113), (116), (122), (214), and (125) of Fe_2O_3 (JCPDS card No. 33-0664) crystal parameters, respectively. In addition, certain relatively small, but not negligible, diffraction peaks near 30.1° , 35.5° , 43.1° , 42.2° , 57.1° , and 62.7° were also observed, attributed to the crystal planes (220), (311), (400), (422), (511), and (440) of Fe_3O_4 , respectively. [JCPDS 19-0629] [50]. These inclinations manifested the successful formation of iron oxides crystals. There are also slight characteristic peaks at 21.16° , attributed to the graphite diffraction peaks [51] in $\text{Fe}_x\text{O}_y/\text{GN}$ because iron oxides can be reduced by carbon species at a high temperature, and the reduced zero-valent iron can induce the formation of graphite, and therefore, only small graphite peaks were observed. How-

ever, compared with $\text{Fe}_x\text{O}_y/\text{GN}$, the nitrogen-doped catalysts were obviously different, indicating a complex distribution that is highly disordered and N-GN successfully maintained its material structure. All the analysis results were consistent with the FTIR phenomena.

3.2.3. Raman

The bonding and microstructures of the C-species were explicitly investigated via Raman spectroscopy. As demonstrated in Fig. 1, two dramatic characteristic peaks and a weak peak were detected, which are assigned to the G, D, and 2D bands [52], respectively. The G-band at 1591 cm^{-1} is related to the stretching vibration of the sp^2 hybridization C atoms. It effectively reflects the graphene layer structure and ordered texture. While the D-band near 1339 cm^{-1} is usually considered as a disordered vibration peak of graphene and employed to characterize the structural defects of graphene. This peak is produced from the lattice vibrations that deviate from the Brillouin zone center, graphite random arrangement, and irregular vibration of the sp^3 hybridization carbon atoms. The observed D-band demonstrates that after oxidation, some of the sp^2 hybridization C atoms were transformed into sp^3 hybridization, and the $\text{C}=\text{C}$ double bonds were destroyed, leading to the formation of a highly expansive and disordered structure. Additionally, the intensity ratio of the D and G bands, I_D/I_G , can be used to characterize the density defects and degree of crystal disorder [53]. After the calculation, the values of the I_D/I_G ratios for $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$, $\text{Fe}_x\text{O}_y/\text{N-GN}$, and $\text{Fe}_x\text{O}_y/\text{GN}$ are ~ 1.079 , 1.167 , 1.117 , respectively. Obviously, after being doped with nitrogen, these increased slightly, which is mainly associated with the fraction of nitrogen that was embedded in the carbon atoms lattice. For comparison, after joining the CNTs, the ratio decreased slightly; this is related to the regular structure and higher uniformity degree of the CNTs, resulting in a 3D structure. Noticeably, for all the manifestations, the carbon skeletons were deformed to a certain degree when nitrogen or iron atoms were introduced, which is favorable for reactant adsorption.

Fig. 1. Raman spectra of the $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$, $\text{Fe}_x\text{O}_y/\text{N-GN}$, and $\text{Fe}_x\text{O}_y/\text{GN}$ compounds.

3.2.4. SEM and TEM

SEM and TEM were applied to determine the particle size and surface morphology, and the corresponding results are shown in Fig. 2. Graphene has a thin flake tissue layer and fold drape textures. It belongs to the oxygen-containing groups, which undermine the formation of the lamellar structure. Fig. 2(a) shows that before the nitrogen doping, the aggregation and agglomeration of the iron oxide was obvious, and the crystal growth of metal oxides was affected by each other, resulting in relatively large particle sizes and a reduction in the degradation efficiency. In contrast, this was improved when a substantial amount of nitrogen was introduced as shown in Fig. 2(b). In the presence of nitrogen atoms, this can lead to a twisting of the two-dimensional graphene plane skeleton, resulting in iron oxide particles that possess a smaller size and are uniformly distributed on the nitrogen doped graphene. Significantly, as shown in Fig. 2(c), after adding CNTs, the graphite layers were spirally tiled and the specific surface areas were further effectively enlarged, leading to the formation of a pore structure and better uniformly dispersed particles.

