N-doped graphene aerogels as efficient heterogeneous catalytic activators for peroxymonosulfate to remove 2-sec-butyl-4,6-dinitrphenol (DNBP) in aqueous solution

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Abstract

The nitrogen-doped graphene aerogels (NGAs) with interconnected hierarchical porous structures were facilely prepared via hydrothermal process in the mixed aqueous solution of ethylenediamine (EDA) and urea and post-freeze-drying treatment. A series of NGAs samples with different GO:urea:EDA mass ratios were obtained and characterized by Raman, FT-IR, XPS, TEM and SEM. The prepared NGAs were employed as metal-free carbocatalysts in the activation of peroxymonosulfate (PMS) for 2-sec-butyl-4,6-dinitrphenol (DNBP) degradation in aqueous solution. The resultant NGA-4 catalyst with GO:urea:EDA mass ratio of 3:2:4 exhibited the best catalytic activity in PMS activation for oxidative degradation of DNBP among the prepared NGAs samples. The effects of temperature, initial pH value, catalyst concentration and PMS dosage on the degradation of DNBP in NGA-4/PMS system were investigated. The catalytic degradation of DNBP followed the pseudo-first-order kinetic and the activation energy of the degradation reaction was calculated to be 31.3 kJ·mol⁻¹. The quenching experiments clearly demonstrated that SO₄⁻³ radicals served as predominant active species in the PMS activation catalytic process. The good applicability made the application of the prepared NGAs materials in PMS activation for removing organic pollutants more practical and feasible.

1. Introduction

The dramatical development of industrialization and rapid depletion of resource lead to environmental detrimental aspects to the eco-environment and human beings [1, 2]. The widespread and potential risky refractory pollutants, especially water pollution, have triggered worldwide concern for environmentalists and researchers [3, 4]. A variety of physical, chemical and biological the-state-of-the-art technologies have been leveraged to address the issues [5], among which adsorption and catalytic oxidation treatment of organic pollutants have intensively investigated and proven to be efficient on wastewater treatment [6, 7]. Adsorption with phase separation performance may cause secondary pollution, because the adsorbed pollutants have not been completely decomposed. On the other hand, advanced oxidation processes (AOPs) have aroused wide concern because of their ability to thoroughly decompose refractory organic pollutants into harmless substances without secondary pollution, mild reaction conditions and high efficiency. AOPs mainly depend on highly reactive radicals with high redox potentials such as hydroxyl radicals (‘OH) and sulfate radicals (SO₄⁻³) to oxidize organic pollutants. Compared with hydroxyl radicals, sulfate radicals generated from peroxydisulfate (PDS) or peroxymonosulfate (PMS) activation have a higher redox potential (2.5 ~ 3.1 V), broader pH applicability, and longer survival time [8–10]. PMS is widely used in the sulfate radical based AOPs (SR-AOPs) due to its asymmetrical structure and easy activation property. As reported in the literature, transition metal ions (Co²⁺, Ag⁺, Fe³⁺, etc), oxides of transition metals (Co₃O₄, MnO₂, CuO, etc) and metal organic frameworks (MOFs) are
generally employed as homogeneous or heterogeneous catalysts to activate PMS to produce SO$_4^-$ radicals for oxidation of various organic pollutants [11–15]. However, the application of transition metal-based catalysts in the activation of PMS was limited due to the potential metal leaching into the ecological environmental system, which may cause secondary pollution and thereby impact human health. Therefore, growing attention has been focused on the development of environmentally friendly metal-free catalysts to activate PMS in SR-AOPs for degradation of organic contaminants [16, 17].

Recently, carbon-based materials have attracted tremendous interest in serving as promising metal-free catalysts for PMS activation because of their environmentally friendly and sustainable features [18]. Carbon-based materials, such as fullerene (C$_{60}$), single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), graphene oxide (GO), hexagonally and cubically-ordered mesoporous carbon, have proven to be effective carbocatalysts for PMS activation in SR-AOPs [19–22]. As a typical class of carbon-based materials, graphene materials have triggered considerable attention due to their outstanding properties, such as sp$^2$ carbon configuration, excellent thermal and electrical conductivity, great mobility of charge carriers, and large theoretical specific surface area. Nevertheless, the employment of graphene materials as carbocatalysts for PMS activation was still limited because graphene with two-dimensional planar structure is apt to stack together in aqueous solution due to the existence of interlayer π–π interactions and hydrophobic character of graphene, which could reduce the effective specific surface area and diminish the active sites of graphene. Moreover, the obstacle of separation of graphene nanosheets from aqueous solution also restricted the application of graphene in SR-AOPs. Therefore, development of graphene-based materials with high catalytic activity and easy separation properties in PMS activation is necessary and important.

