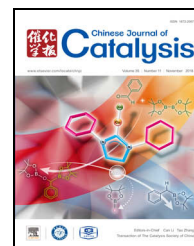


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Article

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

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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

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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.

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