Fig 2(d) shows that in the absence of nitrogen, the particle distribution was extremely uneven and the size spanned from 300 to 500 nm. Furthermore, these were unexpectedly partially stacked together, resulting in substantial agglomeration. Comparatively, Fig. 2(e) reveals that the size uniformity and distribution of $\text{Fe}_x\text{O}_y/\text{N-GN}$ were both significantly modified. The sites were distributed evenly and maintained a certain distance between each other. The diameters of the non-spherical iron oxide particles were $\sim 30\text{--}50\text{ nm}$, with short rod- and rice-like shapes. No particles were detected far away from the graphite structure, indicating that the ionic interactions and hydrogen bonding were not the only causes for the formation of the compounds; chemical reactions between the oxygen groups, iron, and nitrogen also played an important role. These reactive region parts supplied the nucleation sites for particle crystal growth, leading to the formation of defects on the surface of graphene. Thus, the doped-N sites were bonded with iron ions

in Fe–N conjugate arrangements in situ, which indirectly restricted and controlled the size [49]. Ultimately, as displayed in Fig. 2(f), the CNTs with pipe shapes were easily inserted into a graphite structure. After being introduced to the CNTs, two-dimensional graphite and one-dimensional carbon nanotubes not only formed interpenetrating polymer network (IPN)-like textures, which have the merits of three-dimensional materials, but the CNTs also prevented the graphite from collapsing, resulting in a swelling of the sponge-like structure. The high-resolution transmission electron microscopy (HRTEM) of the iron oxides is displayed in Fig. 2(g), belonging to (110) of Fe_2O_3 .

3.2.5. XPS

Fig. 3 shows the XPS survey spectra, which indicates the element chemical states and surface compositions. As displayed in Fig. 3(a), there are four peaks near 285.08, 400.03, 532.05, and 712.09 eV corresponding to C 1s, N 1s, O 1s and Fe $2p_{3/2}$, respectively. In Fig. 3(b), C 1s was split into four peaks near 284.68, 285.13, 286.16, and 289.98 eV, which are the responses to C–C/C=C, C–N, C–O, and O–C=O, respectively. However, it is reported that the combination energy of C–N is closed to C=O so it is difficult to discriminate them. However, it was demonstrated from the FTIR analysis that C=O almost disappeared. Hence, the peak near 285.13 eV is due to C–N, further illustrating that the nitrogen was firmly anchored onto the graphite layers through a chemical bond force. Fig. 3(c) reveals the deconvolution of the O envelope. Two large peaks near 530.38 and 532.08 eV were detected, attributed to C–Fe and C–O, respectively, due to the successful synthesis of the iron oxides and a strong bonding force. Typically, N 1s peaks can be divided into pyridinic, pyrrolic, and graphitic nitrogen [54]. As shown in Fig. 3(d), the peak near 398.28 eV is attributed to pyridinic nitrogen, and that at $\sim 399.68\text{ eV}$ indicates the generation of pyrrolic nitrogen. In addition, the peak at $\sim 401.18\text{ eV}$ belongs to graphitic nitrogen. Commonly, in the case of carbon materials, the higher the amount of pyridinic type nitrogen, the better

Fig. 2. SEM morphology of $\text{Fe}_x\text{O}_y/\text{GN}$ (a), $\text{Fe}_x\text{O}_y/\text{N-GN}$ (b), and $\text{Fe}_x\text{O}_y/\text{N-GN/CNTs}$ (c). TEM images of $\text{Fe}_x\text{O}_y/\text{GN}$ (d), $\text{Fe}_x\text{O}_y/\text{N-GN}$ (e), and $\text{Fe}_x\text{O}_y/\text{N-GN/CNTs}$ (f). HRTEM images of $\text{Fe}_x\text{O}_y/\text{N-GN}$ (g, h).

Fig. 3. XPS spectra of $\text{Fe}_x\text{O}_y/\text{N-GN/CNTs}$ (a) the survey spectrum, (b) C 1s, (c) O 1s, (d) N 1s, (e) Fe 2p.

the catalytic activity, which is attributed to the strong electron-withdrawing ability of pyridinic nitrogen. Additionally, pyrrolic nitrogen is regarded as a substantial active site and used for applications for anchoring transition metals [55]. Graphitic nitrogen is favorable for prompting the interaction between individual elements.