Among the various methods investigated to enhance the catalytic activity of carbocatalysts, chemical modification through heteroatom-doping (B, S, P, and N) has proven to be the most promising and effective one [23]. It has been demonstrated that N-doping in carbocatalysts such as mesoporous carbon, CNTs and rGO could effectively boost the catalytic activity for PMS activation [24–26]. The introduction of N atoms having distinct electronegativity with C into the graphitic lattice can lead to polarization in the sp$^2$-hybridized network and rearrangement of the local electronic state, which in turn improves the chemical activity, electrical conductivity, and adsorption capacity of graphene materials, thus helping to increase catalytic performance in SR-AOPs. In addition, the doping with heteroatoms also increases the number of sites for molecular binding and reactive microenvironment for catalytic reactions, which is beneficial to improve the catalytic activity of graphene materials [27–31]. Strategies that have been taken to tackle the problem of separation of suspended nanoscale graphene nanosheets from aqueous solution after oxidative degradation reactions include the fabrication of 3D graphene-based macrostructures. Among the various 3D graphene-based macrostructures, the free standing graphene-based aerogels (GAs) are of particular interest to researchers due to their large specific surface area, hierarchically interconnected porous structure, versatile surface chemistry, and fast mass transfer. The bulky macrostructure of GAs can not only prevent graphene nanosheets from aggregating in solution, but also help collection of the catalysts in the application of SR-AOPs. On the basis of these characteristics of GAs, it could be expected that N-doped graphene aerogels could be the promising metal-free carbocatalysts to activate PMS for the destruction of organic pollutants.

In this study, a series of N-doped graphene aerogels (NGAs) were facilely fabricated by hydrothermal self-assembly of graphene oxide (GO) nanosheets in the mixed solution of ethylenediamine (EDA) and urea and post-freeze-drying treatment. The prepared NGAs were employed as carbocatalysts to activate PMS for oxidative degradation of organic pollutants. 2-sec-butyl-4,6-dinitrophenol (DNBP), a typical alkyldinitrophenol compound, was selected as a model organic contaminant for the oxidative degradation experiments. DNBP is widely used in agriculture as herbicide and in petrochemical industry as polymerization inhibitor. DNBP can pose a threat to the ecological environmental system and human beings when it is released into water because of its side effects such as toxicity and carcinogenicity [32]. Compared with pristine GO, the as-prepared NGAs exhibited an astonishing improvement in PMS activation for oxidative degradation of DNBP, which made the application of NGAs as efficient metal-free carbocatalysts in SR-AOPs more practical.

2. Experimental

2.1. Materials
Oxone (KHSO$_4$ · K$_2$SO$_4$ · KH$_2$SO$_4$), ethylenediamine (EDA), urea, t-butyl-alcohol (TBA), ethanol (EtOH) were obtained from Sinopharm Chemical Reagent Co., Ltd. 2-sec-butyldinitrophenol (DNBP) was obtained from Tianjin Fine Chemical Co., Ltd. The commercially available graphene oxide (GO) was provided by Tanfeng Technology Inc., China. All the chemicals were used as received without further purification.
2.2. Preparation of N-doped graphene aerogels
The NGAs materials were prepared by a facile one-pot hydrothermal method. A typical procedure for the synthesis of NGAs materials was as follows: 15 ml GO aqueous dispersion (3 mg ml \(^{-1}\)) was well-mixed with requisite amount of mixture of ethylenediamine (EDA) and urea and stirred continuously for 20 min at 25 \(^{\circ}\)C. Then, the as-obtained suspension was transferred into a 25-ml Teflon-lined stainless steel autoclave and heated at 95 \(^{\circ}\)C for 12 h under hydrothermal condition. After completion of the hydrothermal reaction, the as-prepared N-doped GO hydrogel was freeze-dried for 24 h to obtain the final functionalized aerogel. A series of NGAs samples were prepared by changing the GO:urea:EDA mass ratios of the reaction system. The resultant NGAs samples with various GO:urea:EDA mass ratios of 3:3:4, 3:3:8, 3:0:4, 3:2:4 and 3:4:4 were denoted as NGA-1, NGA-2, NGA-3, NGA-4 and NGA-5, respectively.

