Graphene and biomass-based carbocatalysts as high-performance peroxymonosulfate activator for the removal of recalcitrant pollutants in water

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**Graphene and Biomass-Based Carbocatalysts
as High-Performance Peroxymonosulfate
Activator for the Removal of Recalcitrant
Pollutants in Water**

Chen Xiao

School of Civil and Environmental Engineering

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Activator for the Removal of Recalcitrant
Pollutants in Water**

Chen Xiao

School of Civil and Environmental Engineering

Thesis submitted to

The Nanyang Technological University

In partial fulfilment of the requirements for the degree of

Doctor of Philosophy

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

Jul 25th, 2019

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Date

Chen Xiao

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Chen Xiao

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

Jul 25th, 2019

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Date

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Prof Lim Teik-Thye

Authorship Attribution Statement

This thesis contains material from 4 papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 2 is published as X. Chen, W.D. Oh, T.T. Lim. Graphene- and CNTs-based carbocatalysts in persulfates activation: Material design and catalytic mechanisms. *Chemical Engineering Journal* **354**, 941-976 (2018).

The contributions of the co-authors are as follows:

- I wrote the drafts of the manuscript. The manuscript was revised together with Dr. Oh.
- Prof Lim provided the project direction and edited the manuscript.

Chapter 3 is published as X. Chen, W.D. Oh, Z.T. Hu, Y.M. Sun, R.D. Webster, S.Z. Li, T.T. Lim. Enhancing sulfacetamide degradation by peroxymonosulfate activation with N-doped graphene produced through delicately-controlled nitrogen functionalization via tweaking thermal annealing processes. *Applied Catalysis B: Environmental* **225**, 243-257 (2018).

The contributions of the co-authors are as follows:

- I designed the experiment and prepared the manuscript drafts.
- Dr. Oh and Dr. Hu provided guidance in the experimental design and assisted in manuscript revision.
- Dr. Sun and Dr. Li performed the density functional theory calculation.
- Dr. Webster conducted the electron paramagnetic resonance.
- Prof Lim provided the project direction and edited the manuscript.

Chapter 4 is published as X. Chen, X.G. Duan, W.D. Oh, P.H. Zhang, C.T. Guan, Y.A. Zhu, T.T. Lim. Insights into nitrogen and boron-co-doped graphene toward high-performance peroxymonosulfate activation:

Maneuverable N-B bonding configurations and oxidation pathways. *Applied Catalysis B: Environmental* **253**, 419-432 (2019).

The contributions of the co-authors are as follows:

- I designed the experiment and prepared the manuscript drafts.
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- Dr. Oh provided guidance in the manuscript revision.
- Dr. Zhang conducted the transmission electron microscopy.
- Dr. Guan conducted the quantitative structure-activity relationship analysis.
- Prof Lim provided the project direction and edited the manuscript.

Chapter 5 is published as X. Chen, W.D. Oh, R.D. Webster, P.H. Zhang, T.T. Lim. Surface construction of nitrogen-doped chitosan-derived carbon nanosheets with hierarchically porous structure for enhanced sulfacetamide degradation via peroxymonosulfate activation: Maneuverable porosity and active sites. *Chemical Engineering Journal* **382**, 122908 (2020).

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- I designed the experiment and prepared the manuscript drafts.
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- Dr. Webster conducted the electron paramagnetic resonance.
- Dr. Zhang conducted the transmission electron microscopy.
- Prof Lim provided the project direction and edited the manuscript.

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ABSTRACT

Water contamination by refractory organics is one of the most critical and challenging problems in industrialization. Advanced oxidation processes based on peroxymonosulfate (PMS) activation is increasingly becoming popular due to its high ability to completely decompose toxic and refractory organic pollutants. Heteroatom-doped nanocarbons have attracted considerable attention over the conventional metal-based catalysts (e.g., Fe- or Co-based catalyst, etc.) to activate PMS, because carbocatalysts with the environmentally benign nature, corrosion resistance and biocompatibility can overcome the sintering and metal leaching problems caused by metal-based catalysts. The main objective of this study is to fabricate carbocatalysts to activate PMS for the degradation of recalcitrant organic contaminants, especially sulfonamide antibiotics in the aqueous environment.

In the first part of this study, nitrogen-doped graphenes (NG) was fabricated to activate PMS for sulfacetamide (SAM) degradation. The contents of reactive functional groups and catalytic performance of NG were delicately controlled by adjusting thermal annealing temperature. NG600 (NG thermally annealed at 600°C) with the optimized amount of N species and C=O group exhibited a better PMS-activating activity than NGs prepared under other thermal annealing temperatures or via other optimized synthesis methods. Quenching experiment, electron paramagnetic resonance (EPR) study and Density Functional Theory (DFT) calculations revealed that non-radical pathway with surface activated PMS as the key reactive oxygen species (ROS) contributed more to SAM degradation than radical pathway in the NG/PMS/SAM system. The effect of catalyst loading, PMS dosage and common matrix species on PMS activation by NG600 for SAM degradation, the SAM degradation pathway, and the reusability of NG600 were investigated.

In the second part of this study, nitrogen and boron-co-doped graphene was synthesized through two-step thermal annealing (2sNBG) and one-step thermal annealing (1sNBG). Boron-doped graphene was also synthesized via thermal annealing (BG). The carbocatalysts were employed as PMS activators to degrade SAM. The concentration of the main reactive functionalities and catalytic activity of 2sNBGs were delicately maneuvered through tuning the thermal annealing temperatures. 2sNBG800 (prepared at 800°C) with the highest N and B doping levels,

the highest contents of pyridinic N and BC3 (substitutional B) that serve as the main active sites, and absence of hexagonal boron nitride (h-BN), performed best to activate PMS for SAM degradation. By contrast, the 1sNBG contained h-BN which could hamper its catalytic activity. The catalytic performances of the various doped graphenes prepared in this study followed the order of 2sNBG800 > 2sNBG900 > 2sNBG700 > 2sNBG600 > NG600 > 1sNBGs > BG800. Both radical quenching experiment and DFT calculation revealed that the introduction of B into NG can facilitate the shift of reaction pathway from a non-radical oxidation dominating in the NG/PMS system to the coexistence of non-radical and radical oxidations in the 2sNBG/PMS system. The synergistic coupling effect from bonding configuration of B-C-C-C-pyridinic N was the main reason for the enhanced catalytic activity of 2sNBG800 to activate PMS for SAM degradation. The SAM degradation was negligibly influenced by NO_3^- in the 2sNBG800/PMS/SAM system, while Cl^- and humic acid led to 33% and 64% decrease in k_{app} , respectively. The transformation of the aromatic amino group and subsequent mineralization of SAM can effectively minimize the hazardous potentials of sulfonamides to the environment. Nevertheless, the adsorbed intermediates could deactivate 2sNBG to some extent.

In the third part of this study, nitrogen-doped chitosan-derived carbon nanosheets (CNUs) were synthesized as a renewable, cheap and easily accessible alternative to the graphene-based carbocatalyst. The contents of reactive functionalities, graphitization degree and porous structure of CNU can be effectively tailored by pyrolysis temperature (T_p). The outstanding PMS-activating activity of CNU800 (prepared at $T_p = 800^\circ\text{C}$) for SAM degradation can be attributed to its high level of C=O/C and graphitic N/C, relatively high graphitization degree, and its large specific surface area and hierarchically porous structure. The introduction of urea with the presence of NaHCO_3 during chitosan pyrolysis facilitated formation of the graphene-like carbocatalyst with hierarchically porous structure and an enhanced PMS-activating activity. Quenching experiment and EPR collectively revealed that non-radical oxidation with singlet oxygen ($^1\text{O}_2$) as the main ROS was the dominant catalytic pathway in the CNU800/PMS/SAM system. The effect of catalyst loading, PMS dosage and common matrix species on PMS activation by CNU800 for SAM degradation, SAM degradation pathway, and reusability of CNU800 were probed.

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A. Journal articles

1. **X. Chen**, W.D. Oh, Z.T. Hu, Y.M. Sun, R.D. Webster, S.Z. Li, T.T. Lim. Enhancing sulfacetamide degradation by peroxymonosulfate activation with N-doped graphene produced through delicately-controlled nitrogen functionalization via tweaking thermal annealing processes. *Applied Catalysis B: Environmental* **225**, 243-257 (2018). (Impact Factor: 14.229)
2. **X. Chen**, W.D. Oh, T.T. Lim. Graphene- and CNTs-based carbocatalysts in persulfates activation: Material design and catalytic mechanisms. *Chemical Engineering Journal* **354**, 941-976 (2018). (Impact Factor: 8.355)
3. **X. Chen**, X.G. Duan, W.D. Oh, P.H. Zhang, C.T. Guan, Y.A. Zhu, T.T. Lim. Insights into nitrogen and boron-co-doped graphene toward high-performance peroxymonosulfate activation: Maneuverable N-B bonding configurations and oxidation pathways. *Applied Catalysis B: Environmental* **253**, 419-432 (2019). (Impact Factor: 14.229)
4. **X. Chen**, T.T. Lim. Highly-efficient peroxymonosulfate activation for sulfacetamide degradation over nitrogen-functionalized graphene: The effect of thermal annealing temperature on reactive functional groups. *Chemical engineering transactions* **73**, 145-150 (2019). (Impact Factor: 8.355)
5. **X. Chen**, W.D. Oh, R.D. Webster, P.H. Zhang, T.T. Lim. Surface construction of nitrogen-doped chitosan-derived carbon nanosheets with hierarchically porous structure for enhanced sulfacetamide degradation via peroxymonosulfate activation: Maneuverable porosity and active sites. *Chemical Engineering Journal* **382**, 122908 (2020). (Impact Factor: 8.355)
6. W.D. Oh, A. Veksha, **X. Chen**, R. Adnan, J.W. Lim, K.H. Leong, T.T. Lim. Catalytically active nitrogen-doped porous carbon derived from biowastes for organics removal via peroxymonosulfate activation. *Chemical Engineering Journal* **374**, 947-957 (2019). (Impact Factor: 8.355)
7. C.T. Guan, J. Jiang, S.Y. Pang, J. Ma, **X. Chen**, T.T. Lim, Nonradical transformation of sulfamethoxazole by carbon nanotube activated peroxydisulfate: Kinetics, mechanism and product toxicity. *Chemical Engineering Journal* **378**,

122147 (2019). (Impact Factor: 8.355)

B. Conference contributions

1. X. Chen, T.T. Lim. Nitrogen-doped graphene for synergistic catalytic oxidation and adsorption of sulfacetamide in environmental remediation. Poster, 9th International Conference on Materials for Advanced Technologies, June 2017, Singapore.
2. X. Chen, T.T. Lim. Surface construction of nitrogen-functionalized graphene for enhanced sulfacetamide degradation via peroxymonosulfate activation. Oral presentation, Spring 2019 ACS National Meeting, Orlando, April 2019, USA.

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LIST OF SYMBOLS AND ACRONYMS

E_{ads}	Adsorption energy
AOPs	Advanced oxidation processes
NH₂-G	Aminated graphene/NH ₂ -functionalized graphene
E_g	Band gap energy
BJH	Barrett-Joyner-Halenda
BA	Benzoic acid
BPA	Bisphenol A
BG	Boron-doped graphene/rGO
BET	Brunauer-Emmet-Teller
CNT	Carbon nanotube
CVD	Chemical vapor deposition
Chi	Chitosan
CN	Chitosan-derived carbocatalyst from chitosan/NaHCO ₃ mixture
CU	Chitosan-derived carbocatalyst from chitosan/urea mixture
CNU	Chitosan-derived carbocatalyst from chitosan/urea/NaHCO ₃ mixture
CF	Chloroform
E_{coh}	Cohesion energy
DFT	Density Functional Theory
DMSO	Dimethyl sulfoxide
DMPO	5,5-dimethyl-pyrroline N-oxide
DMPOX	5,5-dimethyl-2-pyrrolidone-N-oxyl
DPA	Diphenylanthracene
DPCI	1,5-diphenylcarbohydrazide
DPCO	1,5-diphenylcarbonzone
pK_a	Dissociation constant
EDC	Endocrine-disrupting chemical
EDX	Energy dispersive X-ray spectroscopy
EELS	Electron energy loss spectroscopy
EPR	Electron paramagnetic resonance
ESI	Electrospray ionization
FESEM	Field emission scanning electron microscopy
FFA	Furfuryl alcohol
FTIR	Fourier transform infra-red spectra
GGA	Generalized gradient approximation
GO	Graphene oxide
g-C₃N₄	Graphitic carbon nitride
GND	Graphitic nanodiamond
NG-g	Graphitic N-doped graphene
NBG-g	Graphitic N and B-co-doped graphene
h-BN	Hexagonal boron nitride

CMK-3	Hexagonally ordered mesoporous carbon
HPLC	High-performance liquid chromatography
HOMO	Highest occupied molecular orbital
HTC	Hydrothermal carbonization
LSV	Linear sweep voltammetry
LC-MS/MS	Liquid chromatography tandem mass spectrometry
LDA	Local density approximation
LUMO	Lowest unoccupied molecular orbital
NOM	Natural organic matters
NB	Nitrobenzene
NBT	Nitro blue tetrazolium
NBG	Nitrogen and boron-co-doped graphene/rGO
1sNBG	Nitrogen and boron-co-doped graphene from one-step thermal annealing
2sNBG	Nitrogen and boron-co-doped graphene from two-step thermal annealing
NPG	Nitrogen and phosphorus-co-doped graphene/rGO
NSG	Nitrogen and sulfur-co-doped graphene/rGO
NG	Nitrogen-doped graphene/rGO
RNO	<i>N, N</i> -dimethyl- <i>p</i> -nitrosoaniline
NMDS	Nonmetric multidimensional scaling
<i>l</i>_{o-o}	O–O bond length
ORR	Oxygen reduction reaction
p-BQ	p-benzoquinone
p-CBA	Para-chlorobenzoic acid
PBCs	Periodic boundary conditions
PDS	Peroxydisulfate
PMS	Peroxymonosulfate
PBN	Phenyl- α -t-butyl nitron
P-GNS	Phosphorus-doped graphene nanosheets
PG	Phosphorus-doped graphene/rGO
pH_{pzc}	Point of zero charge
NG-pd	Pyridinic N-doped graphene
NBG-pd	Pyridinic N and B-co-doped graphene
T_p	Pyrolysis temperature
NG-pl	Pyrrolic N-doped graphene
NBG-pl	Pyrrolic N and B-co-doped graphene
ROS	Reactive oxygen species
rGO	Reduced graphene oxide
SIEs	Self-interaction errors
SWCNT	Single-walled carbon nanotube
SSA	Specific surface area
SAM	Sulfacetamide
SMX	Sulfamethoxazole

SNM	Sulfanilamide
STZ	Sulfathiazole
SG	Sulfur-doped graphene/Sulfurized graphene
BMPO	5-tert-butoxycarbonyl-5-methyl-1-pyrroline-N-oxide
BMPOX	5-tert-butoxycarbonyl-5-methyl-2-oxopyrroline-1-oxyl
TBA	Tert-butyl alcohol
TEMP	2,2,6,6-tetramethyl-4-piperidone
TEMPO	2,2,6,6-tetramethyl-4-piperidone-N-oxyl radical
T_a	Thermal annealing temperature
TGA	Thermogravimetric analysis
TOC	Total organic carbon
TEM	Transmission electron microscopy
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

CHAPTER 1: INTRODUCTION

1.1 Background

The occurrence, fate and potential risks of antibiotics in the environment have become a worldwide concern in recent years (Lin et al. 2008, Zhang et al. 2014b, Zhang and Zhang 2011). Annual worldwide antibiotic usage is estimated at 100000-200000 tons (Kummerer 2003). Americans consumed 16,000 tons of antibiotics per year at the beginning of the 21st century, and sulfonamides used in veterinary medicine accounted for approximately 2.3% of the total amount of antibiotics (Sarmah et al. 2006). More than 20,000 tons of sulfonamides per year have been introduced into the biosphere worldwide (Baran et al. 2011). Sulfonamides as sulfanilamide (SNM) derivatives are one group of synthetic antibiotics containing the characteristic sulfonamide group (Calza et al. 2004). Being commonly used as human and veterinary medicines for treating and preventing infections, sulfonamide antibiotics can enter the environment as partially unmetabolised form or biotransformed product from human body and animal organisms, or as the expired and unused drugs discharged into sewage (Baran et al. 2009). Sulfonamides with the amphoteric property exhibit high solubility and chemical stability in water, which leads to their high mobility in the aquatic environment (Baran et al. 2011, Huang et al. 2011a). Sulfonamides are generally present in freshwaters within the ng L^{-1} range (Hughes et al. 2013), and can reach up to mg L^{-1} range in the wastewater (Baran et al. 2011). A widespread distribution of sulfonamides in the aquatic environment can induce the evolution of antibiotic resistant pathogenic bacteria, posing a threat to the ecosystem and human health even at a low concentration (Luo et al. 2010, Pruden et al. 2006). Sulfacetamide (SAM) was selected as the main target pollutant in this study. SAM belongs to sulfonamides which are commonly used in human medicine. Different from the light sensitivity of SNM and sulfamethoxazole (SMX) (Budavari 1989), SAM is a stable substance under normal temperature and pressure conditions (photo- and thermally stable substances at the degradation half-life (DT_{50}) > 1 year) (Baran et al. 2011). SAM is incompatible with strong oxidizing agents (e.g., hydroxyl radical ($\text{HO}^\bullet$)) (Boreen et al. 2004). The solubility of SAM in water is 12.5 g L^{-1}

(37°C). SAM has $pK_{a1} = 1.8$ and $pK_{a2} = 5.4$ (Budavari 1989).

Several reported techniques to reduce sulfonamides in the environment may have ulterior problems (**Table 1.1**), such as low removal efficiency of coagulation/flocculation (Homem and Santos 2011) and biological degradation (Ternes et al. 2007), membrane characteristics-dependence of membrane filtrations (nanofiltration and reverse osmosis among other membrane filtrations exhibit the relatively high reject rate of $> 80\%$) (Exall et al. 2013, Ramli et al. 2015), production of some toxic oxidation byproducts of chlorination and ozonation (Adams et al. 2002, Garoma et al. 2010, Westerhoff et al. 2005), and ultraviolet (UV) light penetration being adversely affected by high turbidity or the lack of sufficiently strong UV absorption in the UV/H₂O₂ and UV photolysis system (Adams et al. 2002, Lian et al. 2015). Thus, more efficient advanced treatment techniques are highly desirable.

Persulfates (including peroxymonosulfate (PMS) and peroxydisulfate (PDS))-activating-based advanced oxidation processes (AOPs) have been garnering increasing attention due to the produced reactive oxygen species (ROS) with highly oxidative activity to mineralize the recalcitrant organic pollutants. Compared with the abovementioned traditional methods for sulfonamides removal in water (e.g., coagulation/flocculation, biological processes, membrane and conventional AOP involving UV and HO[•]), PMS activation-based AOP can work via radical and non-radical pathway, exhibiting merits including the relatively higher reduction potential, higher substrate selectivity, a wider effective pH range, higher efficiency and higher resistance toward scavengers in the complex real water. Sulfate radical (SO₄^{•-}) as the most commonly reported ROS generated from persulfates activation has been documented to be effective to degrade various refractory organic pollutants in water, such as pharmaceuticals and their metabolites (Nfodzo and Choi 2011, Zhang et al. 2015b), endocrine-disrupting chemicals (EDCs) (Sharma et al. 2015) and perfluorinated compounds (Lee et al. 2013b).

The persulfates activation methods include using external energy activators (e.g., ultrasound, heat and UV), transition metals (e.g., Fe, Co, Mn)-based catalysis (homogeneous and heterogeneous), and chemical activators (e.g., bases, phenols and quinones) (Ghanbari and Moradi 2017, Matzek and Carter 2016). Persulfates activation by the external energy is an effective process albeit with some limitations:

1) economic concerns and inaccessibility of scale-up reactor hamper its application on a large scale (e.g., PMS/ultrasound system); and 2) visible light cannot activate PMS (Duan et al. 2015a). The homogeneous transition metals/oxidants system can overcome the mass-transfer limitation and allow the free contact between catalysts and oxidants, but the behaviors of transition metal ions highly depend on the solution pH (Chan and Chu 2009, Zhou et al. 2015a). Although transition metals, especially toxic cobalt ions (the concentration limit of Co^{2+} in the drinking water is 0.05 mg L^{-1} (Förstner and Wittmann 1981)), can be immobilized with supports (e.g., metal oxide or carbon-based supporters), it has been reported that sulfathiazole (STZ) and SMX can be effectively degraded in the Co-doped graphitic carbon nitride (g- C_3N_4)/PMS system (Oh et al. 2017a) and Co/Fe oxide/PMS system (Bao et al. 2019), respectively. However, the metal leaching problem cannot be completely inhibited (Oh et al. 2016).