The results of the deconvolution of Fe are showed in Fig. 3(e). Clearly, the peaks near 711.08 and 724.98 eV agree with the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ regions, respectively [56]. Iron oxide is made up of three forms of iron elements; namely, octahedron Fe^{2+} , tetrahedron Fe^{3+} , and octahedron Fe^{3+} . Specifically, Fe $2p_{3/2}$ was feasibly deconvoluted into three dominant and two satellite peaks. The peaks at ~ 710.08 and 711.38 eV are consistent with octahedron Fe^{2+} and octahedron Fe^{3+} , respectively; the peaks near 713.58 eV correspond to tetrahedron Fe^{3+} ; and the peaks at 717.18 and 719.38 eV agree with the satellite peaks of Fe^{2+} and Fe^{3+} respectively [56]. These results indicate that the synthesized material contains three types of nitrogen and two states of iron, and the binding force between them and GN consisted not only of physical forces but also chemical bonds, which is consistent with the former analysis.

In addition, the XPS analysis of the catalyst after the MB degradation was also characterized and the curve is provided in Fig. S3. Clearly, compared with the fresh catalyst, there were negligible changes to the XPS for C 1s, N 1s, and O 1s, but small changes for Fe 2p. Clearly, octahedral Fe^{2+} increased slightly and octahedral Fe^{3+} decreased, which further illustrates that the possible catalytic mechanism can mainly be attributed to the transformation between different valent irons, leading to electron transfer.

3.2.6. VSM

In consideration of the iron oxides nanoparticles, it does not matter if either Fe_2O_3 or Fe_3O_4 are anchored on the graphitic sheet as the samples possess excellent magnetic properties regardless. Thus, $\text{Fe}_x\text{O}_y/\text{N-GN/CNTs}$ and $\text{Fe}_x\text{O}_y/\text{N-GN}$ were investigated using VSM, and the results are shown in Fig. 4. Clearly, both displayed the typical S-like shaped loops, indicating the presence of magnetic iron oxide particles. However, the main three magnetic parameters are different. As shown, the saturation magnetization (M_s), coercivity (H_c), and remnant magnetization (M_r) are 19.437 emu/g, 175.7 Oe, and 3.54 emu/g for $\text{Fe}_x\text{O}_y/\text{N-GN}$, and 16.467 emu/g, 146.41 Oe, and 0.56 emu/g for $\text{Fe}_x\text{O}_y/\text{N-GN/CNTs}$, respectively, and all have a high H_c and low remnant magnetization. The difference between

Fig. 4. Vibrating sample magnetometer of $\text{Fe}_x\text{O}_y/\text{N-GN}$ and $\text{Fe}_x\text{O}_y/\text{N-GN/CNTs}$.

them may be attributed to the doped CNTs because it is non-magnetic, which inactivates the magnetization process.

3.2.7. Nitrogen sorption isotherms

The specific surface area and pore size distribution of sample were characterized by N₂ adsorption-desorption isotherms, and the corresponding results are shown in Fig. S4. The graph shows a typical type IV hysteresis curve, indicating that this catalyst belongs to mesoporous materials. Moreover, the calculated BET surface area is ~56.294 (m²/g). Additionally, it is not difficult to show that the aperture size is ~4 nm with uniform pores. Therefore, they are beneficial for reactant transfers and adsorption. The relatively large surface and even pores may be caused by the fraction of gases, such as H₂O and CO₂, or NH₃ released from urea; and potentially associated with the IPN-like three-dimensional structure caused by the one-dimensional GN and two-dimensional CNTs, which further demonstrates the outstanding graphite ductility and excellent CNTs expansibility.

3.3. Catalytic activity of Fe_xO_y/N-GN/CNTs

The MB degradation was evaluated through a series of experiments. As shown in Fig. 5(a), a slight concentration (5.54%) was reduced by PMS alone, indicating the extremely stability of PMS. Similarly, the MB removal was merely 24.62% in the existence of catalyst, which was primarily due to the considerable catalyst adsorption, demonstrating that the nitrogen doped graphene/CNTs skeleton has a remarkable surface area and an excellent expanded pore structure. Moreover, it has reported that iron-based materials [39] and nitrogen doped graphene possess admirable catalytic performances [57,58]. Therefore, both of these have been employed to degrade MB. Clearly, as shown in Fig. 5(a), for iron-based materials, 52.73% of MB disappeared in 20 min, which was attributed to the superior surface traction force of the nanoparticles and structural iron. For the nitrogen-doped reduced graphene, the MB is thoroughly degraded at the same time, showing the high efficiency of N-GN. This is because the doped nitrogen caused increasingly active sites and expanded the graphene texture, resulting in the coordination between the adsorption and catalysis. Similarly, the

Table 1

Kinetics rate constant in different systems.