2.3. Characterization
Raman spectra of the samples were investigated on a Thermo Fisher DXR Microscope dispersive argon laser Raman spectrometer. External morphology and internal structure of the prepared materials were studied by field emission scanning electronic microscopy (FESEM, Hitachi S-4800), and high-resolution transmission electron microscopy (TEM, FEI-TECNAI G220STWIN). Fourier infrared spectra were measured on a Nicolet Avatar 360 FT-IR infrared spectrometer in the range of 4000–400 cm \(^{-1}\). Data of x-ray photoelectron spectroscopy (XPS) was obtained using a Thermo Scientific Escalab 250 Xi x-ray Photoelectron Spectrometer system.

2.4. Evaluation of catalytic activity
The catalytic activity of as-prepared NGAs materials was evaluated by oxidative degradation of DNBP in 100 ml batch reactors. Typically, a certain amount of as-prepared carbocatalyst (0.1 g l \(^{-1}\)) was dispersed in 50 ml aqueous solution of DNBP (20 mg l \(^{-1}\)), then the suspension was agitation on a thermostatic water bath oscillator for 60 min to establish complete adsorption/desorption equilibrium on the catalyst surface. Subsequently, PMS solution of certain concentration (6 mmol l \(^{-1}\)) was added to the reaction system to initiate the oxidative degradation reaction. The reaction solutions were sampled at selected time spans and subjected to filtration to remove the catalyst particles. The change in concentration of DNBP in solution was determined by HITACHI Double Beam UV–vis Spectrophotometer (UV-1700) at a maximum wavelength of 375 nm. The total organic carbon (TOC) was measured using a TOC-analyzer (Multi N/C 2100 S, Germany).

3. Results and discussion
3.1. Structural characterization of resultant samples
Raman analysis is widely used for analyzing the structural features of carbon materials [33]. Figure 1 exhibits the Raman spectra of GO and as-prepared NGAs samples. The Raman spectra of all the samples showed two common characteristic peaks belonging to the documented D-band (~1343 cm \(^{-1}\)) and G-band (~1596 cm \(^{-1}\)), respectively [34, 35]. The G-band is related to the in-plane vibration of all the sp\(^2\) hybridized carbon atoms and D-band results from disorder and structural defects of carbon nanomaterials [36]. Therefore, the intensity ratio of the D over G band (I\(_D\)/I\(_G\)) could reflect the disorder and defective degree of carbon materials. Compared with GO (I\(_D\)/I\(_G\) = 0.95), all the synthesized N-doped GAs samples displayed higher I\(_D\)/I\(_G\) values from 1.14 to 1.42,
suggesting that nitrogen doping resulted in an increase of structural defect density and disorder as well as a
decrease of the mean size of sp² domains. The increase of $I_D/I_G$ ratio for GAs with nitrogen doping also
confirmed the decrease of the number of oxygen-containing functional groups in the graphene structure, which
could be attributed to the deoxygenation and reduction of GO by EDA to some extent during preparation
process. The highest $I_D/I_G$ ratio value of NGA-4 among all the synthesized N-doped GAs samples proved the
presence of more defective sites and relatively small average crystallite size of the sp² domains in its graphene
network, which is helpful for improving catalytic activities in PMS activation for oxidative degradation of
DNBP. In addition, the spectral shift of the Raman D and G bands could be observed in all the prepared N-doped
GAs samples in comparison with pristine GO, which is due to the donation of lone electron pairs on doped N
atoms to the graphene network.

The surface functional groups in GO and as-synthesized samples were investigated by FT-IR spectra. As
shown in figure 2, the absorption peaks present on the spectra of GO sample at 3440, 1730, 1620 and 1204 cm
⁻¹ were assigned to stretching vibrations of O−H, C=O, C=C and C−O bonds, respectively [37–39]. After
introducing N atoms, the FT-IR spectra of the N-doped GAs samples exhibited new absorption peak at around
1120 cm⁻¹ corresponding to C−N stretching vibration. Compared with that of GO, the broad peaks of the
N-doped GAs samples at 3000–3700 cm⁻¹ became sharper and stronger due to N doping [40]. Moreover, the
peaks of the N-doped GAs materials at about 1730 cm⁻¹ associated with C=O stretching vibrations
disappeared, while the intensities of broad peaks of the prepared samples in the range of 3000–3700 cm⁻¹ were
remarkably increased in comparison with GO, suggesting the decrease of surface oxygen-containing functional
group content and successful doping of N atoms into the framework of graphene aerogels.