Table 1.1. Summary of conventional treatment technology for sulfonamides removal

Treatment methods	Sulfonamides removal%	Shortcomings
Conventional purification techniques (e.g., filtration, coagulation, flocculation)	20-30% (Homem and Santos 2011)	Low efficiency
Oxidation (e.g., chlorination, ozonation)	> 90% (chlorination (Adams et al. 2002)) 92% SMX (pH = 2, $3.2 \text{ mg L}^{-1} \text{ O}_3$, t = 3 min) (Garoma et al. 2010)	Toxic oxidation by-products are carcinogenic and more toxic than initial compounds
Membrane	Reverse osmosis: 90.2% reject rate (Adams et al. 2002) Nanofiltration: 80% sulfadimethoxine reject rate (pH = 7.2) (Ramli et al. 2015) Ultrafiltration: 20-74% reject rate (addition of micellar solutions of cetyltrimethylammonium bromide as cationic surfactant) (Exall et al. 2013)	Membrane characteristics-dependent
Biodegradation	24-100% removal (Peng et al. 2006, Ternes et al. 2007) Not subject to biodegradation under aerobic and anaerobic (Baran et al. 2006, Halling-Sørensen et al. 1998, Zessel et al. 2014)	Discrepancy in the sulfonamide degradation performance
AOP (e.g., Photo-Fenton, UV photolysis, semiconductor photocatalysis, mainly dependent on $\text{HO}^\bullet$)	Photo-Fenton: 100% sulfamethazine removal (< 2 min) (Perez-Moya et al. 2010) UV photolysis: 100% STZ/SAM removal (4 h, UVA/UVB) (Zessel et al. 2014) UV/TiO ₂ : 100% SAM removal ($\lambda_{\text{max}} = 366 \text{ nm}$, $2.5 \text{ g L}^{-1} \text{ TiO}_2$, t = 300 min) (Baran et al. 2006)	UV light penetration being adversely affected by high turbidity or the lack of sufficiently strong UV absorption

1.2 Motivation and knowledge gaps

To overcome the abovementioned problems, the application of carbocatalysts for persulfates activation has attracted increasing attention over the last decades. Compared with energy activator and transition metals for PMS activation to degrade sulfonamides in water, nanocarbon material can serve as the metal-free, environmentally friendly and biocompatible alternative with less energy consumption and no metal leaching via tuning its surface chemistry, textural and structural properties by adjusting synthesis conditions. It has been reported that nitrogen-doped graphene (NG) performed better than Co_3O_4 (typical metal catalyst) to activate PMS for phenol degradation (Duan et al. 2015b). Single-walled carbon nanotubes (SWCNTs) can act as a superior PDS activator for phenol degradation to some metal oxides (Fe_3O_4 , CuO , Co_3O_4 , and MnO_2) (Duan et al. 2015g).

Among nanocarbon materials, graphene has drawn intensive attention due to their outstanding properties, such as large specific surface area (SSA), high electrical conductivity and mobility of charge carriers, and structural and surface tunability. Graphene has a single two-dimensional (2D) planar sheet with carbon atoms packed in a hexagonal lattice, which can be exfoliated from graphite (Geim and Novoselov 2007, Park and Ruoff 2009). As the mother form of other graphitic materials, graphene opens a new application perspective for the 2D materials. Graphene oxide (GO) can be generated via oxidation and exfoliation of graphite. Reduced graphene oxide (rGO) can be generated via reduction of GO (**Table 1.2**). However, pristine graphene with an intact sp^2 hybridized honeycomb nanocarbon network has the zero band gap, limited functional groups and high chemical potentials, exhibiting its catalytic inertness (Geim and Novoselov 2007, Novoselov et al. 2012). Thus, the catalytic performance of the pristine graphene is weak. Heteroatom doping (e.g., nitrogen (N), boron (B), sulfur (S), etc.) can create surface defects. These surface defects can be beneficial to hosting certain functional groups which are conducive to the redox catalysis. Besides, oxygen-containing functional groups on the GO (one of the most commonly used carbon precursors for graphene-based nanomaterials synthesis) surface can endow nanocarbon network with hydrophilic and cation exchange properties to facilitate doping with other heteroatoms. Thus, doping is expected to enhance the catalytic activity of carbocatalysts for the activation of

persulfates (O-O bonds) via the modification of textural structure and surface chemical properties. To date, it is still disputable in terms of the persulfates-activating performance of heteroatom-doped or co-doped graphene for the degradation of organic pollutants in water.

In addition, apart from $\text{SO}_4^{\cdot-}$, other ROS (e.g., surface activated complex, singlet oxygen ($^1\text{O}_2$)) have been reported in the graphene-based carbocatalysts/persulfates system (Duan et al. 2018c). Moreover, there is a discrepancy in the possibly involved mechanisms for persulfates activation. $\text{SO}_4^{\cdot-}$ (radical pathway) and surface activated complex (non-radical pathway) have both been claimed in the rGO/PMS system. Besides, due to the difference between the intrinsic structures of PMS and PDS (e.g., molecular symmetry and bond energy), PMS (which has an asymmetric structure, the relatively low redox potential and adsorption ability) is more sensitive to the polarized and positively charged carbon region resulting from the introduction of graphitic N in the non-radical carbon-driven AOPs (Duan et al. 2015d, Duan et al. 2018b). Hence, further investigation is needed to explore the catalytic mechanisms in the carbocatalyst/persulfates system.

Although the graphene-based carbocatalysts have been documented to be the effective persulfates activators for degradation of the refractory aqueous organic pollutants (Chen et al. 2018b), GO or graphene as the most commonly used carbon sources for the graphene-based carbocatalyst fabrication possess the limitation in terms of economic feasibility, scalable production and sustainability. Thus, biomass is an ideal alternative as carbon precursor due to its low cost, renewability and easy processability (De et al. 2015, Deng et al. 2016a). So far, the reports about employing biomass-based carbocatalysts to activate persulfates in water decontamination are still limited. Furthermore, comparison between different nanocarbon materials (graphene- and chitosan-based nanocarbon materials) in terms of their SAM degradation kinetics, catalytic mechanisms, resistance toward scavengers in real water matrix and reusability can be conducive to probing the suitable precursors and synthesis methods to achieve the desirable PMS activation and decontamination performance.

Table 1.2. Main properties of graphene-based materials (modified from (Perreault et al. 2015))

Properties	Graphene (G)	Graphene Oxide (GO)	Reduced Graphene Oxide (rGO)
Synthesis	-Chemical vapour deposition -Thermal decomposition of SiC -Graphite exfoliation	-Oxidation and exfoliation of graphite	-Reduction of GO
C:O ratio	No oxygen	2-4	8-246
Young's modulus (TPa)	1 (Lee et al. 2008)	0.2	0.25
Electron mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-2}$)	10000-50000 (Marinho et al. 2012)	Insulator	0.05-200
Electronic conductivity (S m^{-1})	2500 ± 20 (Stankovich et al. 2007)	0.021 ± 0.002 (Stankovich et al. 2007)	2400 ± 200 (Stankovich et al. 2007)
Production cost	High	Low	Low
Theoretical specific surface area ($\text{m}^2 \text{g}^{-1}$)	~ 2620 (Chae et al. 2004)	736.6 (diluted GO aqueous solution) (Montes-Navajas et al. 2013)	466 (Chae et al. 2004) 600-900 (McAllister et al. 2007)

1.3 Objective and scope of works

The general objectives of this study were to address the abovementioned knowledge gaps to probe the feasibility of the nanocarbon materials as PMS activators to degrade sulfonamides in water, which includes (i) development of heteroatom-doped graphene and biomass-based carbocatalyst as PMS activator for the removal of sulfonamides in water; (ii) investigation of the relationship between textural structure and surface chemical properties of the carbocatalyst and its PMS-activating activity; and (iii) exploration of the catalytic mechanisms in the carbocatalyst/PMS/sulfonamides system.

This study includes 3 parts and the respective scopes of work are outlined below:

1. Fabrication of NG and evaluation of its performance in SAM degradation via PMS activation.
 - a. To optimize the synthesis condition for preparing NG through thermal annealing of GO and urea.
 - b. To fabricate NGs through thermal annealing, hydrothermal and low temperature combustion methods with different nitrogen sources, including NG-NH₄NO₃-air, NG-urea-HT, and NG-melamine-N₂.
 - c. To evaluate, compare and optimize the performance of NGs for SAM degradation via PMS activation.
 - d. To investigate the catalytic mechanisms, SAM degradation pathway and reusability of NG in the NG/PMS/SAM system.
2. Fabrication of nitrogen and boron-co-doped graphene (NBG) and evaluation of its performance in SAM degradation via PMS activation.
 - a. To fabricate NBGs via two-step (2sNBG) and one-step (1sNBG) thermal annealing and optimize the synthesis condition.
 - b. To evaluate, compare and optimize the performance of NBGs for SAM degradation via PMS activation.
 - c. To investigate the catalytic mechanisms, SAM degradation pathway and reusability of 2sNBG in the 2sNBG/PMS/SAM system.
3. Fabrication of nitrogen-doped chitosan-derived carbon nanosheet (CNU) and evaluation of its performance in SAM degradation via PMS activation.

- a. To optimize the synthesis conditions for preparing CNU.
 - b. To evaluate and optimize the performance of CNU for SAM removal via PMS activation.
 - c. To explore the role of each agent involved during synthesis on the PMS-activating activity of CNU for SAM degradation.
 - d. To investigate the catalytic mechanisms, SAM degradation pathway and reusability of CNU in the CNU/PMS/SAM system.
4. To compare graphene- and chitosan-based nanocarbon materials in terms of their degradation kinetics, catalytic mechanisms, resistance toward scavengers in real water matrix and reusability for SAM degradation via PMS activation.

1.4 Structure of thesis

This thesis consists of six chapters. This chapter presents a brief background of study, current knowledge gap and research motivation, objectives, scopes of study and the organization of this thesis. **Chapter 2** provides an up-to-date literature review of graphene-based carbocatalyst in persulfates activation covering comparison between PMS and PDS, doping graphene with heteroatoms, characterization techniques for nanocarbons, persulfates-activating activity of carbocatalysts, Density Functional Theory (DFT) for carbocatalyst design, identification of ROS in the radical and non-radical process, and transformation of biomass waste into carbon-based nanomaterials. In **Chapter 3**, the NG fabricated via different synthesis methods and its performance as a carbocatalyst for SAM degradation via PMS activation are described. The catalytic mechanism in the NG/PMS/SAM system is also presented. **Chapter 4** describes the synthesis of 2sNBG and 1sNBG together with their performances as carbocatalysts for SAM degradation via PMS activation. The comparison in the catalytic mechanisms between the NG/PMS/SAM and 2sNBG/PMS/SAM system is also presented. In **Chapter 5**, the pyrolytic synthesis of CNU is described. The performance of CNU for SAM removal in water via PMS activation is presented. Finally, in **Chapter 6**, a summary of all the major findings in this thesis and several recommendations for future work are provided.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Water pollution caused by the emerging contaminants has drawn increasing attention in recent years due to the toxicity and persistence of those emerging contaminants (e.g., pharmaceuticals and personal care products (PPCPs), EDCs and other refractory organics) (Wang and Bai 2017, Wang and Wang 2016). AOPs can be used to degrade most highly recalcitrant and toxic organic contaminants (Andreozzi et al. 1999). The highly reactive species involved in the AOPs can be realized via activating oxidants including PMS, PDS, hydrogen peroxide (H_2O_2) and ozone (O_3). The produced ROS possess higher redox potentials than their parent oxidants (**Table 2.1**). Generation of ROS using persulfates (PMS and PDS) as oxidants have attracted significant interest due to the following merits: 1) persulfates are available in a stable solid form; 2) high yield of ROS can be produced; and 3) various methods can be used to activate persulfates.

Table 2.1. Reduction potential of some common oxidants (Bard et al. 1985, Douglas et al. 1983, Wardman 1989)

Oxidant	Reaction/pH	Reduction potential (V)
Fluorine (F)	$\text{F}_2, \text{H}^+/\text{2HF}$	3.05
Hydroxyl radical ($\text{HO}^\cdot$)	$\text{HO}^\cdot, \text{H}^+/\text{H}_2\text{O}/\text{pH} = 0$	2.80
Sulfate radical ($\text{SO}_4^{\cdot-}$)	$\text{SO}_4^{\cdot-}/\text{SO}_4^{2-}$	2.50-3.10
Peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$)	$\text{S}_2\text{O}_8^{2-}/\text{HSO}_4^-$	2.08
Ozone (O_3)	$\text{O}_3, \text{H}^+/\text{O}_2, \text{H}_2\text{O}/\text{pH} = 0$	2.08
Peroxymonosulfate (HSO_5^-)	$\text{HSO}_5^-/\text{HSO}_4^-$	1.82
Hydrogen peroxide (H_2O_2)	$\text{H}_2\text{O}_2, \text{H}^+/\text{2H}_2\text{O}/\text{pH} = 0$	1.78
Permanganate (MnO_4^-)	$\text{MnO}_4^-, \text{H}^+/\text{MnO}_2, \text{2H}_2\text{O}$	1.68
Chlorine (Cl_2)	$\text{Cl}_2/\text{2Cl}^-$	1.36
Chlorine dioxide (ClO_2)	$\text{ClO}_2/\text{ClO}_2^-$	0.95

As described in the **Chapter 1**, carbonaceous materials are the alternative to external energy activators, conventional transition metals and chemical activators for persulfates activation. Carbocatalysis largely benefits from the availability of novel carbon allotropes, which can be divided into bulk carbonaceous (e.g., activated carbon (AC), carbon fiber and biochar, etc.) and nanocarbon materials (e.g., zero-dimensional (0D) fullerene (C_{60}) and nanodiamond (ND), one-dimensional (1D) carbon nanotubes (CNTs), 2D graphene and three-dimensional (3D) hexagonally

ordered mesoporous carbon (CMK-3), etc.) (Indrawirawan et al. 2015b, Yu et al. 2015). The carbonaceous materials in bulk are characterized by some intrinsic shortcomings such as complex structure and non-stoichiometry, so it is better to use low dimensional nanocarbons with simplified configuration for probing the carbon-driven AOPs. It has been reported that the adsorptive and catalytic performances of pristine nanocarbons with different dimensions for phenol degradation via PMS activation follow the order of 3D CMK-3 > 2D graphene and 1D SWCNT > 0D C₆₀, which is collectively decided by the textural properties (e.g., SSA and pore size), and surface chemistry (e.g., defective level and carbonyl group (C=O)) (Indrawirawan et al. 2015b).

As described in the **Chapter 1**, this study is mainly focused on graphene-based carbonaceous materials. To enhance the persulfates-activating activity, heteroatom doping can tune the surface properties and disorientate the homogeneously conjugated electron network by tailoring the charge/spin distribution of the doped surface, which can enhance the catalytic activity of graphene-based carbocatalysts to activate persulfates. Given the drawbacks of the conventional graphene or GO synthesis methods with respect to high cost, low yield, product impurities, small-scale applicability and being non-environmentally friendly (e.g., mechanical exfoliation, epitaxial growth on SiC, arc discharge, chemical vapor deposition (CVD) (**Table 1.2**)) (Deng et al. 2016b), biomass opens up a new horizon to realize both waste reduction and renewable carbon source for carbocatalyst fabrication.

This chapter addresses the literature review from the perspective of the relationship between the carbocatalyst design and catalytic mechanisms in the graphene/biomass-based carbocatalysts/persulfates system, which mainly includes the following points: 1) disclosing the relevant findings and controversy according to the experimental practice and theoretical calculation; and 2) giving an insight on how to select the suitable synthesis methods to prepare the desirable carbocatalysts, which are engineered with some specific functionalities to induce the desirable mechanisms for the degradation of specific organic substrates via persulfates activation.

Specifically, the following aspects are discussed in this review: 1) the intrinsic properties of PMS and PDS, and their preferences for active sites on catalysts; 2) versatile synthesis methods for O/N/B/S/P/F doping or co-doping, effective bonding

configurations for persulfates activation and the possible characterization techniques; 3) the effect of properties of carbocatalysts, organic substrates, persulfates and reaction conditions on the adsorption in the graphene-based carbocatalysts/persulfates system; 4) the properties of radical reaction pathway and non-radical reaction pathway, and the influencing factors (e.g., the nature of carbocatalysts and organic substrate); 5) the active sites and possible ROS involved with respect to the radical pathway and non-radical pathway in the graphene-based carbocatalysts/persulfates system; 6) the employment of DFT to investigate and predict the structural and electronic properties along with the active sites of carbocatalysts, and the limitations of the standard DFT method; 7) possible quantitative and qualitative methods for the detection of different ROS ($\text{SO}_4^{\bullet-}$, $\text{HO}^{\bullet}$, $^1\text{O}_2$, superoxide anion radical ($\text{O}_2^{\bullet-}$), surface-bound $\text{SO}_4^{\bullet-}$, surface activated complex and electron shuttle); and 8) biomass categories, conversion methods and practical applications.

2.2 Comparison between peroxymonosulfate and peroxydisulfate

Table 2.2 presents the main differences between PMS and PDS. Although persulfates are the thermodynamically powerful oxidants, they are not efficient to degrade most of persistent organic substrates on their own due to their low oxidative potential (**Table 2.1**). Therefore, activation is necessary to generate free radicals or non-radical reactive species with relatively higher reactivity than their persulfates parents in the persulfates/nanocarbon system. The principle of persulfates activation is the activation of the peroxide O-O bond to induce electron transfer between catalysts and persulfates, which is controlled by both the binding energy of bonds and the capability of catalyst to transfer electrons to the bonds in persulfates.

Persulfates have dual functionalities: 1) radical precursors for which the O-O bond in persulfates is susceptible to one-electron reduction to produce $\text{SO}_4^{\bullet-}$; and 2) electron acceptor for which persulfates have the fair reduction potential ($E^\circ (\text{HSO}_5^-/\text{HSO}_4^-) = 1.82 \text{ V}_{\text{NHE}}$, $E^\circ (\text{S}_2\text{O}_8^{2-}/\text{HSO}_4^-) = 2.08 \text{ V}_{\text{NHE}}$) (**Table 2.2**) to withdraw electrons from donors. There is an activator dependence for initiating the functionalities of persulfates. Transition metals as a reducing agent can initiate one-electron reduction of persulfates to produce $\text{SO}_4^{\bullet-}$ (Yun et al. 2017). PMS and PDS

present a preference for different transition metals as their activators due to their different properties (**Table 2.2**). It has been reported that Co^{2+} is more effective for PMS activation to produce $\text{SO}_4^{\bullet-}$, whereas Ag^+ is more effective for PDS activation to produce $\text{SO}_4^{\bullet-}$ (Lin et al. 2016, Sun et al. 2014). Phenol or quinone prefer to activate PDS then PMS to generate $\text{SO}_4^{\bullet-}$ via one-electron reduction (Ahmad et al. 2013, Fang et al. 2013). Carbonaceous materials (e.g., graphene as conductive materials effective for facilitating electron transport) exhibit the potential of mediating electron transfer from organics to persulfates.