Different systems	Kinetics rate constant (K_{app} , min ⁻¹)
PMS	0.002265
Fe _x O _y /N-GN/CNTs	0.01335
Fe ₂ O ₃ +Fe ₃ O ₄ +PMS	0.02668
CNTs+PMS	0.02470
Fe _x O _y /GN+PMS	0.03726
N-GN+PMS	0.04429
Fe _x O _y /GN/CNTs+PMS	0.12026
Fe _x O _y /N-GN/CNTs+PMS	0.33444

CNTs were predicted to have the same effect as N-GN. However, in view of its hollow tissue, it was only tested for adsorption. It was observed that it reached adsorption equilibrium within 6 min, and the rest of the removal was due to a slight degradation from the catalysis of the *sp*³ and *sp*² hybridization carbon bonds. Additionally, when the catalysts had neither nitrogen nor CNTs, the efficiency was affected by different factors. In the absence of nitrogen there were not enough active sites and a poorer electron transfer rate. In the absence of CNTs, the slight reduction in the efficiency was attributed to the collapsed carbon skeleton without CNT extensions. Perhaps the irons were combined with CNTs via covalent bond leading forming active C-Fe sites, and thus, without CNTs these sites were no longer in existence resulting in a lowered performance. More importantly, when Fe_xO_y/N-GN/CNTs was united with PMS, the MB dislodging distinctly accelerated and the efficiency was almost 98.37% in 12 min, which was the approximate sum of the previous efficiencies. Compared with the former case, the results suggest that the remarkable catalytic capability is attributed to the collaborative synergy of the structural iron NPs, CNTs, and N-doped graphene.

Meanwhile, the UV-vis spectra and kinetics models were also investigated, which is clearly illustrated in Fig. 5(b) and (c) as well as Table 1. The characteristic peaks of methylene located at 664 and 292 nm dropped significantly before becoming insignificant, demonstrating the progressive decomposition of MB. The excellent performance in the first few minutes was ascribed to the synergistic effect between the adsorption and

Fig. 5. (a) MB degradation in different systems: (1) PMS, (2) Fe_xO_y/N-GN/CNTs, (3) Fe₂O₃+Fe₃O₄+PMS, (4) CNTs+PMS, (5) Fe_xO_y/GN/CNTs+PMS, (6) N-GN/CNTs+PMS, (7) Fe_xO_y/N-GN+PMS, (8) Fe_xO_y/N-GN/CNTs+PMS; (b) The temporal UV-vis spectra of MB removal; (c) The degradation kinetics models. Reaction conditions: initial MB 100 mg/L, PMS loading 2 mmol/L, catalyst content: 0.4 g/L, pH = 7.62.

catalysis, and in the later periods, the gradually slackened rate was attributed to the production of organic intermediates, which also consumed the sulfate radicals resulting in the curve fluctuation. Conversely, as shown in Table 1, after being calculated and analyzed, the kinetics model roughly follows the pseudo first-order, which can be formulated as $\ln(C/C_0) = -kt$; where C_0 and C are the initial and residual concentrations of MB, respectively, and k symbolizes the first-order kinetics rate constant. In comparison with others, $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$ had a higher level of $\sim 0.33 \text{ min}^{-1}$. In addition, it is not difficult to show that there were some scattered points in the model curves in the presence of PMS due to intermediate influences.

Additionally, TOC was employed to further investigate the catalytic efficiency of MB in the system. As can be seen from Fig. S5, after 16 min of reaction, the TOC removal efficiency was $\sim 59.20\%$ before increasing. Clearly, in the first 4 min, the removal rate was slightly higher than that of the next 5 min, indicating that a quantity of intermediates was generated. Finally, the rates increased to a certain degree, which was mainly because the intermediates, as well as some MB molecules, had

been degraded to CO_2 , leading to the increase of TOC removal rates. Undoubtedly, all the above processes are extremely significant for the degradation mechanism.