The morphology and microstructure of GO and NGA-4 samples were characterized by SEM and TEM as
showed in figures 3(a)–(d). Figures 3(a) and (c) exhibited smooth and wave-like morphology of GO with an
aggregated nanosheet structure and wrinkled edges. After the hydrothermal process and freeze-drying treatment,
the GO nanosheets assembled into N-doped 3D graphene aerogel monoliths via supramolecular interactions. As
illustrated in figure 3(b), the as-synthesized NGA-4 sample presented foam-like morphology with an
interconnected hierarchical porous structure. TEM image of NGA-4 (figure 3(d)) also demonstrated that NGA-
4 displayed as less aggregated crumpled nanosheets compared with GO, which could provide more active sites
and enhance its catalytic properties [41, 42].

The surface composition and chemical states of the elements of as-prepared NGA-4 material were studied by
XPS. As presented in figure 4(a), the full survey scan of NGA-4 confirmed the presence of C 1 s, O 1 s and N 1 s at
284.1 eV, 399.4 eV and 531.1 eV, respectively [43, 44]. The high resolution C 1 s peak in figure 4(b) consisted of
three pronounced signals with binding energies at 284.6, 286.2 and 288.8 eV, corresponding to C=C, C−OH and
O=C=O groups, respectively. As shown in figure 4(c), the O 1 s spectra of NGA-4 presented two peaks centered
at 531.7 and 533.4 eV, assigning to C=O, C−OH groups, respectively. The N 1 s spectra could be deconvoluted
into three major species: pyridinic N (400.0 eV), pyrrolic N (398.8 eV) and graphitic N (401.7 eV). The results of
XPS measurements demonstrated that the N element was successfully doped into the structure of graphene
aerogels.

3.2. Catalytic degradation of DNBP
A series of experiments were performed to investigate the catalytic activities of as-prepared samples for PMS
activation and DNBP degradation in aqueous solution. Figure 5(a) shows the relative concentration of DNBP,
$C_{i} / C_{0}$, for different reaction times $t$ in the different carbocatalyst/PMS systems. As illustrated in figure 5(a), the equilibrium adsorption of as-prepared NGAs carbocatalysts toward DNBP was achieved after 60 min of contact time. PMS in the absence of the carbocatalysts could merely remove less than 14% of DNBP, suggesting that PMS could only oxidize DNBP to some extent without catalytic activation. Similarly, the poor catalytic performance in PMS activation of GO was also found and only 27.6% DNBP were degraded in 180 min in the GO/PMS system. In comparison, the DNBP degradation efficiency greatly increased to more than 86% in the NGA-4/PMS system, which was almost three times higher than in the GO/PMS system. Figure 5(b) presents the typical time evolution of UV–vis spectral variation during adsorption and catalytic degradation of DNBP in NGA-4/PMS reaction system. The characteristic absorption peak of DNBP at 375 nm gradually became weaker and nearly disappeared after 180 min of reaction, clearly demonstrating the incessant destruction of DNBP in the NGA-4/PMS reaction system. The catalytic oxidative degradation of DNBP followed the pseudo-first-order
The kinetics described by the following equation: \( \ln \left( \frac{C_0}{C} \right) = k_{\text{app}}t \), where \( k_{\text{app}} \) is the apparent first-order rate constant. The obtained \( \ln \left( \frac{C_0}{C} \right) \) versus \( t \) plots were linear, confirming the reliability and applicability of the first-order kinetic model for oxidative degradation of DNBP (figure 5(c)). The prepared NGAs samples possessed the interconnected hierarchical pore structure and more N-doped active sites compared with GO, thus inducing an increased reactivity in PMS activation. It has been reported that the contents of GO and graphitic N play an important role in carbon-catalyzed PMS activation \([45]\). Excessive GO in NGAs could increase the compactness of GO nanosheets and thus hinder the mass transfer and reactants accumulation \([46]\). A low level of GO in NGAs was not benefit for the formation of the interconnected hierarchical pore structure. The graphitic N content of NGAs has important influence on PMS activation because graphitic N has high charge density and asymmetric spin density, which could induce the peroxo-bond breakage to generate reactive radicals \([47]\). Based on the area integral of the peak corresponding to graphitic N, the relative atomic percentage of graphitic N in NGAs carbocatalysts was determined by XPS. Figure 5(d) presents the relationship between DNBP removal efficiency and contents of GO and graphitic N in different NGAs samples. Compared with other NGAs samples, NGA-4 had moderate GO concentration and relatively higher graphitic N content. The superior catalytic activity of NGA-4 should be ascribed to the synergistic effects of interconnected porous architecture, appropriate GO content, higher graphitic N level and more N-doped active sites. Therefore, more \( \text{SO}_4^- \) free radicals could be generated in the NGA-4/PMS system to degrade DNBP, which resulted in higher DNBP removal efficiency.