Table 2.2. Differences between PMS and PDS

	PMS	PDS
Distance of O-O bond (Å) (Flanagan et al. 1984)	1.460 (HSO_5^- , 113 g mol ⁻¹)	1.497 ($\text{S}_2\text{O}_8^{2-}$, 192 g mol ⁻¹)
Bond energy (kJ mol ⁻¹)	140-213.3 (Benson 1978, Kolthoff and Miller 1951, Yang et al. 2010)	140 (Kolthoff and Miller 1951)
Molecular symmetry	Asymmetric oxidant, HO-O-SO ₃ (replacement of one H atom in H ₂ O ₂ with a SO ₃ group)	Symmetric oxidant, SO ₃ -O-O-SO ₃ (replacement of two H atoms in H ₂ O ₂ with two groups of SO ₃)
Stable form	A triple salt of 2 KHSO ₅ , KHSO ₄ , K ₂ SO ₄ (Oxone). 1) pH < 6 and pH = 12: PMS is stable. 2) pH = 9: PMS has the lowest stability ($[\text{HSO}_5^-] = [\text{SO}_5^{2-}]$ are equal (pK _{a2} = 9.4)). 3) pH < 1: PMS is hydrolysed to H ₂ O ₂ (Meunier 1992)	Sodium and potassium salts of peroxydisulfate ion are very stable and readily soluble in water
Average estimated lifetime in groundwater (Kolthoff and Miller 1951, Yang et al. 2010)	Hours to days	> 5 months
Solubility in water at 25°C (g L ⁻¹) (Kolthoff and Miller 1951, Yang et al. 2010)	298	730
Redox potential	E° ($\text{HSO}_5^-/\text{HSO}_4^-$) = 1.82 V _{NHE} (Betterton and Hoffmann 1990)	E° ($\text{S}_2\text{O}_8^{2-}/\text{HSO}_4^-$) = 2.08 V _{NHE} (Liang et al. 2003)
Price	US \$ 2.2 per kg Oxone (Anipsitakis and Dionysiou 2003)	US \$ 0.74 per kg K ₂ S ₂ O ₈ (Lau et al. 2007)

2.3 Doping graphene with heteroatoms (O, N, B, S, P, F)

Persulfates activation relies mainly on activating their peroxide O-O bond to induce electron transfer between catalysts and persulfates. The catalytic activity of carbocatalysts, which is closely relative to the defective level and electron states of

the nanocarbon framework, is crucial for persulfates activation. As described in the **Section 2.1**, introduction of adventitious heteroatoms (e.g., O (oxygen), N, B, S, phosphorus (P), fluorine (F)) is a feasible alternative to modify the structural and compositional properties of the carbon network of pristine graphene which has the limited catalytic activity. Substitutional doping, which uses extrinsic heteroatoms with different electronegativities, can modulate structural and chemical properties (e.g. SSA and surface hydrophilicity) (Xue et al. 2012), interrupt graphitic carbon configuration, generate more active sites and change electron states (spin and/or charge density) of the carbon network (Kong et al. 2014). Hence, substitutional doping is conducive to the enhanced performance of graphene-based carbocatalysts for persulfates activation. Defects along the edges of the graphitic carbon network can serve as active sites to accommodate heteroatoms due to their high densities of unpaired electrons (Serp and Machado 2015).

Notably, doping with heteroatoms might lead to a decrease in the SSA of the doped graphene (Chen et al. 2018a, Duan et al. 2015f, Rocha et al. 2015, Wang et al. 2018a) (**Table 2.3**). The lower SSA values after doping may be ascribed to the following reasons: 1) reduction or annealing with the presence of heteroatom precursors might lead to a lower exfoliation degree of the graphitic sheets; and 2) incorporating dopants might disorientate and crumple the graphitic basal planes to a large extent, which inhibits the formation of the few-layered structure (Qu et al. 2010). Urea as a N precursor can create more aggregation than melamine (Rocha et al. 2015). However, the reverse scenario has also been reported. Doping rGO ($10.9 \text{ m}^2 \text{ g}^{-1}$) with N or P atoms can increase the SSA of NG ($20.5 \text{ m}^2 \text{ g}^{-1}$) and phosphorus-doped rGO (PG) ($26.6 \text{ m}^2 \text{ g}^{-1}$) to some extent. Although SSA is not a decisive factor for the catalytic performance of carbocatalysts to activate persulfates, an enhancement in the SSA of carbocatalysts with higher dimensionalities can enable organic substrates and persulfates to approach the active sites on carbocatalysts more easily. Therefore, the catalysis in the graphene-based carbocatalysts/persulfates system can be promoted (Indrawirawan et al. 2015b).

Nonetheless, it is not always energetically favorable for most of the heteroatoms to reside in the hexagonal structure in a substitutional manner due to the strong stability of C-C bond (Tsetseris and Pantelides 2014). Pre-oxidized graphitic carbon

network can facilitate heteroatom doping due to the reaction between its oxygen functional groups and other heteroatoms (e.g., N, B, S, P, F). In comparison to N and B as natural choices for carbocatalyst doping owing to their intrinsic atom properties, doping with S, P and F is relatively less investigated.

Doping of graphene exploits the vast experiences accumulated in the previous studies on doping other carbon materials (e.g., C₆₀ and mesoporous carbons). Basically, it can be divided into two major categories, namely, direct synthesis and post treatment. The direct synthesis starts from the molecular carbon and dopant precursors. These techniques include CVD, segregation growth, solvothermal, epitaxial method and arc-discharge approaches. The post treatment approach is based on the preformed graphene (the most common graphene precursors are GO and rGO). The post treatment techniques include thermal and hydrothermal treatment, thermal exfoliation, pyrolysis, plasma treatment, ball milling method, supercritical method, reflux, electron-beam-based method (**Table 2.3**).

Generally, thermal and hydrothermal methods can incorporate a relatively high N doping level (0.7-9.3 at.%) and graphitic N concentration (0.9-25.9 at.%) into graphene carbon network. It is noteworthy that pyrolysis can significantly facilitate the formation of graphitic N (51.1-65.9 at.%) in the graphitic carbon network albeit with a low N doping level (1.79-2.44 at.%). As for B doping, compared with thermal and hydrothermal methods (0.82-4.82 at.%), CVD method can induce a relatively high B doping level (0.5-19 at.%) (**Table 2.3**). In comparison to N doping, the doping level of B/S/P/F is yet to be increased and the quantitative determination of the specific bonding configurations needs further exploration.

Table 2.3. Different synthesis methods for heteroatom doping on graphene-based nanocarbon materials

Synthesis methods	Catalyst	Synthesis procedure	Doping level/ BET (m ² g ⁻¹)	Bonding configurations by XPS	Application	Ref
Post-synthesis						
Thermal annealing Advantages: high conductivity, low cost, and high yield without metal catalyst Disadvantages: high energy cost	N-doped rGO (NG)	NG: 1.0 g GO + 1.0 g NH ₄ NO ₃ , 350°C, 2 h	NG: N = 7.66 at.% / 20.5	NG: graphitic N: pyrrolic N: pyridinic N = 1:10.77:4.35	Catalytic ozonation for SMX removal	(Yin et al. 2017)
	P-doped rGO (PG)	PG: 1.0 g GO + certain amounts of ammonium phosphate monobasic (NH ₄ H ₂ PO ₄), 350°C, 2 h	PG: P = 9.86 at.% / 26.6	PG: P-O (P2p _{3/2} : 134 eV) > P-O (P2p _{1/2} : 134.8 eV)		
	N-doped graphene (NG)	The mixture of 200 mg GO + 1 g urea was calcined in tubular furnace at 800°C, N ₂ , 30 min (heating rate = 5°C min ⁻¹)	N = 16 wt%/74	Graphitic N = 25.9 at.%, pyrrolic N = 31.8 at.%, pyridinic N = 38.4 at.%, nitric oxide = 3.94 at.%	[SAM] = 10 mg L ⁻¹ , [cat] = 0.2 g L ⁻¹ , [PMS] = 0.5 mM NG: ~10% adsorption, 100% phenol removal in 50 min.	(Chen et al. 2018a)
	N-doped graphene (NG)	1 g GO + 1 g melamine calcined at 450°C for 1 h with the ramping rate of 5°C min ⁻¹ in the muffle furnace. Then the mixture was transferred to the tubular furnace for further calcination at 600°C in a N ₂ atmosphere for 1 h with the ramping rate of 5°C min ⁻¹ .	N = 19.3 wt%/8	Graphitic N = 12.8 at.%, pyridinic N = 52.8 at.%, pyrrolic N = 34.5 at.%	[SAM] = 10 mg L ⁻¹ , [cat] = 0.2 g L ⁻¹ , [PMS] = 0.5 mM NG: ~10% adsorption, 59% phenol removal in 60 min.	(Chen et al. 2018a)
	N-doped graphene (NG)	Graphene nanosheets + ammonia gas (NH ₃) (100 sccm) at 800°C	N = 0.7 at.% / 517.2	-	Electrically conductive adhesives	(Pu et al. 2014)
	N-doped graphene (NG) (transfer doping method)	A polyaniline (PANI)-containing quartz boat was covered by a GO-containing boat and putting them in a tubular furnace with Ar flow. The deoxidation and doping of GO were proceeded by increasing the temperature to 850°C at the rate of 20°C min ⁻¹ , keeping the temperature at 850°C for 60 min.	N = 6.27 at.% / 1119	Pyridinic N (398.3 eV), pyrrolic N (398.8 eV), quaternary N (401.2 eV) and nitric oxide (403.4 eV)	Oxygen reduction reaction (ORR)	(Mo et al. 2014)

Table 2.3 continued

B-doped graphene (BG)	Chemically derived graphene + a gas mixture of BCl ₃ (~99.99%) and Ar (1:4 v/v) at 800°C for 2 h with a total flow rate of 250 mL min ⁻¹	B = 0.88 at.% / 256	B-C bond in BC ₃ nanodomain: ~ 190.0 eV, B-O bond in BC ₂ O nanodomain: 192 eV	Anode material for lithium ion batteries	(Wu et al. 2011)
B-doped graphene (BG)	BPG precursor: tetraphenylphosphonium tetraphenylborate (TPP-TPB) solution + graphene dispersion with magnetic stirring and heating at 60°C	B = 0.82 at.% P = 0.18 at.%	BCO ₂ : 192.5 eV, BC ₂ O: 190.7 eV, BC ₃ : 188.7 eV, B ₄ C: 186.7 eV P-C: 133.7 eV, P-O: 132 eV	ORR	(Jo et al. 2015)
P-doped graphene (PG)	BG (PG): 0.035 g of the BPG precursor thermally decomposed at 900°C (700°C) for 3 h in a tubular furnace under autogenic atmosphere without any gas flow				
P-doped graphene nanosheets (P-GNS)	TPP-GO mixture: 50 mg triphenylphosphine (TPP) (2 mL DMF solution) + 50 mg GO (in 20 mL of H ₂ O), dried at 900°C P-GNS: TPP-GO mixture was then annealed at 800°C under an Ar atmosphere	P = 1.55 at.%	P2s: 190 eV, P2p: 132 eV (P-C: 132.3 eV, P-O: 133.3 eV)	Room temperature NH ₃ sensing	(Niu et al. 2014)
S-doped graphene (SG)	GO + benzyl disulfide (BDS) in Ar, 1050°C	S = 1.3 wt%/ 435	Sulfide (-C-S-C-) (~163.8 eV) = 82.3 at.% Oxidized sulfur groups (-C-SO _x -C) (x = 2,3,4) (167.5-171.5 eV) = 17.7 at.%	ORR	(Yang et al. 2012)

Table 2.3 continued

N-doped graphene (NG)	NG: 1.0 g GO + 1.0 g NH ₄ NO ₃ , 350°C, 1 h	N = 6.54 at.% (NG) / 71.5 (NG), 71.4 (NBG), 83.3 (NPG), 255.4 (rGO)	NG: Pyridinic N = 45.46 at.%, pyrrolic N = 38.35 at.%, graphitic N = 10.38 at.%, nitric oxide = 5.8 at.%	[phenol] = 20 mg L ⁻¹ , [cat] = 0.2 g L ⁻¹ , [PMS] = 2 g L ⁻¹ , T = 298 K.	(Duan et al. 2015e)
N, B-co-doped graphene (NBG)	NBG: 1.0 g GO + 1.0 g NH ₄ NO ₃ + ammonium pentaborate octahydrate (H ₈ B ₁₀ N ₂ O ₁₆ ·8H ₂ O) (0.1% B ₂ O ₃), 350°C, 1 h			7.2% adsorption, 85% phenol removal in 180 min.	
N, P-co-doped graphene (NPG)	NPG: 1.0 g GO + 1.0 g NH ₄ NO ₃ + NH ₄ H ₂ PO ₄ (0.1% P ₂ O ₅), 350°C, 1 h			GO < PG < rGO < BG < NPG < NBG < NG	
N-doped graphene (NG)	NG: 1.0 g GO + 1.0 g NH ₄ NO ₃ , 350°C, 1 h	N = 5.61 at.% (NG), N = 7.69 at.% (NBG)/ 64.1 (NG), 73.2 (NBG), 301 (rGO)	NG: pyridinic N = 29.67 at.%, pyrrolic N = 49.96 at.%, graphitic N = 20.37 at.%	[phenol] = 20 mg L ⁻¹ , [cat] = 0.2 g L ⁻¹ , [Oxone] = 2 g L ⁻¹ , T = 298 K	(Sun et al. 2013a)
N, B-co-doped graphene (NBG)	NBG: 1.0 g GO + 1.0 g NH ₄ NO ₃ + H ₈ B ₁₀ N ₂ O ₁₆ ·8H ₂ O (0.1 wt% B ₂ O ₃), 350°C, 1 h		NBG: graphitic N = 10.75 at.%, pyridinic N = 25.45 at.%, pyrrolic N = 63.81 at.%	NG: 3% adsorption, 100% phenol removal in 45 min.	
N, P-co-doped graphene (NPG)	NPG: 1.0 g GO + 1.0 g NH ₄ NO ₃ + NH ₄ H ₂ PO ₄ (0.1 wt% P ₂ O ₅), 350°C, 1 h			NBG: 8% adsorption, 100% phenol removal in 20 min.	
				NBG > NG > NPG	
N, B-co-doped graphene (NBG) (chemically grafting ionic liquid (IL) to GO, followed by thermal annealing)	IL-grafted GO (IL-GO): 100 mg GO + 300 mg 1-aminopropyl-3-methylimidazolium tetrafluoroborate (IL-NH ₂ (BF ₄ ⁻)) (N, B precursors) + 200 mg N, N'-dicyclohexylcarbodiimide (DCC), dispersed in 200 mL of N, N-dimethylformamide (DMF) solution, under N ₂ atmosphere, then heated at 50°C for 24 h. NBG: thermal annealing under Ar atmosphere from RT to 300 °C in 1 h and kept at 300 °C for 2 h, then from 300 °C to carbonization temperature (T = 1200°C) at 5 °C min ⁻¹ , dwelling for 1 h.	N = 2.50 at.%, B = 3.26 at.%	B1s: B-N and BC ₃ : 191.9 eV BC ₂ O and BCO ₂ : 193 eV Pyridinic N (398.2 eV), C–N–B (399.1 eV), pyrrolic N (400.1 eV), and graphitic N (401.3 eV)	Electrocatalysis for triiodide reduction	(Yu et al. 2016)

Table 2.3 continued

N, B-co-doped graphene (NBG)	NG precursor: 0.5 g GO + 150 g urea, 180°C for 12 h NBG: the mixture of 0.1 g NG + 0.5 g H ₃ BO ₃ was calcined in the tubular furnace at 900°C, Ar, 30 min (heating rate = 10°C min ⁻¹)	N = 6.80 at.%, B = 4.82 at.%	N1s: 400 eV. graphitic N = 18.8 at.%, pyridinic N = 41.3 at.%, pyrrolic N = 39.9 at.%. B1s: 192 eV. BC ₃ (190.0 eV) = 19.5 at.%, B–C–O (including BC ₂ O and BCO ₂ , 191.2 eV) = 59.5 at.%, and B–O (192.7 eV) = 21.0 at.%	ORR	(Tai et al. 2014)
N, B-co-doped graphene (NBG)	NG: annealing GO powder in 20% NH ₃ /Ar at 900°C for 5 h with the ramping rate of 5°C min ⁻¹ NBG: annealing NG with H ₃ BO ₃ in Ar at 900°C for 5 h	N = 4.42 at.%, B = 2.17 at.%	Pyridinic N = 2.03 at.%, pyrrolic N = 1.29 at.%, graphitic N = 0.90 at.%. BC ₃ (188.9 eV) = 2.17 at.%	ORR	(Zheng et al. 2013)
N, P-co-doped graphene (NPG)	Functionalized graphene nanosheets (FGN): GO, 800°C in N ₂ atmosphere for 30 min NPG: 0.15 g FGN + 0.3 g (NH ₄) ₃ PO ₄ at 800°C, N ₂ , 30 min (heating rate = 10°C min ⁻¹)	N = 3 at.%, P = 1.2 at.% / 284	Pyridinic N, pyrrolic N, nitric oxide and graphitic N, C–O–PO ₃ and (C–O) ₃ PO (134.1 eV): P is not directly bonded to C. C ₂ –PO ₂ (132.8 eV) or CPO ₃ (133.5 eV) C ₃ PO (132.3 eV)	High performance supercapacitors	(Xia et al. 2017)
N, S-co-doped graphene (NSG)	1.0 g GO + 1.0 g NH ₄ NO ₃ + 0.3 g diphenyl disulfide, 623K, 1 h	N = 8.15 at.%, S = 0.69 at.% / 69.1 (NSG), 81.5 (NG), 255.4 (rGO), 29.9 (GO)	Pyridinic N = 39.8 at.%, pyrrolic N = 51.6 at.%, graphitic N = 8.6 at.%. S2p _{3/2} : C–S–C: 164.0 eV S2p _{1/2} : C–S–C: 165.2 eV S2p _{3/2} : C–SO _x –C: 167.8 eV S2p _{1/2} : C–SO _x –C: 169.9 eV (x = 2,3,4)	[PMS] = 6.5 mM, [phenol] = 20 mg L ⁻¹ , [cat] = 0.2 g L ⁻¹ , T = 298 K, ~ 15% adsorption, 100% phenol removal in 90 min. GO < rGO < S-rGO < N-rGO < SNG	(Duan et al. 2015f)

Table 2.3 continued

	N, S-co-doped graphene (NSG) (bioinspired thermal annealing)	PDA-rGO: 1.0 mg mL ⁻¹ GO + 2.0 mg mL ⁻¹ dopamine (N precursor): self-polymerization Cys-PDA-rGO: PDA-rGO (ca. 2.0 mg mL ⁻¹) in 10 mM Tris-buffer (pH 8.0) containing 10 mg mL ⁻¹ of cysteine (S precursor) NSG: annealing freeze-dried Cys-PDA-rGO composite at 800°C in Ar atmosphere for 3 h with a heating rate of 5°C min ⁻¹	N = 2.12 at.%, S = 1.70 at.% / 140.3	Pyridinic, pyrrolic, and quaternary N C-S-C (S2p _{3/2} : 164.1 eV and S2p _{1/2} : 165.2 eV) S-O: 168.2 eV (very likely originated from the incorporated sulfate ions during the synthesis of GO from graphite)	ORR	(Zhang et al. 2015a)
	N, S-co-doped graphene (NSG)	0.2 g GO + 0.2 g thiourea + 100 µL KOH (1 mol L ⁻¹) under N ₂ atmosphere at 800°C for 5 h	N = 2.77 at.%, S = 2.48 at.% / 140.3	Pyridine N = 39.9%, pyrrolic N = 28.8%, graphitic N = 22.6%, nitric oxide = 8.6% C-S-C (S2p _{3/2} : 163.6 eV and S2p _{1/2} : 164.8 eV): S atoms bound in aromatic carbon structures -C-SO _x -C- (x=1, 2): sulfur oxides generated at the edges of graphene	Ultrasensitive and selective determination of cyclophosphamide	(Huang et al. 2017)
Hydrothermal method Advantages: high conductivity, low cost, and high yield	N-rGO (NG)	0.1 g GO + 2 mL 30% ammonia, 180°C, 24 h	N = 7.77 at.% / 317	Pyridinic N = 53.2 at.%, pyrrolic N = 37.7 at.%, graphitic N = 9.1 at.%	[Bisphenol A (BPA)] = 0.385 mg L ⁻¹ , [cat] = 120 mg L ⁻¹ , [PDS] = 0.6 mM, pH = 6.6, T = 298 K. 50% BPA adsorption in 10 min and 100% BPA removal in 7 min	(Wang et al. 2015)

Table 2.3 continued

without metal catalyst Disadvantages: high energy cost	B-rGO (BG)	2.5 mmol boric acid (H ₃ BO ₃) (BG) or cyanamide (C ₂ H ₂ N ₄) (NG) into 60 mL of rGO (~2.5 mg mL ⁻¹), 180°C, 12 h	B = 2.4 at.%, N = 3.6 at.% / 81.26 (B-rGO), 93.68 (N-rGO)	BC ₂ O (192.6 eV) > BCO ₂ (193.1 eV) > BC ₃ (190.5 eV) Pyridinic, pyrrolic, and quaternary N	Separators for high performance Li-S batteries	(Han and Manthiram 2017)
	N-rGO (NG)					
	N-doped graphene (NG)	0.5 g GO + 150 g urea, 180°C for 12 h	N = 9.34 at.%	Pyridinic N = 41.8 at.%, pyrrolic N = 47.4 at.%, graphitic N = 10.8 at.%	ORR	(Tai et al. 2014)
	N-doped graphene (NG)	Dispersing GO (200 mg) in 200 mL of distilled water and to this 600 mg of sodium diethyldithiocarbamate was added and refluxed for 24 h.	N/C = 18.1%	N2p: 400.6 eV	A glassy carbon electrode for sensing 4-nitrophenol at nanomolar levels	(Giribabu et al. 2014)
	F-doped graphene (FG)	40 mL GO dispersion (2 mg mL ⁻¹) + 0.5 mL HF (40 wt%), 180°C for 30 h	C/F = 2.1 at.%	F1s of C-F: 686.2 eV F1s of HF: 690.1 eV ionization energy of HF: 695.9 eV	-	(Wang et al. 2012d)
Low temperature combustion Facile protocol of thermal treatment, mild conditions and energy-saving	phenylboronic acid functionalized rGO (rGO-PBA)	8 mL GO (0.5 mg mL ⁻¹) solution + 25 mg 3-aminophenylboronic acid at 70°C for 3 h + 50 µL hydrazine monohydrate and 50 µL ammonia solution (25%) at 80°C for 1 h	-	-	Glucose sensing	(Basiruddin and Swain 2016)
	N-doped graphene (NG)	The mixture of 0.5 g GO + ammonium nitrate (NH ₄ NO ₃ , containing 0.02 mol N atoms) was calcined in the muffle furnace at 350°C, N ₂ , 30 min (heating rate = 5°C min ⁻¹)	N = 8.5 at.% / 120.2	Pyridinic N = 47.7 at.%, pyrrolic N = 42.4 at.%, graphitic N = 9.9 at.%	[PMS] = 6.5 mM, [phenol] = 20 mg L ⁻¹ , [cat] = 0.4 g L ⁻¹ , T = 298 K, 79.4% phenol removal in 120 min.	(Li et al. 2017a)