3.4 Effect of various factors

In this section, the degradation performance is evaluated by controlling variables to optimize the reaction conditions, including different initial dye concentrations, oxidizing agent dosage, catalyst loading, and oxidizing radical species. Fig. 6(a) displays the effect of different initial MB concentrations. This coincided with an initial concentration ranging from 30 to 500 mg/L, with removal efficiencies of approximately 99.83%, 98.95%, 98.44%, 95.37%, 90.12%, and 81.26% within 16 min. Straightforwardly, the degradation efficiency is inversely proportional to the initial concentration. The reasons for this are as follows. Along with the augment of concentration, the increasing number of dye molecules compete with each other to combine with a limited amount of radicals. Meanwhile, a growing number of organic intermediates were generated, which also

Fig. 6. Effects of different initial MB concentrations (a), oxidizing agent dosage (b), catalyst loading (c), and radical quenchers (d). Reaction conditions: initial MB 100 mg/L, PMS loading 2 mmol/L, catalyst content: 0.4 g/L, pH = 7.62.

scramble for radicals, thus lowering the MB removal efficiency.

Similarly, Fig. 6(b) illustrates the oxidant concentration effect. Although there was little difference in the oxidant dosage, the degradation rate disparity was more evident. When the concentration increased from 0.5 to 2.0 mmol/L, the efficiency improved from 67.32% to 98.70%, which perhaps could be the reason that the higher the amount of oxidant used, the more radicals generated. Moreover, the increased number of oxidants would be simultaneously activated by catalysts, and hence make full use of the active sites. Whereas, when the concentration further increased to 5.0 mmol/L, there was no significant improvement, decreasing at 6 minute. This is because the extra $\text{SO}_5^{\cdot-}$ combined with the sulfate radicals, leading to the formation of low active radicals $\text{SO}_5^{\cdot-}$ (Eq. (1)). Moreover, the sulfate radicals quench themselves (Eq. (2)), resulting in the formation of $\text{S}_2\text{O}_8^{2-}$. In summary, both of reduce the radicals content, leading to unsatisfactory results.

Compared with the oxidants, the influence of the catalyst dosage is not obvious. As indicated in Fig. 6(c), for the loaded 0.8 g/L catalyst, the degradation efficiency reached ~98.65%, which was higher than the loading of 0.1 g/L whose efficiency was 72.13%. Obviously, the more catalysts that are added, the higher the degradation efficiency. The reason is because more catalysts provide more active sites, leading to an easier catalyzing of PMS. Nevertheless, when increasing the amount to 0.8 g/L, the degradation efficiency only slightly improved, which was ascribed to two reasons: on the one hand, when the active sites reached saturation, the impact was mainly dependent on the oxidant, which had an insufficient supply for the catalysts; on the other hand, the excessive active sites reacted with sulfate radicals resulting in the production of $\text{SO}_5^{\cdot-}$.

Fig 6(d) shows the contribution of the radical species. It is reported that sulfate, proxy sulfate, and hydroxyl radicals play decisive roles in organic pollutants degradation [59]. In addition, due to the relatively inferior oxidation activity and lower redox potential, peroxy sulfate was not explored. Moreover, it has been suggested that ethanol containing alpha hydrogen atoms could be enacted as scavengers not only for $\text{OH}^{\cdot}$ but $\text{SO}_4^{\cdot-}$ with rate constants of $1.2\text{--}2.8 \times 10^9$ and $1.6\text{--}7.7 \times 10^7$ mol/(L s), respectively [60]. By comparison, *t*-BuOH without alpha hydrogen atom gives priority to the combination with hydroxyl radicals with a rate constant of $3.8\text{--}7.6 \times 10^8$ mol/(L s), which is about 1000-fold faster than $\text{SO}_4^{\cdot-}$ ($4.0\text{--}9.1 \times 10^5$ mol/(L s)) [60]. Accordingly, these can be taken advantage of to verify the existence of radicals. As displayed in Fig. 6(d), without any quenching agents, the efficiency reached 98.72%, however, when 50 and 10 mmol ethanol were added, the efficiency decreased to 34.88% and 66.73%, respectively. A degradation of 34.88% was mainly was attributed to absorption, which agrees with Fig. 5(a). This demonstrates that the process was dominated by the radicals, either sulfate or hydroxyl. Moreover, after different doses of tert-butanol was injected, the efficiency decreased. Compared with the addition of ethanol, there were no substantial changes but the contribution of hydroxyl radicals cannot be ignored. Clearly, all the

Scheme 2. Mechanism of the degradation reaction over synthesized materials.

above-mentioned results demonstrate that both the sulfate and hydroxyl radicals were involved in the organic dyes degradation.