Mineralization of DNBP before and after oxidative degradation treatment in different catalysis reaction systems was also evaluated by TOC content of DNBP wastewater (figure 6). The decrease of TOC content of DNBP solution was found to be 65.46%, 19.35% and 10.45% in the presence of NGA-4/PMS, GO/PMS and PMS only, suggesting the destruction of the molecular structure of DNBP and better catalytic activity of the prepared NGA-4 catalyst for PMS activation.

The effect of temperature on DNBP degradation in the NGA-4/PMS reaction system was studied by varying the temperature from 5 to 35 °C (figure 7). It was found that the DNBP degradation in the NGA-4/PMS system was accelerated significantly with increasing temperature, indicating that the catalytic activation of PMS by NGAs is an endothermic process. The apparent reaction rate constant \( k_{\text{app}} \) increased from \( 5.64 \times 10^{-3} \) to...
2.05 \times 10^{-2} \text{ min}^{-1} \) with the rise in temperature from 5 to 35 °C, which means the NGA-4 sample exhibited better catalytic performance at high temperature than at low temperature. The oxidative degradation of DNBP increased with the increasing of temperature for the NGA-4/PMS system could be attributed to the enhanced diffusion rate of DNBP in solution and more available surface active centers of the catalyst at elevated temperatures. The degradation of DNBP in the NGA-4/PMS system could be considered as an Arrhenius-type process and the apparent activation energy \( E_a \) of the oxidative degradation reaction was calculated to be 31.3 kJ mol\(^{-1}\) (figure 7 inset).

Figure 8 shows the role of initial pH on adsorption and PMS activation for DNBP degradation in NGA-4/PMS catalysis reaction system over a pH range of 1–12. As exhibited in figure 8, the adsorption capacity of NGA-4 for DNBP reached optimum values under near neutral conditions. The adsorption of DNBP onto the NGA-4 sample dropped obviously under strong acidic or basic conditions. The decrease in the uptake of DNBP under strong acidic conditions resulted from the competitive adsorption of H\(^+\) ions and DNBP on NGA-4. DNBP mainly exists in the forms of anion under strong basic conditions because the pK\(_a\) of DNBP is 4.62. The pHzpc of NGA-4 was determined to be 8.28 and the surface of NGA-4 is negatively charged under strong basic conditions. Therefore, the adsorption of DNBP decreased under strong basic conditions due to the electrostatic repulsion between the DNBP anions and the negative NGA-4 surface charge. The pH values have no significant influence on the catalytic activity of NGA-4 in PMS activation for DNBP degradation except that at initial pH of 1.0. At initial pH 1.0, the DNBP degradation efficiency decreased to 71.4% within 180 min, which may be due to the fact...
that large quantities of \( H^+ \) ions under strong acidic conditions could react with active \( SO_4^{2-} \) radicals to produce \( HSO_4^- \) ions, which caused a distinct decrease on DNBP removal efficiency at the initial pH of 1.0.

Figure 9 shows the effect of catalyst dosage on DNBP degradation in NGA-4/PMS system by changing the catalyst concentration from 0.05 to 0.20 g l\(^{-1}\). As showed in figure 9, the adsorption and DNBP degradation efficiency increased significantly with an increase in catalyst dosage from 0.05 to 0.10 g l\(^{-1}\). This could be due to the availability of more active sites to active PMS with increasing NGA-4 dosage and thus more active \( SO_4^{2-} \) radicals are generated to degrade DNBP. However, the removal efficiency of DNBP changed slightly with further increasing dosage of NGA-4 due to stacking and aggregation of the excessive NGA-4 catalyst which could reduce the effective specific surface area and diminish the number of available active sites. Therefore, an optimum catalyst dosage of 0.10 g l\(^{-1}\) is necessary for the effective degradation of DNBP in NGA-4/PMS system.