Table 2.3 continued

Thermal exfoliation Simple and scalable	B-doped graphene (BG)	GO + boron trifluoride diethyl etherate (BF ₃ Et ₂ O), thermal exfoliation in an atmosphere of N ₂ /H ₂ at 1000°C for 12 min	B = 23 mg L ⁻¹ (prompt γ -ray analysis (PGAA))	The trace amounts of B below the detection limit of X-ray photoelectron spectroscopy (XPS)	-	(Wang et al. 2013b)
	S-doped Hummers GO (HU-S)	100 mg graphite oxide + SO ₂ and H ₂ S (S precursor) flow (1 L min ⁻¹) + N ₂ flow (1 L min ⁻¹), 12 min, 600°C	S = 7.03 (% in the total elemental composition at the surface of HU-S)	S2p: ~167 eV	-	(Poh et al. 2013)
Pyrolysis Advantages: large yield, and utilizing biological waste materials Disadvantages: high energy cost, special atmosphere and low doping content	Metal organic framework derived N-doped graphene (NG)	4 g dicyandiamide (DCDA) + 0.25 g MIL-100 (Fe) (a metal organic framework), 800°C, 2 h, N ₂ → N-C-Fe, then washed with H ₂ SO ₄ (0.5 M) at 80°C for 24 h to exhaust the unsecured iron species → NG	N = 2.31 at.% / 351.2	Pyridinic N = 27.45 at.%, graphitic N = 65.86 at.%, nitric oxide = 6.69 at.%	[PMS] = 3.25 mM, [phenol] = 50 mg L ⁻¹ , [cat] = 0.1 g L ⁻¹ , T = 298 K. ~ 10% adsorption, 100% phenol removal in 30 min.	(Liang et al. 2017)
	N-doped graphene (NG)	GO-PANI: 200 mg GO + 1M HCl + 100 mg aniline monomer + 0.17 g (NH ₄) ₂ S ₂ O ₈ (catalyst), 24 h NG: 1000°C, 30 min under Ar atmosphere	N = 2.44 at.% / 377	Graphitic N = 51.1 at.%, pyridinic N, pyrrolic N, nitric oxide	ORR	(Lin et al. 2013)
	N-doped graphene (NG-20)	3 g glucose (carbon precursor) + 3 g FeCl ₃ ·6H ₂ O (template and catalyst) + urea (10% mass ratio of urea in the mixture) (N precursor), vaporized at 80°C in air and further dried in an oven for 24 h to get a black solid, which was calcined at 700°C for 6 h under a N ₂ flow of 50 mL min ⁻¹	N = 1.79 at.% / 165.8	Pyridinic N = 79.2 at.%, pyrrolic N = 29.8 at.%	[phenol] = 20 mg L ⁻¹ , [cat] = 0.2 g L ⁻¹ , [PMS] = 2 g L ⁻¹ , T = 298 K. ~ 4% adsorption, 98% phenol removal in 180 min	(Wang et al. 2016a)

Table 2.3 continued

	S-doped graphene (SG)	1 g polyacrylonitrile nanospheres (PANS) + sulfur at 900°C for 1 h in high-purity Ar gas	S = 9.52 wt%	Oxidized S (168.5 eV) = 35.3 at.%, thiophene-S (S2p _{3/2} : ~ 163.9eV, S2p _{1/2} : ~ 165.1eV) = 64.7 at.%,	ORR	(You et al. 2014)
Ball-milling Advantages: simple, versatile, scalable, cost-effective and ecofriendly Disadvantages: just edge-nitrogenated	N-doped graphene (NG) (all-solid-state ball-milling)	5 g graphite + 100 g urea + 250 g stainless steel grinding balls (5 mm) under Ar atmosphere. Ball-milling at 290 rpm for 45 h on a planetary ball-milling equipment	N = 3.15 at.%/127.1	Graphitic N = 5.61 at.%, pyridinic N = 21.25 at.%, pyrrolic N = 73.14 at.%	Lithium ion battery anode	(Liu et al. 2017)
	N-doped graphene (rGO-U, rGO-M)	0.6 g GO + 0.26 g melamine/urea ball-milled 4 h, 15 vibrations/s. The mixture then thermal annealed under N ₂ flow (100 cm ³ min ⁻¹) until 873 K (at 2 K min ⁻¹), dwelling for 1 h.	rGO-M: N = 9.3 at.%/102 rGO-U: N = 7.5 at.%/47	rGO-M: pyrrolic N/pyridinic N = 0.6, graphitic N = 17 at.%. rGO-U: pyrrolic N/pyridinic N = 0.5, graphitic N = 25 at.%	Catalytic ozonation for oxalic acid and phenol removal	(Rocha et al. 2015)
	Sulfurized graphene (SG)	Graphite flakes + the mixed acid of nitric acid and sulfuric acid (1:1 in volume), 5 h. then heated at 700°C. The as-prepared chemical modified graphite flakes mixed with sulfur powder in a planetary mill (stainless steel balls with diameter of 5 mm, setting agitation of capsule at 500 rpm for overnight).	S = 3.4 at.%	S2p: C-S (163.4 eV, 164.8 eV), -C-SO ₃ -C- (168.25 eV), and -C-SO ₄ -C- (169.55 eV) S2s: five-membered C-S (233 eV), hexatomic C-S (228 eV)	Reduction of 4-nitrophenol to 4-aminophenol	(Wang et al. 2017b)
Supercritical method Advantages: facile and low temperature Disadvantages: Toxic gas, expensive instruments and	N-doped graphene (NG)	GO + 30% NH ₃ (aq.) (0.25: 3 weight ratio) 250°C, 30 MPa, and 1 h H ₂ O-rich phase condition (GO + sc NH ₃ + H ₂ O): NG-1 NH ₃ -rich phase condition (GO + sc NH ₃): NG-2	N = 9.82 at. % (NG-1) N = 10.58 at. % (NG-2)	NG-1: pyridinic N (398.3 eV) = 23.58 at.%, amino N (399.2 eV) = 29.78 at.%, pyrrolic N (400.1 eV) = 33.86 at.%, graphitic N (401.4 eV) = 10.31 at.%, nitric oxide (403.7 eV) = 2.47 at.%. NG-2: pyridinic N (398.3 eV) = 22.36 at.%, amino N (399.2	CO ₂ adsorption and ORR	(Baldovino et al. 2016)

Table 2.3 continued

rigorous conditions				eV) = 32.40 at.%, pyrrolic N (400.1 eV) = 31.64 at.%, graphitic N (401.4 eV) = 11.96 at.%, nitric oxide (403.7 eV) = 1.64 at.%		
Reflux (liquid process) Mass production and cost-effectiveness	B-rGO (BG)	3 mg GO/1 mL water + borane-THF (BH ₃ -THF) adduct (1.5 mL) in an oil bath, and the brown suspension was stirred under reflux with a magnetic stirring bar for 4 days	B = 1.1 at.% / 466	BC ₂ : 192 eV	Supercapacitor	(Han et al. 2013)
	B-substituted graphene (B-SuG)	100 mg defective graphene (THF solution 100 mL) + BH ₃ -THF (1.2 mL) in an oil bath, 80°C, 24 h (other borylating agents, namely NaBH ₄ , B(OH) ₃ , carborane, and B ₂ O ₃ , NH ₃ BH ₃)	B = 1.85 at.%	B–B < B–C < B–O ≈ B–N in the range of ~188–198 eV	Hydrogen evolution reaction	(Sathe et al. 2014)
Electron-beam-based method Advantages: green, cost-effective and high-quality. Disadvantages: low yield, low doping content and special equipment	N, S-co-doped graphene (NSG-210)	500 mg GO + 500 mg L-cysteine (precursors of N and B) + 75 mg polyethylene glycol + 20 mL (a scavenger of oxidative radicals) + pH adjusted to 9 + GJ-2-II electron accelerator at room temperature at 1.8 MeV with an irradiation dose = 210 kGy (irradiation rate = 5 mA S ⁻¹)	N = 6.4 at.%, S = 2.66 at.% / 324.6	Pyridinic N = 1.10 at.%, pyrrolic N = 2.69 at.%, graphitic N = 2.64 at.% C-S-C (S2p _{3/2} : 163.5 eV and S2p _{1/2} : 165 eV) = 2.38 at.% C-SO _x -C (x = 2,3,4) (168.1 eV) = 0.28 at.%	Supercapacitors	(Cheng et al. 2018)

Table 2.3 continued

Plasma Controllability and selectivity, time and cost effectiveness, clean, non-destructive and adjustable process	NG-60	GO was placed into the plasma chamber which was evacuated to 2 Pa, then N ₂ gas (1 L min ⁻¹) was introduced into the chamber to create N ₂ plasma with RF power of 180 W at 50 Pa for various time at room temperature, 60 min	N/C = 7.68 at. %	Pyridinic N = 69 at. %, pyrrolic N = 24.7 at. %, graphitic N = 6.3 at. %	The effect of N doping on the room temperature ferromagnetism of NG	(Qin and Xu 2017)
Direct synthesis						
CVD Advantages: high quality, few layers, and controllable doping content and dopant species Disadvantages: low yield and metal catalyst residuals	N-doped graphene (NG) (atmospheric pressure CVD (APCVD))	Solid imidazole or mixture of imidazole and melamine powder + Cu foil + Ar and H ₂ (98:2.5 sccm) gas mixture, 1020°C	N = 4.2 at. % (mixture precursor)	Pyridinic N, pyrrolic N, and quaternary N Overall N content and graphitic N content of NG from mixture precursor > those of NG from imidazole	-	(Vishwakarma et al. 2016)
	Single-layer B-doped graphene (BG)	Carborane (C ₂ B ₁₀ H ₁₂) (10 ⁻⁶ mbar) + Ni (111) film, 600-630°C, 20 min	B = 19 at. %	B ₀ (Ni _x B: B atoms under the B-graphene layer): 188 eV, B ₁ : 187.4 eV	Atomic structure of B dopants	(Usachov et al. 2015)
	B-doped graphene (BG)	A flow of 6 sccm of CH ₄ + 1-5 sccm of B ₂ H ₆ (1% B ₂ H ₆ in H ₂) (7.0 Torr) + Cu foil at 1000°C for 30 min.	-	Signals of 192.0 and 200.0 eV in the near edge X-ray absorption fine structure spectroscopy (NEXAFS) spectrum: the π and σ states of sp ² bonded graphitic B	Local atomic and electronic structure of B dopants in monolayer graphene	(Zhao et al. 2013a)
	B-doped graphene (BG)	Cu foil substrates annealed at 960°C under flow of 500 sccm Ar and 500 sccm H ₂ for 45 min + 4 methoxyphenylboronic acid, at around 300°C	-	Auger electron spectroscopy of BG: B signal at 179 eV. The B/C signal ratio remains very	The effect of using phenyl-containing molecules as precursors on BG	(Ovezmyradov et al. 2015)

Table 2.3 continued

	to trigger its sublimation + CH ₄ at the rate of 50 sccm along with the flow of Ar at 500 sccm and H ₂ at 500 sccm for 2 min		close to the initial state after Ar ⁺ sputtering, which indicates the successful B and C incorporation		
B-doped graphene (BG)	Graphene + trimethylboron (TMB) ionized by the low-energy microwave plasma in a plasma-enhanced CVD chamber, 20min	B = 13.85 at.% (secondary ion mass spectroscopy (SIMS))	XPS: B-C (substitutionally doped into the graphenes): ~189.7 eV, B-B: ~ 187.9 eV. Electron energy loss spectroscopy (EELS): K-shell ionization edges of B: 189.5 eV: a detectable π^* peak along with a σ^* band, implying B atoms and their C counterparts possess the similar status of sp ² hybridization.	The effect of B doping on the band gaps and p-type transport properties of BG	(Tang et al. 2012)
B-doped graphene (BG)	Sublimation of phenylboronic acid powder (C ₆ H ₇ BO ₂) at 130°C with 10 sccm H ₂ as the carrier gas. 20 min of growth on the annealed Cu foil (950°C) before cooling down to ambient temperature.	B = 1.5 at. %	BI _s : 190.9 eV the main bonding form of B atoms should be BC ₃	-	(Wang et al. 2013a)
B-doped graphene (BG)	Boron powder (ethanol solution) + ethanol (carbon source 10 μ L min ⁻¹) + Cu substrate, 950°C for 10 min	B = 0.5 at. %	Graphitic B: 200.5 eV > boron silane B (boron atoms which are located in a π -conjugated system and contribute to the π -conjugated system with one p electron): 198.5 eV	p-n junction solar cells	(Li et al. 2012a)
B-doped graphene (BG) (bubbler-assisted CVD)	Triethylborane (TEB)/hexane solution was bubbled with 1 sccm Ar into the reactor at 1000°C for 5 min, Cu foil	B = ~1.75 at. %	Substitutional B atoms: 186.4 eV, edge oxidized B atoms: 190.3 eV	Gas sensor	(Lv et al. 2015)

Table 2.3 continued

Segregation growth Easy control of dopants concentration and location, allowing for the direct growth of pattern-doped graphene and heterojunctions	N-doped graphene (NG)	Vacuum annealing a sandwiched Ni(C)/B(N)/SiO ₂ /Si substrate at high temperature under N ₂ atmosphere (800-1100°C, slowly at a rate of 15-20°C min ⁻¹). Maintaining the samples at desired temperature for 0-60 min with a pressure of 10 ⁻³ -10 ⁻⁴ Pa, then cooling down to room temperature at a rate of 2-50°C min ⁻¹	N = 0.95 at. %	Pyridinic N (398.2 eV), pyrrolic N (400.3 eV), graphitic N (401.5 eV) pyridinic N and pyrrolic N: dominant	-	(Zhang et al. 2011)
Arc discharge Advantages: few defects, convenient and metal-free. Disadvantages: special equipment, high cost and low doping content	N-doped graphene (NG)	DC arc discharge apparatus: N ₂ atmosphere, 800°C, 2min (arc discharge time), 30-32 V (discharge voltage), 25-30 A (current), 0.5-1 mm (gap between the graphite electrodes).	N = 1 at. % (Energy dispersive X-ray spectroscopy) (EDX)	N: ~399 and ~403 eV can be attributed to π^* -states associated with pyridine-like and graphite-like N, respectively (EELS)	-	(Guan et al. 2011)
Epitaxial growth Advantages: simple methodology and high quality Disadvantages: special	N-doped graphene (NG)	Epitaxial graphene: the 4H-SiC (0001) substrates were annealed on a graphite susceptor at around 1550°C in Ar pressure of less than 800 mbar for 10 min in an infrared rapid thermal annealing chamber. NG: epitaxial graphene was exposed to N ₂ under cooling at room temperature for 15 min.	N = 1.2 at. %	Graphitic N = 3.7 at. %, pyridinic N = 21.3 at. %, pyrrolic N = 75 at. %	The effect of N atoms on the electronic properties of epitaxial graphene	(Boutchich et al. 2014)

Table 2.3 continued

Solvothermal Advantages: simple operation, mild conditions, scale-up synthesis and a high doping content Disadvantages: defects inside the graphitic network and functional edges of graphene	substrate, low yield and high cost	N-doped graphene (NG)	Graphene: annealing n-type 6H-SiC (0001) wafers under UHV conditions up to certain temperatures NG: graphene + high-purity NH ₃ (25 mL min ⁻¹) in a high-pressure gas cell at 500°C for 1 h	N = 0.62% per C atom (Low temperature scanning tunnelling microscopy (LT-STM))	-	-	(Wang et al. 2013d)
		B-doped graphene (BG)	B ₄ C particles with a size of about 0.5 µm were annealed at 1600-1900°C in a vacuum furnace (~10 ⁻⁴ Torr). The annealed powder was dispersed onto a carbon film of the microgrid	-	EELS spectra: B–K edge peaks: the presence of π* and σ* peaks in the B edge, suggesting sp ² -bonding of B	-	(Norimatsu et al. 2012)
		B-doped graphene (BG), N-doped graphene (NG)	BG: boron tribromide (BBr ₃ , 156 µL) (B source) + tetrachloromethane (CCl ₄ , 3.0 ml) (C source) + potassium (K, 4.0 g) (catalyst), 210°C, 20 h NG: lithium nitride (Li ₃ N, 1.0 g) and CCl ₄ (2.0 ml) at 200°C for 20 h	N = 9.72 at.%, B = 0.51 at.%	Pyridinic, pyrrolic, and quaternary N 189.10 eV: B-B 190.34 eV (main component): B substitution in the graphene (sp ² hybridization) 191.51 eV: oxidation of B	Field effect transistors	(Zhu et al. 2013)
		N, B-co-doped graphene (NBG)	Freshly distilled CCl ₄ (4.0 mL) + K (7.60 g, 1.1 eq. based on the halogens) + BBr ₃ (0.39 mL) were put into a stainless-steel autoclave under a N ₂ atmosphere. The reaction was run at 270°C for 30 min. The product was dispersed in an HCl solution for 1d with stirring to remove residual metals and potassium from the reactor	N = 2.66 at.%, B = 2.38 at.% / 201.5	B1s: B-C/B-N = 2 :1	Field-effect transistor	(Jung et al. 2014)

2.3.1 Oxygen-containing functional groups

Oxygen-containing functional groups can endow nanocarbon network with hydrophilic and cation exchange properties to facilitate doping with other heteroatoms. The oxidation methods include gas-phase oxidation and liquid phase-oxidation (Stein et al. 2009). The oxidants employed in the gas-phase oxidation encompass O_2 , O_3 , air or nitric oxides. Air oxidation is a weak method to mainly form weakly acidic groups (e.g., phenols). By contrast, liquid-phase oxidation is a more complex and robust method using oxidants (e.g., HNO_3 , H_2O_2 , K_2MnO_4 , H_2SO_4) to incorporate oxygen-containing functional groups into graphitic nanocarbon materials. HNO_3 can introduce carboxylic groups ($-COOH$), along with small amounts of N (in the form of nitro groups) which probably bond with C atoms at the edges of graphitic carbon network. By contrast, H_2O_2 mainly introduces the groups of phenols (Salame and Bandosz 2001). It is noteworthy that the carbon structure can be completely destroyed by HNO_3 at its boiling point (Gerber et al. 2011).

Oxygen-containing functionalities fall into acidic/neutral/basic types (**Figure 2.1**). The acidic oxygen-containing functional groups include $-COOH$ (decomposition temperature (Gonçalves et al. 2010): $200-450^\circ C$) and anhydrides ($450-650^\circ C$), lactols or lactones ($550-700^\circ C$), and phenols ($600-750^\circ C$), which can increase the work functions of nanocarbon materials up to 5.1 eV by interrupting π -conjugation system and giving rise to the surface dipole moments (Ago 1999). The neutral oxygen-containing functional groups are $-C=O$ ($700-950^\circ C$) and ethers. The basic oxygen-containing functional groups encompass quinone ($700-950^\circ C$), chromene and pyrone. Pyrone-like functionalities at the edge of graphitic layers present a wide range of dissociation constant (pK_a) values of 4-13, which depends on the relative position of its ketone and etheric rings.

The type and concentration of the surface groups determine the acidity/basicity of carbon materials. It is worth noting that the basicity of carbonaceous surface remains debatable. In general, the basicity of carbon surface stems from the basic oxygen-containing groups (e.g., chromene, pyrone and quinone), and non-heteroatomic Lewis basic sites which are distributed within π electron-rich areas of graphitic carbon network instead of at the edges (Fuente et al. 2003).