3.5. Mechanism of the degradation reaction

The reaction mechanism and degradation steps are showed in Scheme 2. According to previous reports there are several possible reactions [59–62]:

The organics degradation reaction follows a redox mechanism, namely, PMS, and is activated by the valence transformation of the transition metals *M* (such as, chromium, manganese, iron, cobalt, nickel, and copper,) (Eqs. (3) and (4)). Thus, in this research, $\text{HSO}_5^{\cdot-}$ is most probably catalyzed by $\equiv\text{Fe}^{\text{III}}$ to produce $\text{SO}_5^{\cdot-}$, capturing an electron, resulting in the formation of low valent iron species $\equiv\text{Fe}^{\text{II}}$. Simultaneously, $\equiv\text{Fe}^{\text{II}}$ was oxidized by $\text{SO}_5^{\cdot-}$, leading to the loss of an electron to generate $\text{SO}_4^{\cdot-}$ (Eqs. (5) and (6)). A portion of $\text{SO}_5^{\cdot-}$ are attracted to each other to produce $\text{SO}_4^{\cdot-}$ (Eqs. (7)). In addition, the $\text{OH}^{\cdot}$ formation was attributed to the reaction between $\text{SO}_4^{\cdot-}$ and H_2O (Eqs. (8)). On the basis of the standard reduction potentials of iron (Eqs. (9)) and the Gibbs free energy, a reduction and oxidation between $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$ is feasible [56], which was favorable for promoting MB degradation. Furthermore, research has indicated that pyridinic nitrogen can be considered as Lewis basic reaction sites [55], which is profitable for the generation of $\text{SO}_4^{\cdot-}$ and $\text{OH}^{\cdot}$. Compared with the C atom, graphitic nitrogen

has a higher electronegativity and smaller covalent radius, which is beneficial for the nucleophilic addition of HSO_5^- .

$\text{SO}_4^{\bullet-}$ and $\text{OH}^{\bullet}$ then simultaneously attack the MB and intermediates molecules with a series of reaction principles, which can be divided into three categories as follows. The first is the hydrogen abstraction reaction that is the main reaction process between radicals and, e.g., alkanes, alcohols, organic acids, ethers, and lipids. The second is the electron transfer reaction that is the reaction between radicals and benzene ring or aromatic organics, and is mainly ascribed to electron transfer because the superior oxidizing agent can despoil aromatic organics electrons and destroy the original paired electrons. The third is the addition reaction of unsaturated olefin, alkynes, or compounds containing C=C double bonds, and is widely regarded as the dominant process due to $\text{SO}_4^{\bullet-}$ that can actively attack unsaturated bonds to break them up. Finally, after being completely degraded, MB was transformed into pollution-free small molecules.

3.6. Reusability and stability

The reusability degradation curves are shown in Fig. 7(a). After the fifth utilization, the degradation efficiency still maintained a high level, indicating an outstanding stability. Clearly, fluctuations emerged in the fourth and fifth removals, which were dependent on the slight abscission of particles whose catalytic performance was better than that of the structural irons (Eqs. (11) and (12)). Notwithstanding, it was incredibly unstable.

A histogram is provided in Fig. 7(b) that shows that only a slight reduction was detectable after recycling three times and the distinction between fourth and fifth runs was extremely small. This is due to the chemical actions and physical interactions that were involved in the formation of the heterojunctions, thus promoting a powerful combination of various elements.