Figure 10 presents the effect of PMS concentration on DNBP degradation in NGA-4/PMS system. The results showed that the removal rate of DNBP was 40.7% in the absence of PMS due to the adsorption effect of NGA-4. The catalytic degradation efficiencies of DNBP in the presence of PMS were obviously enhanced from 63.62% to 86.85% within 180 min as the concentration of PMS increased from 3 to 6 mmol l\(^{-1}\). The higher PMS concentration is propitious to generating more active \( SO_4^{2-} \) radicals which could contribute to higher degradation rate of DNBP. Nevertheless, a further increase in PMS concentration had no obvious influence on DNBP degradation efficiency, which could be due to the fact that the generated \( SO_4^{2-} \) radicals could be self-consumed and captured by excess PMS [48]. Thus, 6 mmol l\(^{-1}\) of PMS was chosen as the optimal concentration in the experiments.

The lifetime and structural stability of the prepared NGA-4 catalyst was also examined by the reptitive use test. For the reptitive use test, the used NGA-4 catalyst was collected from the solution by simple filtration after
degradation reaction, washed with deionized water, freeze-dried and utilized for the next cycle. The DNBP removal efficiency decreased from 86.85% for the 1st run to 48.58% and 26.64% for the 2nd and 3rd runs, respectively. The decrease in catalytic activity could be due to pore-blocking, intermediates coverage as well as structural damage of the catalyst. It is worth noting that although the introduction of EDA and urea could improve the structural stability of NGAs, the aerogel carbocatalyst NGA-4 started to crumble during the 4th run of operation. Therefore, further increase the structural strength and stability is an important issue in practical application of NGAs as carbocatalysts for industrial wastewater treatment.

3.3. Catalytic mechanism

The literature showed that the main types of active species generated in SR-AOPs include sulfate (SO$_4^{2-}$), peroxy-sulfate (SO$_5^{2-}$) and hydroxyl (·OH) radicals [49]. In order to identify the controlling active species and elucidate the catalytic degradation mechanism in the NGA-4/PMS system, the quenching experiments were performed by introducing different scavengers to the reaction system under the same conditions. It has been demonstrated that $\text{t}$-butyl-alcohol (TBA) prefers to react rapidly with ·OH radicals with the rate constant of $3.8 \times 10^8 - 7.6 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$ rather than with SO$_4^{2-}$ radicals with the rate constant of $4.0 \times 10^5 - 9.1 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$ [50]. Differently, ethanol (EtOH) tends to capture SO$_4^{2-}$ with the rate constant of $3.5 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$ instead of ·OH with the rate constant of $9.1 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$ [10, 51]. Therefore, TBA and EtOH were employed to trap ·OH and SO$_4^{2-}$ radicals, respectively. As depicted in figure 11, DNBP degradation efficiency decreased to 67.6% and 50.8% when 0.1 mol l$^{-1}$ TBA and EtOH were introduced to the NGA-4/PMS system. The addition of TBA slightly affected the degradation of DNBP during the activation of PMS by NGA-4, whereas the addition of EtOH obviously inhibited the generation of active species and reduced degradation.
efficiency. The experimental results proved that $\text{SO}_4^-$ radicals were the dominant species responsible for oxidative degradation of DNBP in the NGA-4/PMS system.

4. Conclusions

In summary, a series of NGAs carbocatalysts have been successfully synthetized by a facile hydrothermal process in the mixed aqueous solution of EDA and urea and post-freeze-drying treatment. EDA and urea employed as nitrogen precursors could not only prevent GO sheets from stacking, but also reduce and functionalize GO. The presence of more defective sites, small average crystallite size of the sp$^2$ domains and interconnected hierarchical porous structure of the prepared NGAs catalysts are favorable for improving catalytic activity in PMS activation for DNBP degradation. The resultant NGA-4 catalyst with GO:urea:EDA mass ratio of 3:2:4 exhibited superior performance in catalytic degradation of DNBP compared to other prepared NGAs samples. The quenching experiments proved that the $\text{SO}_4^-$ radicals played a critical role in catalytic degradation of organic pollutants in the NGA-4/PMS system. The good applicability makes the prepared NGAs materials as promising metal-free PMS activators for organic pollutants degradation more practical.

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Conflict of interest

The authors declare that they have no conflict of interest.

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