Figure 2.1. Schematic representation showing active catalytic sites in the graphitic carbon network relative to heteroatom incorporation

Among different types of oxygen-containing functional groups, the electron-rich C=O group terminated at the defective edges of graphitic carbon network is of paramount importance to the activation of persulfates for ROS generation in the graphene-based carbocatalysts/persulfates system. The activation of PMS/PDS can be realized through the scission of the O-O bond by the electrons transferred from the C=O group. The C=O group can act as Lewis basic sites, which is characterized by lone-pair electrons (**Section 2.5.2**).

It is noteworthy that the excessive oxygenated functionalities in carbocatalysts (e.g., GO) might be detrimental to the catalytic activity. GO with an extreme oxygen content (≥ 40 wt% O) has oxygen moieties such as the -COOH group, epoxides, ketones, and other oxygenated functionalities, which decreases the reductive degree of graphitic carbon network. The excessive oxygen-containing functional groups lead

to almost complete absence of the aromaticity and conjugated C=C double bonds. As a result, it adversely affects the charge transport ability of the graphitic carbon network, electron density of carbon atoms at the edging sites, and the C=O group with respect to a redox reaction. Meanwhile, the excessive oxygen moieties might occupy the defective sites and therefore encumber the oxidant activation via steric hindrance (Dreyer et al. 2010, Dreyer et al. 2014).

2.3.2 N-doping

N atom is the most ubiquitous dopant for tuning the catalytic activity of carbocatalysts. Doping nanocarbons with N atoms can promote their anion-exchanging activity and catalytic capability toward redox reaction. The electron donor/acceptor properties of N functionalities contribute to the acidity/basicity of carbon materials (Serp and Machado 2015). Point of zero charge (pH_{pzc}) of the pristine graphitic carbon is generally near or below 7, which is dominated by the weak acidic oxygen functionalities imparted from the exposure to ambient conditions (Maldonado et al. 2006). It has been reported that 4.0% N-doping can induce an alkaline pH_{pzc} value close to 9 owing to the prevalence of negatively charged N dopants (Serp and Machado 2015). Pyridinic N, pyrrolic N, graphitic N (or quaternary N) and nitric oxide comprise the four common N doping species in N-doped carbocatalyst (**Figure 2.1**).

Pyridinic N means the sp^2 hybridized N atom in a 6-membered ring bonded with two C atoms at the edges or defects of graphene, which can contribute one p-electron to the conjugated π -system. Pyridinic N can induce the presence of localized states below or above the Fermi level, and therefore generate either a p- or n-type doping, which depends on the N doping level (Serp and Machado 2015). Besides, pyridinic N might be conducive to an increase in the density of π states near the Fermi level and a decrease in the work function of graphitic nanocarbon materials. Thus, pyridinic N can effectively alter the valence band structure of graphitic nanocarbon materials (Luo et al. 2011). Furthermore, pyridinic N, which has lone-pair electrons and can act as a Lewis base, can react with a proton. Thus, pyridinic N exhibits a basic character.

The sp^2 hybridized pyrrolic N can contribute two p-electrons to the 5-

membered-ring aromatic system, which can be considered as a Lewis basic site and lead to a p-type doping (Cruz-Silva et al. 2009, Ewels and Glerup 2005, Hong and Jeong 2004). The sp^2 hybridized graphitic N atom replaces one C atom in the graphitic basal plane and neighbors three sp^2 C atoms. Graphitic N can contribute one electron to the conjugated π -system of graphitic carbon network, which leads to the delocalized electrons of N atom. Moreover, graphitic N can induce the sharp localized states above the Fermi level owing to the presence of additional electrons. Hence, graphitic N leads to n-type conduction, which enables N-doped nanocarbon materials to strongly react with electron acceptor molecules. However, graphitic N cannot contribute to the basicity of N-doped graphitic nanocarbon materials. Because removing an electron from graphitic N (e.g., N atom takes in H^+) may reduce the aromatic level of the conjugated carbon network, which is energetically infeasible.

Nitric oxide, also known as pyridinic N-oxide, is a carbon nitrogen covalent bond whereby N atom neighbors two C atoms and O atom. Nitric oxide presents an acid character with pKa below 3 (Balón et al. 1989). Besides, amine species with a X-ray photoelectron spectroscopy (XPS) binding energy of 399 eV are difficult to detect because the amine peak overlaps the adjacent peaks of pyridinic N and pyrrolic N (Kundu et al. 2010).

The type of N functionalities in NG depends on the synthesis temperature and the type of N sources. Temperature is a decisive factor for the formation of N functionalities due to the different thermal stabilities of N dopants (Bai et al. 2016). The low temperatures (< 800 K) mainly induce slightly acidic N groups (e.g., lactams, imides and amines), whereas the high temperatures can generate pyrrolic N, pyridinic N and graphitic N to enhance the surface polarity and basicity of graphitic carbon materials (**Figure 2.1**). Graphitic N is the most thermally stable, while pyrrolic N shows the lowest thermal stability (Li et al. 2009). Pyrrolic N and pyridinic N as the Lewis basic sites can improve the interaction between the nanocarbon surface and acid molecules via dipole-dipole, hydrogen bonding and covalent bonding, etc.

N precursors for doping graphene can be divided into gas phase (e.g., ammonia) and liquid phase in water or alcoholic solutions (e.g., polyaniline, diethyldithiocarbamate, ammonium nitrate (NH_4NO_3), melamine, urea) (**Table 2.3**). NG prepared with urea as a N precursor performs better to activate PMS than those

synthesized with melamine and NH_4NO_3 , which might be ascribed to the higher concentration of N dopants incorporated, the higher reducibility of graphitic lattice, and the less polymerization of urea achieved during synthesis (Chen et al. 2018a, Li et al. 2017a).

2.3.3 B-doping

B atom with a smaller size can be easily incorporated into the nanocarbon lattice, which can be substituted in both sp^2 and sp^3 configuration (**Figure 2.1**). B atoms substituted in the graphitic lattice facilitate the graphitization while constrain the oxidation of nanocarbons, which reinforces the sp^2 structure of graphitic carbon network (Serp and Machado 2015). B precursors for doping graphene include gas phase (e.g., BCl_3 , carborane ($\text{C}_2\text{B}_{10}\text{H}_{12}$) and trimethylboron), liquid phase (e.g., boron trifluoride diethyl etherate ($\text{BF}_3\text{Et}_2\text{O}$), boron tribromide and triethylborane) and solid phase (e.g., H_3BO_3 , B_2O_3 , NaBH_4 , NH_3BH_3 , B_4C , phenylboronic acid, 3-aminophenylboronic acid, boron powder and ammonium pentaborate octahydrate ($\text{H}_8\text{B}_{10}\text{N}_2\text{O}_{16}\cdot 8\text{H}_2\text{O}$)) (**Table 2.3**).

The most widely explored boron-doped graphene (BG) synthesis method involves thermal treatment of carbon precursors (e.g., graphite powder, GO) and B precursors (mainly H_3BO_3 , B_2O_3 , B_4C) (**Table 2.3**). In such case, B bonding configurations depend on the carbon sources and synthesis temperature. Substitutional B-doping can mainly occur when the pure graphite and the synthesis temperature of $> 2000^\circ\text{C}$ are adopted, whereas a more complex material with substitutional B (C_3B), boronic (CBO_2) and borinic (C_2BO) esters, and boronic acid (BO_3C) (**Figure 2.1**) can be produced when GO and lower temperatures ($900\text{--}1200^\circ\text{C}$) are employed (Agnoli and Favaro 2016).

N and B atoms are natural choices for the heteroatom doping of graphene, because 1) N ($0.71\text{ \AA}$) and B ($0.85\text{ \AA}$) atoms with the similar single-bond covalent atomic radii to C atom ($0.75\text{ \AA}$) (Pyykkö and Atsumi 2009) are the nearest neighbors of C atom in the periodic table. Thus, when replacing one C atom with N atom and another C atom with B atom, the total number of electrons in the hexagonal carbon network remains unchanged; and 2) the electron-rich N atoms and electron-deficient B atoms can induce n-type doping and p-type doping, respectively (Jana et al. 2013),

which leads to synergistic effects for the N, B-co-doped nanocarbon materials.

It has been reported that N and B co-doping can lead to the formation of a dipole moment whereby N dopants are conducive to the charge transport and B dopants promote the interaction between persulfates and carbon surface (Zheng et al. 2013). Moreover, the B-doping level and the relative position of the incorporated B dopants regarding the host N dopants are the decisive factors to affect the synergistic coupling effect. It has been reported that only a low B-doping level (0.1 wt% B_2O_3) can improve the catalytic activity of NG to activate PMS for phenol degradation (Sun et al. 2013a). Incorporating B and N atoms simultaneously into an adjacent position (B bonded with N in the same benzene ring) in the honeycomb lattice of graphene may induce a neutralization due to the complementary effect between n- and p-type dopants (Grundmann 2006, Zhao et al. 2013c). However, a B-C-N heterostructure can effectively activate the neighboring C atom and break the electroneutrality of sp^2 bonded graphitic nanocarbon system (Duan et al. 2015e).

2.3.4 S-doping

Compared with N and B atoms as natural choices, S atom is a relatively emerging dopant for doping graphene to tune its catalytic activities. S-doping can tailor the surface chemistry (e.g., electrochemical, adsorptive and catalytic properties) and fundamental physicochemical properties (e.g., semi-conductivity, magnetic behavior) of carbocatalysts simultaneously, which is because: 1) the introduction of S atoms (the electronegativity of $\chi_S \approx \chi_C \approx 2.5$) can decrease the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which enables electrons to be excited and transferred to oxidants more easily; 2) the S groups located at the edges can redistribute the spin and charge densities, which renders the neighboring C atoms higher spin and charge densities; and 3) S doping process can generate more active sites (Glenis et al. 1999, Kurita et al. 1992, Liang et al. 2012). Besides, S doping can enhance the sintering-resistance of the carbocatalysts (Serp and Machado 2015).

S precursors for doping graphene include benzyl disulfide and diphenyl disulfide (**Table 2.3**). The possible S bonding configurations encompass sulfonic, thiophenol, thioketone, sulfoxide, sulfide, disulfide, and thiolactone (**Figure 2.1**).

From XPS analysis, S2p can be deconvoluted into two adjacent peaks S2p_{1/2} and S2p_{3/2}. The bond of C-S-C corresponds to the two neighboring peaks at 165.2 eV and 164.0 eV. Another two neighboring peaks at 169.9 eV and 167.8 eV represent C-SO_x-C bond (x = 2,3,4) (Cheng et al. 2018, Huang et al. 2017). Zhang et al. (Zhang et al. 2018) employed the radical as a precursor to realize single-form sulfur-doped graphene (SG) (only containing C-SO_x-C bond albeit without C-S-C bond) and revealed that the C atoms beside -SO₂ species and -SO₂ species itself were the active sites for acetaminophen degradation.

It is noteworthy that the enhancement of catalytic activity for persulfates activation by S doping alone in graphene is limited. Further doping NG with S can improve the catalytic activity of carbocatalysts for persulfates activation. Duan et al. (Duan et al. 2015f) reported that only a low amount (0.69 at.%) of S can be incorporated into the graphene sheets, compared with N doping level (8.15 at.%) in nitrogen and sulfur-co-doped graphene (NSG), for which the fact that S atoms possess a larger single-bond covalent atom radius than C and N atoms (1.03 Å (S) > 0.75 Å (C) > 0.71 Å (N)) (Pyykkö and Atsumi 2009) might account. However, only heating in a reducing H₂ atmosphere at a high temperature (> 1000 K) can completely remove S from the carbon matrix due to the extreme stability of S bonding with carbon matrix (Serp and Machado 2015). The catalytic capability of S-doped carbon materials is closely related to the S doping level. Superabundant S atoms may lead to a break in the charge balance and disruption in the charge distribution in the covalent nanocarbon network, which suppresses the synergistic effect between N and S in NSG.

2.3.5 P-doping

Compared with N atom, P atom has the same number of valence electrons albeit with a larger atomic radius. Thus, P atom often exhibits similar chemical properties to N atom albeit with a higher electron-donating capability, which renders it an excellent dopant. P doping can improve the catalytic capability of carbocatalysts because 1) the introduction of P atoms can enhance the charge delocalization of C atoms and therefore the electron-donating properties of carbocatalysts (Choi et al. 2012); 2) P incorporation energetically favorably impacts the band gap of graphene

more than S atoms (Denis 2013); 3) P doping process creates more edges acting as active sites for catalysis; and 4) P doping introduces the acidic surface groups and endows the carbocatalyst with cation exchange properties to improve the oxidation stability (Serp and Machado 2015). Triphenylphosphine and ammonium phosphate monobasic ($\text{NH}_4\text{H}_2\text{PO}_4$) (Duan et al. 2015e, Yin et al. 2017) have been reported to be used as P sources for doping or co-doping graphene via thermal treatment (**Table 2.3**). P species include C-O- PO_3 and $(\text{C-O})_3\text{PO}$ (134.1 eV) (P is not directly bonded to C), $\text{C}_2\text{-PO}_2$ (132.8 eV) or CPO_3 (133.5 eV), C_3PO (132.3 eV) (**Figure 2.1**).

2.3.6 F-doping

F as the most electronegative element ($\chi_{\text{F}} = 3.98 > \chi_{\text{O}} = 3.44 > \chi_{\text{N}} = 3.04$) possesses the strong electron-withdrawing ability, which can induce high positive charge density on the adjacent C atoms to produce active sites. Wang et al. (Wang et al. 2012d) explored a hydrothermal method whereby F atoms can be incorporated into the basal plane of graphene. The performance of F-doped carbocatalysts for the activation of persulfates needs further investigation (**Table 2.3**).

2.4 Characterization techniques for nanocarbons

The surface morphology of carbocatalysts, doping level and specific bonding configurations of dopants (**Figure 2.1**) collectively impact the application performance of nanocarbon materials doped with heteroatoms. Although various characterization techniques can be exploited to accurately analyze the carbocatalysts (**Table 2.4**), the following subsections focus on the characterization techniques intended for the microcosmic properties of carbocatalysts, such as the bonding configuration of dopant atoms, defective level, electronic structure of carbocatalysts, and distribution and charge density of dopant atoms.

2.4.1 X-ray photoelectron spectroscopy

XPS is a non-destructive tool to qualitatively and quantitatively investigate the chemical states and composition of elements present on the thin surface of the catalyst (up to 5 nm). The element type can be determined by the specific binding energy. The

specific bonding configurations of each element can be acquired by the deconvolution of the high-resolution XPS spectrum of each element. However, the peak position of each bonding configuration can vary widely according to different studies, which might be due to their various environments of dopants (Wang et al. 2012b).

Table 2.4. Characterization techniques for nanocarbons

Characterization techniques	Function
Scanning electron microscopy	<ul style="list-style-type: none">• Secondary electron imaging for investigation of the morphology and surface texture.• Backscattered electron imaging for high-resolution compositional mapping.
Transmission electron microscopy	<ul style="list-style-type: none">• Electron beam transmission for investigation of the structure, defects and electronic properties.• High resolution TEM for direct imaging of the catalyst at the atomic scale.• Selected area electron diffraction analysis for identification of crystal structure, structural interfaces and defects.
Scanning tunneling microscopy	<ul style="list-style-type: none">• An imaging technique on the surface of the catalyst at the atomic level.
Atomic force microscopy	<ul style="list-style-type: none">• High resolution techniques based on forced measurement for imaging and surface manipulation.
Zeta potentiometry	<ul style="list-style-type: none">• Determination of the pH_{pzc} of the catalyst.
Porosimetry	<ul style="list-style-type: none">• Investigation of the textural characteristics of the catalysts such as SSA, average pore radius, pore size distribution, and total pore volume.
CHNS elemental analysis	<ul style="list-style-type: none">• Determination of the C, H, N and S composition in the catalyst.
X-ray crystallography	<ul style="list-style-type: none">• X-ray diffraction technique to study the crystal structure/phase, quantify composition and provide information on the physical properties of materials.
Temperature programmed techniques	<ul style="list-style-type: none">• Various techniques such as temperature programmed desorption (with NH_3), temperature programmed reduction (with H_2), isothermal microcalorimetry, and temperature programmed oxidation (with air/O_2) can be used to investigate the physical and chemical phenomena which include phase transition, thermal stability, purity of carbon catalyst.

Electrochemical techniques	<ul style="list-style-type: none"> Investigation of the electrochemical properties such as reducibility and conductivity of carbon materials which can be linked to doping intensity, surface defects, and electron transfer rate. Some examples of electrochemical techniques include cyclic voltammetry and electrochemical impedance techniques.
Particle size analysis	<ul style="list-style-type: none"> Determination of particle size distribution (size range) and average particle size of the catalyst.
Raman spectroscopy	<ul style="list-style-type: none"> Observation of the low-frequency, vibrational and rotational modes of the catalyst under laser irradiation. Various details such as degree of defects and disorder of carbon materials can be quantified.
Energy dispersive X-ray spectroscopy (EDX)	<ul style="list-style-type: none"> Semi-quantitative method for elemental mapping and determination of elemental composition.
Infrared spectroscopy	<ul style="list-style-type: none"> Infrared spectrum can be used to investigate surface functional groups of carbon materials.
UV-Vis spectroscopy	<ul style="list-style-type: none"> Investigation of the UV-Vis absorption and electronic transitions of carbon materials.
X-ray photoelectron spectroscopy (XPS)	<ul style="list-style-type: none"> Investigation of the chemical states and composition of elements present on the thin surface of the catalyst (up to 5 nm).
Electron energy loss spectroscopy (EELS)	<ul style="list-style-type: none"> Advanced technique for the identification of elements and imaging of chemical states of single atoms.
Ion-scattering spectroscopy	<ul style="list-style-type: none"> Characterization of the surface of the catalyst through ion scattering. The information provided can be used to determine the geometric arrangement of atoms and their masses.
Auger electron spectroscopy	<ul style="list-style-type: none"> Application of Auger effect to determine the surface elemental composition of the catalyst.
Photoluminescence spectroscopy	<ul style="list-style-type: none"> Investigation of the optical property and electronic structure (through photoexcitation) of carbon materials.

Figure 2.2(a)-(c) show the XPS analysis for NBG. In the XPS survey spectra, C1s, O1s, N1s and B1s are represented by the peaks appearing at around 284, 531, 400, 189 eV. N1s spectrum can be further deconvoluted into three common N bonding configurations: pyridinic N (397.95-399 eV), pyrrolic N (398.76-400.3 eV), and graphitic N (400.9-401.7 eV). B1s spectrum can be further deconvoluted into three B bonding features: BC₃ (189-190 eV), B-C-O (BC₂O: 190.6-191.2 eV, BCO₂: 191.2-192 eV) and B-O (192-193 eV) (Tai et al. 2014).

Figure 2.2. (a) XPS survey spectra of NG and NBG; (b) High-resolution N1s XPS spectrum of NBG; (c) High-resolution B1s XPS spectrum of NBG (Tai et al. 2014).

2.4.2 Raman spectroscopy

Raman is a useful tool to probe the structure of the doped carbocatalysts. Two pivotal features in the Raman spectrum of the doped carbocatalysts are D band (1320-

1350 cm^{-1}) and G band (1570-1585 cm^{-1}) (Wang et al. 2012b). The D band ($\sim 1350 \text{ cm}^{-1}$) reflects the defective level of graphene platelets caused by zigzag/armchair edges, vacancies, functional groups and heteroatom doping. Vacancies are easier to adsorb PMS than edging sites but have a lower electron-transfer capability from graphene to PMS for PMS activation. Zigzag/armchair edges can activate PMS to produce $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$ via peroxide O-O bond cleavage (Duan et al. 2016c). The G band ($\sim 1580 \text{ cm}^{-1}$) is associated with E_{2g} mode vibration of the intact honeycomb-like sp^2 hybridized carbon network (Wang et al. 2013c). The ratio of I_D/I_G reveals the defective degree of carbon materials.

Generally, the introduction of heteroatoms, such as N, B and S, into the graphitic carbon network can increase the I_D/I_G ratio due to the different bond lengths between C-C and C-N/C-B/C-S/B-O, which leads to an increment in the asymmetric level of graphitic carbon network (Duan et al. 2015f, Zheng et al. 2013). As shown in **Figure 2.3**, the I_D/I_G ratio increases from 1.11 of GO to 1.16 of NG. Further co-doping NG with B can enhance the I_D/I_G ratio to 1.24. Moreover, the downshift of G band has been reported after doping graphene with N, which might be attributed to the electron-donating ability of N atoms (Lin et al. 2012b).

Figure 2.3. Raman spectra of GO, NG and NBG (Tai et al. 2014).