4. Conclusions

In summary, multifunctional $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$ heterojunctions were successfully prepared using the hydrothermal method and extensively applied to evaluate the degradation of MB collaborating with PMS. The results indicated that 98.75% of MB could be removed within a short reaction time of only 12 min with a synergistic effect between adsorption and catalysis. The degradation process can be described by the pseudo-first-order kinetics with a high rate constant 0.33 min^{-1} . Moreover, it showed that the MB removal was affected by the initial dye concentration, PMS dosage, and $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$ content. A radical quenching investigation showed that both $\text{SO}_4^{\bullet-}$ and $\text{OH}^{\bullet}$ acted as the main active components. The formation mechanism of the radicals showed that the remarkable capability was attributed to the collaborative effect of the structural iron NPs, CNTs, and N-doped graphene. The transformation between $\equiv\text{Fe}^{\text{III}}$ and $\equiv\text{Fe}^{\text{II}}$ was regarded as the crucial catalytic reaction mechanism. After being tested for more than five cycles, only a slight reduction (ca. 3.53%) was observed, demonstrating excellent reusability and increased stability. In light of being employed as microwave absorber and with its relatively remarkable qualities, the Fe/N co-rich hierarchical porous carbon skeleton favored electron transport and storage. Therefore, $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$ heterojunctions are potential catalysts for practical applications and may open up new areas of application, such as supercapacitors, energy storage, CO_2 capture, and oxygen reduction electrocatalysts.

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Fig. 7. (a) Degradation of MB using more than five utilization times and (b) histogram Reaction conditions: initial MB 100 mg/L, PMS loading 2 mmol/L, catalyst content: 0.4 g/L, pH = 7.62.

Graphical Abstract

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One-step preparation of $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$ heterojunctions as a peroxymonosulfate activator for relatively highly-efficient methylene blue degradation

Xin Zhao, Qing-Da An *, Zuo-Yi Xiao, Shang-Ru Zhai *, Zhan Shi
Dalian Polytechnic University; Jilin University

Multifunctional $\text{Fe}_x\text{O}_y/\text{N-GN}/\text{CNTs}$ heterojunctions that behave as peroxymonosulfate (PMS) activators for relatively high-efficient organic pollutants degradation, were prepared via a single-step solvothermal method.

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一步法制备铁氧化物/氮改性氧化石墨/碳纳米管异质结及其用于催化活化过一硫酸氢钾降解亚甲基蓝模型染料

赵 鑫^a, 安庆大^{a,*}, 肖作毅^a, 翟尚儒^{a,#}, 施 展^b

^a大连工业大学轻工与化学工程学院, 辽宁大连116034

^b吉林大学化学学院无机合成和制备化学国家重点实验室, 吉林长春130012

摘要: 随着较差的生物相容性和更高毒性有机染料的应用, 如酚类化合物和抗生素, 水污染和食品污染变得极其严重. 这不仅危害人类健康, 而且严重污染自然环境. 过硫酸盐去污技术利用自由基活化降解过程, 成为处理一系列污染物非常有效的方法; 然而设计具有多功能性的高性能催化剂仍然面临着巨大的挑战. 因此, 本文借鉴铁基材料、氮改性石墨和碳纳米管独特的物化性质, 以尿素、铁盐、氧化石墨、碳纳米管为原材料, 通过一步水热法成功制备了三维多功能铁氧化物/氮改性氧化石墨/碳纳米管异质结, 用作活化过一硫酸氢钾复合盐以降解有机模型污染物亚甲基蓝(MB), 研究了高级氧化法(AOPs)作用机理和优化反应条件. XRD、红外光谱、SEM和XPS结果表明, 铁氧化物通过物理静电作用力和化学键结合力已经被牢牢固定在了氮修饰的氧化石墨结构框架内. 当加入了碳纳米管之后, 它会与石墨形成类似于互穿聚合物网络的结构, 从而具有三维材料的优点, 且提升电子转移电导率, 使得催化剂的结构和性能有了很大的改善. 此外, 优化了降解系统、PMS负载量、初始有机污染物浓度和催化剂用量等因素. 结果表明, 处于催化剂/PMS系统时, 亚甲基蓝可以在12 min之内有效地完全降解, 可归结于碳、氮以及主要活性物质铁氧化物之间的协同作用. 基于数据拟合分析, 污染物氧化降解系统与拟一阶动力学相符合, 其速率常数约为0.33 min⁻¹. 淬灭实验证明, 硫酸根自由基和羟基自由基是主要的反应活性物种. 这种同时富含铁/氮分级的多孔碳骨架异质结物质不仅可用作过渡金属催化剂, 而且为制备其他异质结提供参考, 以用于超级电容器、储能材料、电催化剂等领域.

关键词: 异质结; 有机污染物降解; 氮掺杂石墨烯; 协同作用

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*通讯联系人. 电子信箱: anqingdachem@163.com

#通讯联系人. 电子信箱: zhairschem@163.com

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