2.4.3 Electron microscopy

The combination of the aberration-corrected scanning transmission electron

microscopy (STEM) and electron energy loss spectroscopy (EELS) is a powerful method to identify the individual dopant atom and explore the local bonding region, which can reveal the change in the electronic structure of carbocatalysts after heteroatom doping. STEM works via the contrast variation in the medium-angle annular dark-field (MAADF) images. The variation of intensity is proportional to the atomic number, which can be used to identify the individual dopant atom. As shown in **Figure 2.4(a)**, the statistically calculated intensity ratio of 1.3 proves the bright atom is the N dopant (Nicholls et al. 2013).

Recording EELS spectrum simultaneously can give rise to the supplemental bonding information. **Figure 2.4(b)** demonstrates the typical EELS edge spectrum of NG (Liu and Antonietti 2013). π^* peak and σ^* band of the C K-edge suggests the graphitic carbon network of NG with high crystallinity (Cho et al. 2011, Guan et al. 2011). The π - π^* transition peak at 401 eV in the N K-edge implies the incorporation of N atom into sp^2 C hexagonal rings (Liu and Antonietti 2013). Notably, EELS edges and fine structures of some dopant atoms are difficult to detect (e.g., N K-edge with small cross section). Instead, the K-edge of C atoms surrounding the abovementioned individual dopant atom can be employed to characterize the electronic structure of the doped carbocatalysts due to the measurable changes in the C K-edge fine structure. As shown in **Figure 2.4(c)**, the subtle extra feature appearing at around 290 eV in the EELS spectrum of NG region surrounding the N atom outlined by the red box in Figure 2.4(a) suggests the existence of C-N bond in NG.

Figure 2.4. (a) MAADF image of NG and (b) EELS spectrum of NG (Liu and Antonietti 2013). (c) C K-edge of NG region (outlined by the red box in (a)) surrounding the N atom and C K-edge of pristine graphene (Nicholls et al. 2013).

Besides, scanning electron microscope (SEM) can be used to probe the morphology of carbocatalysts. High-resolution transmission electron microscope (HRTEM) can provide the information on the layer numbers of graphitic sheets based on the edge images. Energy dispersive X-ray spectroscopy (EDX) can provide the elemental mapping and determine the elemental composition. Selective area electron diffraction (SAED) can be used to determine the crystal structural of carbocatalysts via diffraction pattern. A well-ordered crystalline structure can be reflected by the hexagonal diffraction spots (Jin et al. 2011), whereas ring-like diffraction spots imply the distorted structure caused by doping (Qu et al. 2010).

2.4.4 Scanning probe microscopy

Scanning tunneling microscopy (STM) is an effective tool to provide information about 1) the topography with atomic resolution and the distribution of dopant atoms (**Figure 2.5(a)**) (Tison et al. 2015); 2) the bonding configurations of dopant atoms (**Figure 2.5(b)-(g)**); and 3) the charge-carrier density at the Fermi level and the Dirac point of dopant species based on the curves of dI/dV (derivative of current versus the voltage). Atomic force microscope (AFM) can be used to probe the layer numbers of graphitic sheets based on the interlayer distance.

Figure 2.5. (a) STM image of N species in NG; (b) 1-2 N bonding configuration in (a); (c) 1-3 N bonding configuration in (a); (d) 1-4 N bonding configuration in (a); (e) 1-8 N bonding configuration in (a); (f) P in (a) referring to pyridinic N bonding configuration; (g) simulation of the substitutional N atoms (Tison et al. 2015).

2.5 Persulfates-activating activity of carbocatalysts

2.5.1 Adsorption of organic substrate/persulfates by carbocatalysts

A synergy between adsorption and catalysis has been demonstrated. The enhanced adsorption can facilitate the enrichment of organic substrates onto the carbocatalyst surface, increasing their proximity to active sites (especially conducive to the formation of charge-transfer complex in the surface-dominated non-radical pathway (**Section 2.5.2.1**)) or the contact with the short-lived free radicals to accelerate organic substrates degradation. Conversely, the fast degradation of the adsorbed organic substrates can release more sites on carbocatalysts for re-adsorbing residual organic substrates in the solution (Chen and Carroll 2016, Wang et al. 2015). It has been reported that up to 40% of SMX (Chen and Carroll 2016) or 50% of bisphenol A (BPA) (Wang et al. 2015) can be removed via adsorption by NG, which is conducive to the fast degradation of organic substrates in the carbocatalysts/persulfates systems. Thus, carbocatalysts with synergistic adsorptive and catalytic functionality have drawn attention for persulfates activation and organic substrates degradation.

Generally, the adsorption performance can be influenced by the properties of carbocatalysts, organic substrates, and persulfates along with the reaction conditions

(e.g., pH and ionic strength of the aqueous solution). Physisorption functions via π - π interaction (Mattson et al. 1969) and electrostatic attraction (Coughlin and Ezra 1968), which is related to the physiochemical properties of carbocatalysts (e.g., porosity, SSA). While chemisorption occurs via specific interactions (e.g., hydrogen bonding, acid/base reaction, complexation) and formation of chemical bonding, which is associated with the functional groups in the carbonaceous materials (Serp and Machado 2015). The properties of organic substrates (polarity, stereochemistry, etc.) also affect adsorption. Organic substrates with one or more benzene rings facilitate the π - π interaction (Wang et al. 2015).

Carbocatalysts with different structural dimensions exhibit distinct capabilities in electron conductivity, mechanical strength and porosity (Yu et al. 2015, Zhi et al. 2013), which can influence adsorptive ability toward organic substrates. Generally, the adsorptive performance of 2D and 3D carbocatalysts are better than that of 1D and 0D carbocatalysts. **Table 2.5** presents the adsorption performances in the graphene-based carbocatalysts/persulfates systems. rGO (60%) and SWCNT (40%) exhibit a better adsorption ability to remove phenol than other nanocarbon materials (< 10%) (graphite, graphite oxide, GO, C₆₀, multiple-walled carbon nanotubes, graphitic nanodiamond (GND)), which might be ascribed to their relatively high SSA and favorable surface functionalities for adsorption process (Lee et al. 2016). It has been reported that N functional groups can improve adsorption performance due to 1) mitigating aggregation of N-doped carbonaceous materials; 2) serving as Lewis-base sites beneficial to binding acidic organic molecules; and 3) enhancing the π - π interaction between sp² hybridized covalent π system of graphene and aromatics (Pei et al. 2013, Wang et al. 2014b, Xu et al. 2012b). Notably, the large SSA and porosity albeit with a low density of functional groups cannot guarantee a good adsorption performance (Sun et al. 2014).

Persulfates show a preference to be adsorbed on N-doped graphitic domain (e.g., graphitic N) via outer-sphere interaction (electrostatic bonding). As such, the O-O bond in persulfates can be activated to form surface activated complex (**Section 2.5.2.1.1**),

followed by readily oxidizing the coexisting adsorbed organic substrates and therefore consumption of persulfates via non-radical pathway in the carbocatalysts/persulfates system (Zhang et al. 2014c). Besides, addition of persulfates can affect the adsorption behavior of organic substrates on carbocatalysts due to competition for the limited adsorption sites on carbocatalysts (Cheng et al. 2017).

In addition, the adsorption extent of organic substrates by a carbocatalyst could be collectively influenced by pH, pK_a of organic substrates, and pH_{pzc} of the carbocatalyst. The solution pH impacts both the existing species of organic substrates and the surface charge of carbocatalysts ($pH < pH_{pzc}$: positively charged, $pH > pH_{pzc}$: negatively charged), therefore influencing the electrostatic interaction and chemisorption between organic substrates and carbocatalysts (Chang et al. 2014, Rocha et al. 2015, Wang et al. 2018a, Wang et al. 2015, Wang et al. 2016b).

Generally, carbocatalysts are inferior to most of the metal catalysts in terms of the long-term stability due to the reconstruction of carbon structure. In addition, the adsorbed organic substrates and their degradative intermediates could partially account for the deactivation of nanocarbons (e.g., rGO, NG, NBG, NSG) (Lee et al. 2016). It has been reported that the catalytic performance of NG-700 diminished from 100% phenol removal in the first run (45 min) to 31% in the third run (180 min) in the NG-700/PMS/phenol system (Duan et al. 2015b). Besides, the catalytic performance of rGO-900 decreased from 100% phenol removal in the first run (30 min) to 57.7% in the third run (180 min) in the rGO-900/PDS/phenol system.

Post treatments, such as UV-C irradiation (Lee et al. 2016), thermal annealing (Duan et al. 2015e, Duan et al. 2016b, Wang et al. 2018a, Wang et al. 2016b, Yin et al. 2017) or hydrogenation at a mild condition (Duan et al. 2015b), can be performed to remove the adsorbed organic substrates and intermediates as well as recover the reductive degree of carbocatalysts from oxidation. Sun et al. (Sun et al. 2013a) reported that ultrasonication performs better to recover the catalysis capability of NG than washing and thermal annealing.

Table 2.5. Radical pathway and non-radical pathway in the graphene-based carbocatalysts/persulfates system

Reaction system and relative mechanism	Synthesis method	Catalyst properties	Application conditions	Active sites/reactive species	Performance	Ref
Radical pathway						
rGO/PMS/phenol	Hydrothermal reduction of GO with ammonia solution (37%) at 453 K for 18 h	$I_D/I_G = 1.48$	$[\text{phenol}] = 2.215 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{cat}] = 0.2 \text{ g L}^{-1}$, $[\text{Oxone}] = 3.188 \times 10^{-3} \text{ mol L}^{-1}$, $T = 298 \text{ K}$	Zigzag edges, C=O at the edges / $\text{SO}_4^{\cdot-}$ $\text{C}=\text{C}=\text{O} + \text{HSO}_5^- \rightarrow \text{SO}_4^{\cdot-} + \text{C}=\text{C}-\text{O}^+ + \text{OH}^-$ $\text{C}=\text{C}-\text{O}^+ + \text{HSO}_5^- \rightarrow \text{SO}_5^{\cdot-} + \text{C}=\text{C}=\text{O} + \text{H}^+$	~ 10% adsorption, 70.4% phenol removal in 3 h	(Sun et al. 2012)
rGO-900/PMS/phenol	Thermal annealing of GO under inert atmosphere at 900°C for 1 h	$I_D/I_G = 1.69$ Oxygen content = 2.95 at.%	$[\text{phenol}] = 20 \text{ mg L}^{-1}$, $[\text{cat}] = 0.2 \text{ g L}^{-1}$, $[\text{PMS}] = 6.5 \text{ mM}$, $T = 298 \text{ K}$	Vacancies, edges, C=O at the edges / $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$	~ 10% adsorption, 100% phenol removal in 150 min with a decomposition rate of 0.027 min^{-1}	(Duan et al. 2016c)
rGO900/PDS/phenol	Thermal annealing of GO under N_2 atmosphere at 900°C for 1 h	$I_D/I_G = 1.70$ Oxygen content = 6.0 at.%,	$[\text{PDS}] = 6.5 \text{ mM}$, $[\text{phenol}] = 20 \text{ mg L}^{-1}$, $[\text{cat}] = 0.2 \text{ g L}^{-1}$, $T = 298 \text{ K}$	1) a sp^2 hybridized graphitic lattice and a number of vacancies, zigzag edges and functionalities (especially proper amount of C=O); 2) the activated PDS oxidizes water to produce $\text{HO}^{\cdot}$; 3) carbon matrix also acts as excellent electron bridge to facilitate electron transfer/ large amount of $\text{HO}^{\cdot}$ and a small portion of $\text{SO}_4^{\cdot-}$	21.3% phenol adsorption and 100% phenol removal in 30 min	(Duan et al. 2015g)
NSG/PMS/phenol	1.0 g GO + 1.0 g NH_4NO_3 + 0.3 g diphenyl disulfide, 623 K, 1 h	$I_D/I_G = 1.30$ N = 8.15 at.%, S = 0.69 at.%, O = 11.11 at.%	$[\text{PMS}] = 6.5 \text{ mM}$, $[\text{phenol}] = 20 \text{ mg L}^{-1}$, $[\text{cat}] = 0.2 \text{ g L}^{-1}$, $T = 298 \text{ K}$,	1) the positively charged C atoms might be the active sites to adsorb PMS and cleave its O-O bond for activation; 2) synergistic effect between S and N dopants can efficaciously interrupt the chemical inertness of graphitic lattice,	~ 15% adsorption, 100% phenol removal in 90 min. $\text{GO} < \text{rGO} < \text{SG} < \text{NG} < \text{NSG}$	(Duan et al. 2015f)

which is conducive to transferring electron from the activated sp^2 carbon lattice to PMS to generate radicals/ $SO_4^{\cdot-}$ and $HO^{\cdot}$

Surface activated complex (non-radical pathway)

rGO-900 (defective graphene)/PMS/phenol

Thermal annealing of GO under N_2 atmosphere at $900^\circ C$ for 1 h with a heating rate of $5^\circ C\ min^{-1}$

$I_D/I_G = 1.70$
Oxygen content = 6.0 at. %

[PMS] = 6.5 mM,
[phenol] = 20 $mg\ L^{-1}$,
[cat] = 0.1 $g\ L^{-1}$, T = 298 K

Defects, especially zigzag edges in a bordered graphene sheet /surface activated complex directly attacks organics via electron abstraction

4.9% adsorption, 100% phenol removal in 10 min

(Duan et al. 2016a)

NG/PMS/SAM

Thermal annealing of GO with urea at $600^\circ C$ for 1 h in N_2 atmosphere

$I_D/I_G = 1.12$
O/C = 8 at. %,
N/C = 18.3 at. %

[SAM] = 10 $mg\ L^{-1}$,
[cat] = 0.2 $g\ L^{-1}$,
[PMS] = 0.5 mM, pH = 7

Non-radical pathway: the positively charged C atoms adjacent to N atoms lead to formation of surface activated PMS via out-sphere interaction/surface activated complex

~10% SAM adsorption and 100% SAM removal in 50 min

(Chen et al. 2018a)

Radical pathway: 1) defects (zigzag edges, vacancies); 2) Lewis basic sites (C=O, pyridinic N and pyrrolic N); 3) sp^2 carbon network activated by lone-pair electrons of N dopants via conjugation/ $SO_4^{\cdot-}$, $HO^{\cdot}$

1O_2 (non-radical pathway)

Metal organic framework derived NG/PMS/phenol

Thermal treatment of MIL-100 (Fe) and dicyandiamide under N_2 atmosphere at $800^\circ C$ for 1 h, washed with H_2SO_4 (0.5 M) at $80^\circ C$ for

Hollow onion-like graphitic carbon
 $I_D/I_G = 0.9$
Oxygen content

[PMS] = 3.25 mM,
[phenol] = 50 $mg\ L^{-1}$,
[cat] = 0.1 $g\ L^{-1}$, T = 298 K

C=O at the edging sites of graphene network (similar to a redox cycle induced by p-benzoquinone (p-BQ))/ 1O_2 (dominant species), trace amount of $SO_4^{\cdot-}$ and $HO^{\cdot}$

~ 10% phenol adsorption, 100% phenol removal in 30 min

(Liang et al. 2017)

	24 h to exhaust the unsecured iron species	= 2.99 at.%, Nitrogen content = 2.31 at.%				
<u>Surface bound radicals (non-radical pathway)</u>						
NG/PDS/SMX						
	Commercial	Oxygen content = 7-7.5%, Nitrogen content = 3-5%	[SMX] = 5 mg L ⁻¹ , [cat] = 50 mg L ⁻¹ , [PDS] = 1 mM, pH = 6	(1) electron-rich N functional groups, such as pyridinic-N, quaternary-N; (2) N functional groups are active sites for both adsorption and catalysis; (3) SMX enrichment on NG surface, increasing proximity to PDS activation sites and therefore SMX overall removal/non-radical (surface-bound radical)	40% SMX adsorption and 100% SMX removal in 120 min	(Chen and Carroll 2016)
Aminated graphene (NH₂-G)/PDS/SMX						
	Commercial	Oxygen content = 23%, Nitrogen content = 7%	[cat] = 50 mg L ⁻¹ , [PDS] = 1 mM, [SMX] = 5 mg L ⁻¹ , pH = 6	Amine groups mainly responsible for catalysis/ non-radical (surface-bound radical)	~ 10-20% SMX adsorption and 40% SMX removal in 180 min (NG/PDS/SMX > NH ₂ -G/PDS/SMX)	(Chen and Carroll 2016)
NG/PDS/BPA						
	Hydrothermal treatment of GO and ammonia at 180°C for 24 h	I _D /I _G = 1.08 Oxygen content = 12.9 at.%, Nitrogen content = 7.77 at.%	[BPA] = 0.385 mg L ⁻¹ , [cat] = 120 mg L ⁻¹ , [PDS] = 0.6 mM, pH = 6.6, T = 298 K	N dopants function as active sites for both the adsorption of bisphenols and the activation of PDS, leading to synergistic interaction between adsorption and catalysis/surface-bound SO ₄ ^{•-}	50% BPA adsorption in 10 min and 100% BPA removal in 7 min	(Wang et al. 2015)

2.5.2 Activation of persulfates

2.5.2.1 Free radical and non-radical pathway

Basically, the catalytic oxidation mechanisms involved in the graphene-based carbocatalysts/persulfates systems encompass free radical pathway and non-radical pathway, which is schematically illustrated in **Figure 2.6**. The main differences between radical pathway and non-radical pathway are presented in **Table 2.6**.

2.5.2.1.1 Difference between mechanisms of free radical pathway and non-radical pathway

Free radicals are usually believed as the primary ROS (e.g., $\text{SO}_4^{\bullet-}$, $\text{HO}^{\bullet}$ and $\text{O}_2^{\bullet-}$) in AOPs. $\text{HO}^{\bullet}$ can oxidize organics through three mechanisms: 1) hydrogen abstraction from saturated compounds (e.g., alkanes); 2) electron extraction; and 3) electrophilic addition and substitution reaction with unsaturated and aromatic compounds. Hydrogen abstraction proceeds at a lower rate than electrophilic substitution. The reaction between $\text{HO}^{\bullet}$ and highly reactive organic substrates is limited by the diffusion rate of $\text{HO}^{\bullet}$ in water ($\sim 7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) due to the short half-life of $\text{HO}^{\bullet}$ ($< 1 \text{ } \mu\text{s}$). $\text{HO}^{\bullet}$ as a relatively nonselective ROS can react with most organics at the diffusion-controlled rate. By contrast, $\text{SO}_4^{\bullet-}$ exhibits a stronger tendency toward electron abstraction than $\text{HO}^{\bullet}$, favoring one-electron oxidation (Yang et al. 2014b). Aromatic compounds with ring activation groups (e.g., anisole, p-hydroxybenzoic acid) demonstrate reactivity with $\text{SO}_4^{\bullet-}$ at the near-diffusion-controlled rate, whereas aromatic compounds with ring deactivating groups (e.g., nitrobenzene (NB) and p-nitrobenzoic) can hardly react with $\text{SO}_4^{\bullet-}$ (Watts and Teel 2006).

Radical pathway is based on electron transfer along with the resultant activation and dissociation of the O-O bond in persulfates to produce $\text{SO}_4^{\bullet-}$ and $\text{HO}^{\bullet}$ for the oxidation of organic substrates. The transferred electrons can be categorized into: 1) delocalized π electrons from the defects of carbocatalysts (e.g., vacancies and zigzag/armchair edges) (Duan et al. 2016c, Oh et al. 2016); 2) lone-pair electrons in Lewis basic sites, such as O atom in the C=O group, pyrrolic N and pyridinic N

(Frank et al. 2009); and 3) the free-flowing π -electrons abundant in the sp^2 hybridized carbon lattice and their activation by the lone-pair electrons from N doping species via conjugation (Sun et al. 2013a).

Non-radical pathway has drawn increasing attention in recent years. Compared with free radical pathway, non-radical pathway with a relatively mild oxidative potential in the carbocatalysts/persulfates system is a surface-confined reaction, which occurs via electron transfer (electron abstraction or electron shuttle) and becomes more selective to electron-rich substances (e.g., dyes, phenol, chlorophenols and big molecule antibiotics) for an electrophilic attack (Duan et al. 2018b). The non-radical pathway can be induced through the following mechanisms (as schematically illustrated in **Figure 2.6**):

(1) surface-active species including

i) surface activated complex (Lee et al. 2015b). Specifically, the higher electronegativity of N atoms than that of C atoms ($\chi_N = 3.04$ and $\chi_C = 2.55$) may result in the electron transfer and the formation of active sites which comprise N atoms with negative charges and the neighboring C atoms with positive charges. In such case, PMS can be adsorbed and activated with a minor change in the electron structure of PMS molecule (without cleavage into radicals) (Chen et al. 2018a, Choi et al. 2012).

ii) surface-bound $SO_4^{\cdot-}$ (Duan et al. 2016b, Wang et al. 2015). The surface-active species can directly attack organics via electron abstraction. Notably, radical pathway in this study refers to the free radicals, such as $SO_4^{\cdot-}$ and $HO^{\cdot}$, which can exist in the bulk solution after generation. As for the surface-bound $SO_4^{\cdot-}$, it is another metastable state of the activated PDS, which is more related to the surface-confined reaction and shows resistance to the commonly used free radical scavengers. Thus, it is more reasonable to categorize surface-bound $SO_4^{\cdot-}$ into non-radical pathway. This classification is also adopted by other researchers (Duan et al. 2018b, Duan et al. 2018c).

(2) sp^2 hybridized carbon network as electron shuttle. Specifically, carbocatalysts work as an electron shuttle via a surface electron-transfer mechanism whereby electrons transport from the adsorbed organic substrates to the oxidants through carbocatalyst surface (Yun et al. 2017);

(3) generation of 1O_2 (Cheng et al. 2017, Liang et al. 2017).

Table 2.6. Main differences between free radical pathway and non-radical pathway

	Free radical pathway	Non-radical pathway
Selectivity	HO [•] : low-selective with a low half-life of 20 ns SO ₄ ^{•-} : unsaturated/aromatic structures with a high half-life of 30-40 μs (Zhou et al. 2015a)	Electron-rich organics with electron-donating groups on the aromatic ring (e.g., dyes, phenol, chlorophenols and big-molecule antibiotics, such as carbamazepine, propranolol, SMX and acetaminophen)
Oxidative potential	HO [•] : 1.8-2.7 V (Buxton et al. 1988) SO ₄ ^{•-} : 2.5-3.1 V (Neta et al. 1988)	Mild redox potential compared with free radicals (Duan et al. 2018b)
Active species	Free radicals (e.g., SO ₄ ^{•-} , HO [•] and HO ₂ [•] /O ₂ ^{•-}) as electron acceptor to oxidize organics (electron donor). SO ₄ ^{•-} exhibits a stronger tendency toward electron abstraction than HO [•] (Yang et al. 2014b)	Surface activated complex (Lee et al. 2015b) Surface-bound SO ₄ ^{•-} (Duan et al. 2016b, Wang et al. 2015) Electron shuttle (Yun et al. 2017) ¹ O ₂ (Cheng et al. 2017, Liang et al. 2017)
Deactivation tolerance of system	Inorganic ions (HCO ₃ ⁻ , NO ₃ ⁻ /NO ₂ ⁻ , halides, etc.) and natural organic matters (NOMs) in the complex water matrix may serve as radical scavengers to free radicals	More resistant to the scavengers in the complex real water
pH range	HO [•] : pH < 3 for convention Fenton process, SO ₄ ^{•-} : in a wide pH range (PMS-based oxidation system: neutral and basic conditions)	Acidic/neutral/basic
Treatment efficiency	Activators continue to fruitlessly decompose persulfates even after complete removal of organic substrates	The concentration of residual organics determines the kinetic rate of persulfates reduction (electron shuttle)

¹O₂ is a non-radical ROS due to its properties, such as milder oxidative potential (lower than that of SO₄^{•-} and HO[•]), substrate-specificity (e.g., pharmaceuticals and EDCs with electrophilic nature) and resistance to the commonly used free radical scavengers, which are similar to those of surface activated persulfates and surface-bound SO₄^{•-} (reactive intermediates in the non-radical processes). ¹O₂ generation has been reported in the NG/PMS systems (**Table 2.5**). Apart from the activation of persulfates, ¹O₂ can also be produced by PMS self-decomposition with a rate constant *k* of about 0.2 M⁻¹ s⁻¹ as shown in Eq 2.5.2.1.1.1 (Ball and Edwards 1956, Evans and Upton 1985).

In such case, alkaline condition favors $^1\text{O}_2$ formation due to an increase in the SO_5^{2-} concentration.

Notably, the determination of the reaction mechanism regarding $^1\text{O}_2$ in the carbocatalyst/persulfates system may be interfered with by $\text{O}_2^{\bullet-}$. Because recombination of $\text{O}_2^{\bullet-}$ can produce $^1\text{O}_2$. $\text{O}_2^{\bullet-}$ can be produced by the hydrolysis of PDS alone as shown in Eqs 2.5.2.1.1.2 - 2.5.2.1.1.3 (Furman et al. 2010, Tan et al. 2013).

By contrast, upon the introduction of carbocatalyst, which acts as a carbocatalyst facilitating PDS hydrolysis, the generation of $\text{O}_2^{\bullet-}$ follows a different pathway in the carbocatalyst/persulfates system, as shown in Eq 2.5.2.1.1.4. The subsequent recombination of $\text{O}_2^{\bullet-}$ to form $^1\text{O}_2$ is illustrated by Eqs 2.5.2.1.1.5 - 2.5.2.1.1.7. Thus, the consumption of 3 mol PDS can produce 1 mol $^1\text{O}_2$, which is not directly generated via PDS activation by carbocatalyst (Cheng et al. 2017, Pignatello et al. 2006, Zhou et al. 2013).

The involvement of $\text{O}_2^{\bullet-}$ in the $^1\text{O}_2$ production causes difficulties in identification and differentiating whether $\text{O}_2^{\bullet-}$ just serves as an intermediate for $^1\text{O}_2$ generation or a dominant ROS in the persulfates/carbocatalysts system.

Non-radical pathway can readily oxidize organic substrates at the initial stage due to its milder oxidative potential, while free radicals are more capable of mineralizing organic substrates into CO_2 and H_2O , which leads to the fact that the mineralization of organic substrates entails both radical and non-radical pathways collectively. Besides, because of the higher selectivity and moderate oxidative potential of non-radical ROS, they are more resistant to the influence of diverse inorganic ions (HCO_3^- , $\text{NO}_3^-/\text{NO}_2^-$, halides, etc.) and NOMs omnipresent in the real water, which are detrimental to free radicals due to the scavenging effects. By contrast, the $\text{C}=\text{O}$ group (Zhou et al. 2015b) and vicinal hydroxyl groups (Bokare and Choi 2015) in NOMs favor the formation of $^1\text{O}_2$, making the non-radical pathway

more suitable for reaction in the real water matrix (e.g., surface water, ground water and seawater).

The statistical approaches can be used to visualize and assess the similarity of the degradation mechanisms of organic substrates in different experimental systems. Nonmetric multidimensional scaling (NMDS) functions via investigating the inter-sample distance regarding intermediate distribution or substrate-specificity in the NMDS plot as an indicator of similarity between different systems. Two-way clustering analysis is another statistic method using dendrogram with a heat map to visualize the difference in the degradative mechanism (Yun et al. 2017).

2.5.2.1.2 Factors influencing reaction pathway

Nature of carbocatalyst

The nature of carbocatalysts, persulfates and organic substrates simultaneously determine the reaction pathway in the carbon-catalyzed AOPs system. Carbocatalysts with a high reactivity toward redox reaction readily trigger radical formation from oxidants, whereas those with a lower redox potential favor the non-radical process. The intrinsically structural and chemical complexities of carbocatalysts (which determines their catalytic reactivities) depend on dimensions, carbon configurations (sp , sp^2 , and sp^3), distinct graphitic degree, curvature structure, and point defects (e.g., edges/vacancies, oxygen moieties and doped heteroatoms).

Carbon configuration is a decisive factor for catalytic activity of carbonaceous materials. The sp^2 hybridized nanocarbons (e.g., graphene and CNTs) exhibit a better catalytic activity than sp^3 and amorphous carbon (nanodiamond) toward electron transfer in the nanocarbons/persulfates activation system (Duan et al. 2015d). The conjugated π system of graphitic carbon networks is conducive to both the activation of persulfates for radical production and the electrophilic attack of the aromatic rings of organics during non-radical process.

Point defects are the imperfect units on the carbocatalyst disturbing the homogeneous and inert carbon network with high chemical potentials. The role of edging sites remains controversial with respect to the catalytic mechanisms (radical (Duan et al. 2016c, Sun et al. 2012) or non-radical pathway (Duan et al. 2016a)) induced in the same system of rGO/PMS/phenol. This discrepancy in the possible

catalytic mechanisms induced by the edging sites in the rGO/PMS/phenol system and the corresponding phenol degradation performances (pseudo-first-order kinetic reaction rate of phenol degradation: 1.125 min^{-1} (non-radical pathway) $> 0.027 \text{ min}^{-1}$ (radical pathway)) might be partially related to the differences in 1) the synthesis methods; 2) the properties of the resulted rGOs (e.g., the corresponding concentration and type of oxygen-containing functional groups and defective level (reflected by the I_D/I_G ratio)); and 3) the application conditions (catalyst loading, PMS dosage) (**Table 2.5**). Further investigation is needed to explore the edging sites of the graphitic carbon network for persulfates activation. The C=O group has been reported to be capable of generating free radicals (Duan et al. 2016c) or $^1\text{O}_2$ (Cheng et al. 2017, Liang et al. 2017) (**Table 2.5**). Compared with pyridinic N and pyrrolic N, graphitic N might contribute more to non-radical pathway via the formation of surface activated persulfates (**Section 2.5.2.1.1**).

Nature of organic substrates

Apart from the intrinsic nature of carbocatalysts, catalytic oxidation can also be influenced by the properties of persulfates (**Section 2.2**) and organic substrates. As for the nature of organic substrates, the charge density of the organic substrate can be significantly influenced by the properties (electron-donating/withdrawing) of the substituent groups in the benzene ring, which determines the electronic properties of organic molecular structure toward redox reaction and adsorption of organics on the nanocarbon network.

Compared with organics (e.g., NB, benzoic acid (BA) and furfuryl alcohol (FFA)) with electron-withdrawing groups (e.g., $-\text{NO}_2$, $-\text{COOH}$), electron-rich organics with electron-donating groups (e.g., dyes, aniline, phenols, chlorophenols and big-molecule antibiotics, such as carbamazepine, propranolol, SMX and acetaminophen) are more readily oxidized via electrophilic reaction in the non-radical pathway than radical pathway in the graphene-based carbocatalysts/persulfates system (Lee et al. 2016, Lee et al. 2015b). Moreover, phenolic compounds (e.g., 4-nitrophenol, para-hydroxyl benzoic acid and acetylsalicylic acid) might mainly consume $\text{O}_2^{\cdot-}$ and $^1\text{O}_2$, whereas $\text{HO}^{\cdot}$ is the responsible ROS for degradation of aliphatic compounds (e.g., oxalic acid, acetic acid and formic acid) (Wang et al. 2018b).

In such case, we can design a carbocatalyst favoring the non-radical pathway for the degradation of those electron-rich organic substrates, such as NG with a high content of graphitic N, the formation of which is favored by a higher thermal temperature. Because the surface activated complex (Lee et al. 2015b) as one mechanism type of non-radical pathway might be induced by the graphitic N (**Section 2.5.2.1.1**). As such, the abovementioned electron-rich organic substrates can serve as an electron donor, while the surface activated persulfates can act as an electron acceptor to induce the degradation of organic substrate and simultaneous consumption of the persulfates.

2.5.2.2 Activation of persulfates by graphene-based carbocatalysts

2.5.2.2.1 Catalytic mechanisms involved in graphene-based carbocatalysts/persulfates system

In the graphene/persulfates system, the reported degradative mechanisms include free radicals ($\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$), surface activated complex, $^1\text{O}_2$, and surface-bound $\text{SO}_4^{\cdot-}$ (**Table 2.5**). Free radical pathway has been reported in the rGO/PMS/phenol system (Duan et al. 2016c, Sun et al. 2012). The active sites of rGO900 ($I_D/I_G = 1.69$, oxygen content = 2.95 at.%) (**Table 2.5**) for PMS activation to generate $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$ include zigzag edges, vacancies and the $\text{C}=\text{O}$ group at the edges. The zigzag edges with a localized state enable their π electrons not to be confined by the edge carbons, leading to their high chemical activity and functionality as an active site for the radical process. The appropriate amount of electron-rich $\text{C}=\text{O}$ group (which terminates at the edges of graphitic carbon network and acts as a Lewis basic site with lone-paired electrons) can facilitate the generation of $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$ in the rGO/PMS system via directly transferring electrons to persulfates (Duan et al. 2016c). The redox cycle induced by the $\text{C}=\text{O}$ group is shown in Eqs 2.5.2.2.1.1 - 2.5.2.2.1.2 (Sun et al. 2012).

It is interesting that $\text{HO}^{\cdot}$ has been revealed as the main ROS instead of $\text{SO}_4^{\cdot-}$ in the rGO900/PDS/phenol system due to water oxidation by the activated PDS (Duan

et al. 2015g). However, Duan et al. (2016a) reported that rGO900 as a defective graphene with few functional groups ($I_D/I_G = 1.70$ oxygen content = 6.0 at.%) (**Table 2.5**) can activate PMS by zigzag edges in a graphene sheet. The edging sites can confine the delocalized π system with ‘a localized state’, which leads to a strongly interaction with small molecules to form surface activated complex for the non-radical pathway rather than free radicals in the rGO-900/PMS/phenol system.

Besides, Liang et al. (2017) revealed that the C=O group at the edging sites of graphitic carbon network is the active site for PMS activation to produce 1O_2 instead of $SO_4^{\bullet-}$ and $HO^{\bullet}$ as the main ROS in the NG/PMS/phenol system, which is similar to a redox cycle induced by p-benzoquinone (p-BQ) (**Figure 2.6**). Hence, it remains debatable regarding the relationship between the active sites and corresponding reaction pathway. Surface-bound $SO_4^{\bullet-}$ has also been detected in the systems of NG/PDS/SMX, aminated graphene (NH_2 -G)/PDS/SMX (Chen and Carroll 2016) and NG/PDS/bisphenols system (Wang et al. 2015). N dopants and amine functional groups are believed to be the active sites for both adsorption and PDS activation.

2.5.2.2.2 Comparisons in catalytic performances of doped or co-doped graphene for persulfates activation

As for the single doping, it has been reported that the catalytic performance for PMS activation follows the order of $NG > BG \approx PG \approx SG \approx rGO$ (**Table 2.3**). Compared with B/P/S doping, N doping can boost the catalytic activity of graphene significantly. The graphitic N might be more reactive than other N bonding configurations (e.g., pyridinic N and pyrrolic N) in the activation of persulfates (Duan et al. 2015b)

However, it remains controversial with respect to the catalytic capabilities of graphene co-doped with heteroatoms for persulfates activation. Duan et al. (2015e) reported that catalytic performances of co-doped carbocatalysts to activate PMS for phenol degradation follow the order: nitrogen and phosphorus-co-doped rGO (NPG) (0.1 wt% P_2O_5) < NBG (0.1 wt% B_2O_3) < NG (**Table 2.3**). N dopants contribute more to activating PMS to generate $SO_4^{\bullet-}$ and $HO^{\bullet}$ than the oxygen-containing functional groups (e.g., the C=O group). By contrast, Sun et al. (2013a) claimed a different order of catalytic activities: NBG (0.1 wt% B_2O_3) > NG > NPG (0.1 wt% P_2O_5) (**Table**

2.3). Pyrrolic N or pyridinic N at the edge sites might contribute more to activating PMS than the activated π electrons after doping.

The introduction of S atom at the optimized doping level (0.3 g diphenyl disulfide) can greatly enhance the catalytic capability of NG because the synergistic effect of N and S efficaciously breaks up the inertness of sp^2 hybridized nanocarbon network to facilitate charge transfer from carbocatalyst to PMS to generate $SO_4^{\cdot-}$ and $HO^{\cdot}$ (**Table 2.5**). However, iodine (I) as a co-dopant of NG fails to facilitate an enhancement in the catalytic performance of NG (Duan et al. 2015f). Thus, further investigation on the synthesis conditions and the possible effective bonding configurations of other heteroatoms except for N atom is needed to gain a deeper insight on the impact of co-doping with heteroatoms on the catalytic activity and mechanism of persulfate activation by carbocatalysts.

2.6 Density Functional Theory for carbocatalyst design

DFT is useful to 1) investigate and predict the structural and electronic properties (mainly the ground state) of nanomaterials qualitatively, sometimes even quantitatively; and 2) favor characterization, justification of experimental results, and probing their promising applications. The Hohenberg-Kohn theorem serves as the basis of DFT, which describes how the natures of a system relate to the electron density. The exchange and correlation (XC) potential relative to the quantum nature of the electrons can be estimated by functionals (e.g., the generalized gradient approximation (GGA), the local density approximation (LDA), and hybrid functionals) (Tang et al. 2015).

Quintessentially, periodic boundary conditions (PBCs) are applied to all the supercell structures. Compared with the cluster type quantum mechanical calculations (finite models), PBCs as infinite models can describe the system more realistically to circumvent the problem of cluster boundaries in the case of finite models. However, the cluster approach exhibits the merit of the lower computational costs due to the reduction in the molecular size in the finite models. Meanwhile, the cluster approach can adequately depict the local characteristics (e.g., vibrational frequencies and geometries). Thus, a combination of cluster approach and PBCs can offer a comprehensive understanding of the origin of the catalytic activity of

investigated systems via comparison and contrast between information provided by two approaches (Ricca et al. 2018).

Cohesion energy (E_{coh}) can be used to indicate the stability of the doped carbocatalysts, as shown in Eq 2.6.1.

$$E_{\text{coh}} = (E_{\text{doped carbocatalyst}} - \sum_i^N E_i)/N \quad (2.6.1)$$

where $E_{\text{doped carbocatalyst}}$ refers to the total energy of the doped carbocatalyst, E_i refers to the energies of each element i (e.g., C, N, B, S, P), and N is the total atomic amount in the supercell. It has been reported that NBG retains the graphene structure. Doping graphene with N and B even reinforces the crystalline structure of graphene, especially in the case of all B atoms ortho to N atoms incorporated (larger E_{coh} values) (Ricca et al. 2018).

The adsorption of persulfates or the generated ROS in the carbocatalysts/persulfates system along with the spin and charge density distributions of the doped carbocatalysts can be used as criteria for determination of active sites. The adsorption energy (E_{ads}) can be computed as shown in Eq 2.6.2.

$$E_{\text{ads}} = E_{\text{adsorbate/carbocatalyst}} - (E_{\text{carbocatalyst}} + E_{\text{adsorbate}}) \quad (2.6.2)$$

Where $E_{\text{adsorbate/carbocatalyst}}$ is the total energy of the combined adsorbate/carbocatalyst system. $E_{\text{carbocatalyst}}$ and $E_{\text{adsorbate}}$ are the energies of carbocatalyst and of the isolated adsorbate, respectively. The higher E_{ads} indicates the higher catalytic activity the investigated sites possess.

The electron states (charge density and spin density) of the neighboring C atoms to dopants can be probed by DFT calculation based on the rational and semi-empirical selection of the size of carbon matrix, bonding configurations of dopants and the relative position of dopants in the carbon matrix. The positively charged sites might serve as possible active sites. It has been reported that introducing S atoms alone into graphene lattice can induce a high spin density to the adjacent C atoms albeit without a significant increase in their positive charges (**Figure 2.7(a) and (b)**). The introduction of N atoms into graphene lattice can induce both a high spin density and a high positive charge density to the adjacent C atoms (**Figure 2.7(c) and (d)**). By contrast, the introduction of S atoms into NG to form NSG can further increase the positive charge densities to the adjacent C atoms albeit without the variation in spin density due to the compensating effect of the spin pairing from S and N (same spatial

densities but opposite spins) (**Figure 2.7(e) and (f)**). However, further introducing S atoms into NSG might lead to a considerable reduction in the positive charge densities of the neighboring C atoms due to the disruption of the balance of charge density in the conjugated graphitic carbon network caused by surplus S atoms (Duan et al. 2015f).

(c)

(d)

Figure 2.7. SG: on-site bader charge (a) and spin density isosurface (b); NG: on-site bader charge (c) and spin density isosurface (d); NSG: on-site bader charge (e) and spin density isosurface (f) (Duan et al. 2015f).

Electronic properties, which can be reflected by the HOMO-LUMO gap or the

band gap (E_g) of the carbocatalysts, can be investigated or predicted by DFT calculation. Kinetic stability can be reflected by the HOMO-LUMO gap. Thus, a decrease in the HOMO-LUMO gap might indicate an enhanced reactivity (Aihara 1999). Doping with heteroatoms can induce a smaller HOMO-LUMO gap, which implies a higher reactivity. It has been reported that, compared with the pristine graphene, introducing N and B atoms into graphene can give rise to HOMO and LUMO with higher energies, regardless of the bonding configurations, which facilitates the excitation and transfer of electrons to oxidants (**Figure 2.8**).

In addition, the systematic periodic DFT calculations reveal that doping with heteroatoms can also lead to the opening of E_g , which might be ascribed to the deformation in the symmetry of the undoped graphitic lattice resulting from the rearranged surface charge caused by doping. A larger E_g value refers to a higher deformation level, which indicates the larger charge redistribution conducive to the catalytic activity of the doped carbocatalysts.

Figure 2.8. Comparison in HOMO and LUMO energies calculated by the cluster approach between the undoped graphene and NBG with different bonding configurations (a)-(g) (Ricca et al. 2018).

Moreover, DFT can be used to probe the intricate interaction between persulfates and carbocatalysts to further elucidate the possible reaction mechanism. The E_{ads} , electron transfer (Q) between the adsorbed persulfates and carbocatalysts, and the variation in the O–O bond length (l_{O-O}) of the persulfates are usually calculated as indicators to predict or verify the possible mechanism in the carbocatalysts/persulfates system. It has been reported that the O–O bond was directly

dissociated into $\text{SO}_4^{\bullet-}$ and $\text{HO}^{\bullet}$ with the stronger adsorption, more rapid electron transfer ($E_{\text{ads}} = -7.96$ eV, $Q = -1.078$ e) in the CMK-3 (C=O group)/PMS/phenol system, which suggested a free radical pathway. By contrast, the moderate level of E_{ads} , Q and $l_{\text{O-O}}$ (e.g., $E_{\text{ads}} = -2.58$ eV, $Q = -0.782$ e, $l_{\text{O-O}} = 1.439$ Å in the rGO (zigzag edges)/PMS/phenol system) might indicate a non-radical pathway without the scission of O-O bond in persulfates (Duan et al. 2015b, Duan et al. 2015d, Duan et al. 2016a).

Furthermore, the degradation pathway of organic substrates can be explored by DFT calculation. Basically, the local descriptors of f_{A}^+ and f_{A}^- of the Fukui function can act as indicators for the most susceptible bonds in the organic substrates to be attacked by the nucleophilic and electrophilic species produced in the carbocatalysts/persulfates system, respectively. Therefore, the function is conducive to predicting the possible intermediates and degradation pathway. The larger values of the f_{A}^+ or f_{A}^- of all optimized organic molecule structures simulated by DFT indicate the higher reactivity of the sites.

However, the standard DFT method still exhibits some intrinsic shortcomings in terms of the accuracy and efficiency when investigating the electronic and structural natures of 2D nanomaterials. Firstly, the severely underestimated E_{g} of semiconducting materials can be caused by the most widely employed local and semilocal approximations to the exchange-correlation functional. Thus, the calculated E_{g} are just suitable for qualitative comparison with the experimental results based on the fact that the tendency of the E_{g} variation forecast by the standard DFT method are fairly reliable. Compared with LDA and GGA, the exchange hybrid density functional (HSE06) might serve as an alternative to improve the accuracy of the computed E_{g} albeit with more calculation time (Heyd et al. 2003).

Secondly, the standard DFT method fails to reliably determine the substantial nonlocal long-range dispersion interactions in the 2D materials. The widely used semilocal correlation functionals in the standard DFT method are intended for the strong covalent and ionic bonds. The DFT+D approaches (DFT-D1, DFT-D2) supplemented with semiempirical dispersion corrections are supposed to be an effective solution to the problem regarding accurate prediction of dispersion interactions in the 2D materials (Gräfenstein and Cremer 2009, Grimme 2006).

The third drawback relates to the self-interaction errors (SIEs) due to the inexact exchange energy approximation in DFT, which leads to the overly delocalized electron densities. The DFT+U method is used as an effective solution to correct SIE whereby an averaged intra-atomic interaction potential is employed between the strongly correlated electrons (Cococcioni and De Gironcoli 2005).

2.7 Identification of reactive oxygen species in the radical and non-radical process

The main ROS in the radical processes include $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$. While $^1\text{O}_2$, surface-bound $\text{SO}_4^{\cdot-}$, surface activated complex and carbon matrix as an electron shuttle function predominantly in the non-radical processes. The main techniques for ROS identification include using ROS scavengers, chemical probes, and spin trapping agents.

2.7.1 $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$

The commonly used scavengers to quench both $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$ include methanol, ethanol and phenol (**Table 2.7**). Compared with methanol/ethanol, phenol is easier to react with the produced $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$ due to its higher hydrophobicity, which renders phenol accessible to the surface of nanocarbon materials in the heterogeneous system (Lindsey and Tarr 2000, Ziajka and Pasiuk-Bronikowska 2005). Besides, anisole, isopropanol and atrazine are also employed as scavengers for both $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$ due to their high second order rate constants (**Table 2.7**). These chemical scavengers can be used to constrain the contribution of both $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$ to determine their existence and contribution in the degradation of organic substrates.

Table 2.7. Second-order rate constants for reactions of selected quenchers with different ROS (Cheng et al. 2017, Ghanbari and Moradi 2017, Liang et al. 2017)

Quenching agents	Reaction rate constant ($M^{-1} s^{-1}$)			
	$SO_4^{\bullet-}$	$HO^{\bullet}$	1O_2	$O_2^{\bullet-}$
Methanol	2.5×10^7	9.7×10^8	-	-
Ethanol	10^7	10^9	-	-
Anisole	4.9×10^9 (Padmaja et al. 1993)	5.4×10^9 (Buxton et al. 1988)	-	-
Isopropanol	8.2×10^7 (Clifton and Huie 1989)	1.9×10^9 (Buxton et al. 1988)	-	-
Atrazine	$(2.6-3.5) \times 10^9$ (Khan et al. 2014, Lutze et al. 2015a, Manoj et al. 2007)	$(2.5-3.0) \times 10^9$ (Acero et al. 2000, Balci et al. 2009)	-	-
TBA	$(4-9.1) \times 10^5$	$(3.8-7.6) \times 10^8$	-	-
FFA	-	1.5×10^{10}	1.2×10^8	-
NaN₃	1.2×10^{10}	2.5×10^9	1×10^9	-
L-histidine	-	-	3×10^7 (D ₂ O, pD = 7) (Wilkinson et al. 1995)	-
DPA	-	-	1.3×10^6	-
Phenol	8.8×10^9	6.6×10^9	-	-
BA	1.2×10^9	4.2×10^9	-	-
NB	$< 10^6$	$(3-3.9) \times 10^9$	-	-
NaCO₃	-	-	-	1.5×10^9 (Ross and Neta 1979)
p-BQ	-	-	-	9×10^8 (Bielski et al. 1985)
NBT	-	-	-	$(1.9 \pm 0.4) \times 10^9$ (Bielski et al. 1985)
CF	-	-	-	3×10^{10} (Buxton et al. 1988)

The relative contribution of $\text{SO}_4^{\bullet-}$ can be deduced by eliminating $\text{HO}^{\bullet}$ contribution (Eq 2.7.1.1) (Oh et al. 2017c, Oh et al. 2016) via introducing scavengers selective to $\text{HO}^{\bullet}$ (at least 3-order of magnitude higher in the second order reaction rate with $\text{HO}^{\bullet}$ than with $\text{SO}_4^{\bullet-}$), such as tert-butyl alcohol (TBA), NB and BA (Table 2.7).

$$\begin{aligned} & \% \text{ concentration of } \text{SO}_4^{\bullet-} \\ &= \frac{\% \text{removal (or rate constant) with } ^{\bullet}\text{OH scavenger}}{\% \text{removal (or rate constant) without scavenger}} \times 100\% \end{aligned} \quad (2.7.1.1)$$

Notably, TBA can also react with PDS (Liang and Su 2009). Apart from adopting the proper chemical scavengers, their concentration should be considered, which is attributed to the competition between the target organic substrates and chemical scavengers to react with $\text{SO}_4^{\bullet-}$ or/and $\text{HO}^{\bullet}$ (e.g., the molar ratio of 1:20 of organic substrate to chemical scavenger) (Oh et al. 2016). 4-hydroxybenzoic acid, typically resulting from the reaction between BA and $\text{HO}^{\bullet}$, can be used to confirm the existence of $\text{HO}^{\bullet}$ (Lee et al. 2016).

Besides the competitive kinetic method involving the abovementioned adoption of chemical scavengers to determine the contribution of ROS, chemical probes and spin trapping agents can be used to directly quantify ROS via detecting the byproducts or ROS-adducts generated by the reaction between ROS and chemical probes or spin trapping agents through diversified analytic methods, such as high-performance liquid chromatography (HPLC), fluorescence spectrometer and spectrophotometer.

Dimethyl sulfoxide (DMSO) has been reported to act as a $\text{HO}^{\bullet}$ probe in the GND/PDS/phenol system. DMSO can react rapidly with $\text{HO}^{\bullet}$ ($k_{\text{HO}^{\bullet}+\text{DMSO}} = 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Klein et al. 1981) to generate the $^{\bullet}\text{CH}_3$ radical, formaldehyde and methanesulfinic acid (MSA) as shown in Eqs 2.7.1.2 - 2.7.1.5 (Burkitt and Mason 1991, Navalon et al. 2011, Navalon et al. 2013). The quantitatively generated formaldehyde can react with 2,4-dinitrophenylhydrazine (DNPH) to form the corresponding hydrazone (HCHO-DNPH) which can be analyzed by liquid chromatography-UV to determine the amount of the produced $\text{HO}^{\bullet}$ (Tai et al. 2004). However, it is noteworthy that DMSO can be oxidized by PMS to form dimethyl sulfone, which interferes the $\text{HO}^{\bullet}$ quantification in the carbocatalysts/PMS system (Betterton 1992).

Coumarin can also be used as a $\text{HO}^\bullet$ probe due to the quantitative conversion of the non-fluorescent coumarin to the fluorescent 7-hydroxycoumarin with a maximum emission at $\lambda = 456 \text{ nm}$ (Luo et al. 2009). Terephthalic acid is another chemical probe for a photoluminescence technique. $\text{HO}^\bullet$ can quantitatively convert the non-fluorescent terephthalic acid to the highly fluorescent 2-hydroxyterephthalic acid with a maximum emission at $\lambda = 425 \text{ nm}$ (Xiao et al. 2008, Yu et al. 2009). Parachlorobenzoic acid (p-CBA) can also act as a $\text{HO}^\bullet$ probe due to the following reasons: 1) p-CBA reacts rapidly with $\text{HO}^\bullet$ ($k_{p\text{-CBA}+\text{HO}^\bullet} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Elovitz and von Gunten 1999); and 2) p-CBA cannot be significantly adsorbed on most of organic materials (Sánchez-Polo et al. 2006). Salicylic acid can react with $\text{HO}^\bullet$ to form the stable and quantifiable 2,5-dihydroxybenzoic acid (2,5-DHBA) (Eq 2.7.1.6) which can be analyzed with HPLC for concentration (Kaneko et al. 2000, Li and Wang 2004).

N,N-dimethyl-*p*-nitrosoaniline (RNO) presents a high-rate reaction with $\text{HO}^\bullet$. The formation of $\text{HO}^\bullet$ intermediates (Eq 2.7.1.7) can be monitored via the bleaching of the RNO solution, which uses the UV-Vis spectrophotometer traced at $\lambda = 350 \text{ nm}$ (Martínez-Huitle et al. 2004).

1,5-diphenylcarbohydrazide (DPCI) has been reported to act as a $\text{HO}^\bullet$ probe via the oxidation-extraction photometry method (OEP). In this method, DPCI can oxidize $\text{HO}^\bullet$ into 1,5-diphenylcarbonzone (DPCO) that can be extracted by using the

mixed benzene and CCl₄ solvents. DPCO exhibits a strong absorbance at $\lambda = 563$ nm and can be easily detected using UV-Vis spectra (Wang et al. 2011).

5,5-dimethyl-pyrroline N-oxide (DMPO) is a commonly used spin trapping agent in the electron paramagnetic resonance (EPR) for SO₄^{•-} and HO[•] via formation of specific adducts (DMPO-HO[•]: a typical 4-line EPR spectrum with the relative intensity ratio of 1:2:2:1 due to the equivalent hyperfine splitting constants $\alpha_N = \alpha_H = 14.9$ G; DMPO-SO₄^{•-}: $\alpha_N = 13.2$ G, $\alpha_H = 9.6$ G, $\alpha_H = 1.48$ G, $\alpha_H = 0.78$ G (Timmins et al. 1999). DMPOX (5,5-dimethyl-2-pyrrolidone-N-oxyl) with a heptet ($\alpha_N = 7.3 \pm 0.1$ G, $\alpha_H = 3.9 \pm 0.1$ G) (Floyd and Soong 1977, Verstraeten et al. 2009) can be formed after the oxidation of DMPO, which might be an possible indirect indicator of the existence of SO₄^{•-} and HO[•] (**Figure 2.9(a)**) (Floyd and Soong 1977, Ma et al. 2019, Ma et al. 2018, Yin et al. 2018, Zhang et al. 2017).

Figure 2.9. Schematic representation showing possible pathways for the conversion of (a) DMPO to DMPOX (Chen et al. 2018a, Yin et al. 2018) and (b) BMPO to BMPOX (Wang et al. 2017a).

Apart from DMPO, 5-tert-butoxycarbonyl-5-methyl-1-pyrroline-N-oxide (BMPO) can be used as a spin trapping agent for $\text{SO}_4^{\bullet-}$ and $\text{HO}^{\bullet}$. The formation of 5-tert-butoxycarbonyl-5-methyl-2-oxopyrroline-1-oxyl (BMPOX) (7-line spectra with hyperfine splitting constants $\alpha_{\text{N}} = 7.35$ G, $\alpha_{\text{H}} = 3.65$ G and $\alpha_{\text{H}} = 3.65$ G) may act as an indirect indicator for the existence of $\text{SO}_4^{\bullet-}$ (Wang et al. 2017a). The possible conversion pathway of $\text{BMPO-SO}_4^{\bullet-}$ adduct to BMPOX is shown in **Figure 2.9(b)**. In addition, phenyl- α -t-butyl nitron (PBN) ($\alpha_{\text{N}} = 15.5$, $\alpha_{\text{H}} = 2.7$) has also been reported to be used as a $\text{HO}^{\bullet}$ spin trapping agent. However, PBN is not suitable for $\text{HO}^{\bullet}$ quantification due to consumption of PBN by $\text{HO}^{\bullet}$ (Espinosa et al. 2015).

2.7.2 $^1\text{O}_2$ and $\text{O}_2^{\bullet-}$

The $^1\text{O}_2$ scavengers include sodium azide (NaN_3), FFA (Gsponer et al. 1987), and L-histidine (Wilkinson et al. 1995). However, NaN_3 and FFA can also react with $\text{SO}_4^{\bullet-}$ and $\text{HO}^{\bullet}$ with higher second order rate constants than that with $^1\text{O}_2$ (**Table 2.7**). It is noteworthy that although these ROS scavengers may react with the coexisting oxidants (e.g., persulfates, the coexisting ROS), they still can be used as long as no significant decrease in the oxidation efficiency for pollutant removal is induced. It has been reported that NaN_3 can boost PMS decomposition (Liang et al. 2017).

However, the resulted decrease in PMS concentration (~ 24%) due to the reaction between PMS and NaN₃ cannot remarkably affect the phenol decomposition in the NG/PMS/phenol system. But admittedly, the concentration of NaN₃ can be inadvertently and significantly affected, which limits its scavenging effect. Thus, the dosage of NaN₃ entails a proper adjustment.

Diphenylanthracene (DPA) has been reported as a chemical probe for ¹O₂ detection via liquid chromatography/mass spectrometry (LC/MS). DPA can react specifically with ¹O₂ to form a stable DPA endoperoxide (DPAO₂) ($k_{DPA+^1O_2} = 1.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) (Corby and Taylor 1964, Miyamoto et al. 2003, Turro et al. 1981). Nevertheless, the reaction of NaN₃, FFA or DPA with O₂^{•-} or other non-radical reactive intermediates (e.g., surface activated persulfates) which may co-exist with ¹O₂ is still unclear and yet to be explored.

2,2,6,6-tetramethyl-4-piperidone (TEMP) is the commonly used spin trap for ¹O₂. A stable adduct 2,2,6,6-tetramethyl-4-piperidone-N-oxyl radical (TEMPO) can be formed with a 3-line EPR spectrum with equal intensity ($\alpha_N = 1.69 \text{ mT}$, $g = 2.0054$) (Hideg et al. 2011). The lifetime of ¹O₂ in H₂O is ~ 4.2 μs. Its life-time can be extended by up to ~10 times (~ 55 μs) in D₂O solution compared with in the aqueous solution (Haag and Hoigné 1986). It is noteworthy that O₂^{•-} may interfere with the EPR detection of ¹O₂ by reacting with TEMP to form a similar 3-line EPR spectrum. Besides, TEMP as an alkaline chemical may induce persulfates activation by base (PMS: pH > 9 (Qi et al. 2016); PDS: pH > 11 (Matzek and Carter 2016)) to generate ¹O₂/ O₂^{•-} (Konovalova et al. 2004, Poupko and Rosenthal 1973).

O₂^{•-} presents insensitivity to general radical scavengers (e.g., methanol, ethanol or TBA). Selective ROS scavengers or probes for O₂^{•-} include sodium carbonate (NaCO₃), p-BQ (Kishikawa et al. 2009, Yin et al. 2009), nitro blue tetrazolium (NBT) and chloroform (CF) (**Table 2.7**). CO₃²⁻ can react with O₂^{•-} to produce carbonate radical ([•]CO₃⁻) as shown in Eqs 2.7.2.1 - 2.7.2.2 (Bielski et al. 1985).

NBT can be used as a chemical probe for O₂^{•-}. NBT shows a great selectivity toward O₂^{•-}, since NBT cannot react with other ROS except for HO[•]. The absorbance

intensity of the product from the reduction of NBT by $O_2^{\cdot-}$ at $\lambda = 560$ nm can be used for concentration determination of $O_2^{\cdot-}$ (Auchère and Rusnak 2002).

DMPO can be also used as a spin trapping agent for $O_2^{\cdot-}$ with a sextet EPR spectrum. The adoption of absolute ethanol as the reaction medium instead of the aqueous solution can prolong the half-life of $O_2^{\cdot-}$ as well as scavenge $HO^{\cdot}$ (Wang et al. 2016b). BMPO has been reported to act as a spin trapping agent for $O_2^{\cdot-}$ with absolute ethanol as solvent (Wang et al. 2018a, Wang et al. 2018b). Compared with DMPO, BMPO is more suitable for the detection of $O_2^{\cdot-}/HO_2^{\cdot}$ due to the following reasons: 1) BMPO can react faster with these radicals than DMPO to generate adducts with a higher stability and half-life (DMPO-superoxide adduct: $t_{1/2} = 45$ s, BMPO-superoxide adduct: $t_{1/2} = 23$ min); 2) BMPO-superoxide adduct cannot decay into a hydroxyl adduct, avoiding the confusion between $O_2^{\cdot-}/HO_2^{\cdot}$ and $HO^{\cdot}$; 3) a higher signal-to-noise ratio is characteristic of the EPR spectra of BMPO-derived adducts; and 4) the highly purified crystalline BMPO can be handled and stored for the extended periods of time (Eaton et al. 2010, Eaton et al. 2005, Zhao et al. 2001).

2.7.3 Surface-bound $SO_4^{\cdot-}$, surface activated complex and electron shuttle

Potassium iodide (KI) has been reported as a scavenger for surface-bound $SO_4^{\cdot-}$ (Huang et al. 2014, Xu and Wang 2012). Methanol can serve as a chemical probe to quantify surface-bound $SO_4^{\cdot-}$ due to the oxidation of methanol to formaldehyde by surface-bound $SO_4^{\cdot-}$, as shown in Eqs 2.7.3.1 - 2.7.3.2 (Bartlett and Cotman 1949).

Methods to confirm the existence of surface activated complex include thermogravimetric analysis (TGA), Fourier transform infra-red (FTIR) spectroscopy, investigating the effect of the increased ion strength in the solution, chronoamperometry and linear sweep voltammetry (LSV) (**Table 2.4**). TGA functions via the comparison between the mass-loss rates of carbocatalyst, carbocatalyst/persulfates and carbocatalyst/persulfates/organic substrates, which is based on the facts that persulfates and organic substrates strongly bound to the carbocatalyst surface become liberated as temperatures are elevated (Lee et al. 2016). FTIR can provide information about surface functional groups. Compared with the

FTIR spectrum of the carbocatalyst, the increased peaks at around 1171 and 1074 cm^{-1} may be attributable to the symmetric and asymmetric vibrational modes of $\text{S}=\text{O}=\text{S}$ bond in PDS in the FTIR spectrum of carbocatalyst/PDS, which can be used to confirm the adsorptive interaction between PDS and carbocatalyst surface (Júnior et al. 2013). Adsorbed phenol can introduce an absorption peak at 730 cm^{-1} due to the out-of-plane bend of the aromatic C-H bond in the FTIR spectrum of carbocatalyst/PDS/phenol (Lee et al. 2016).

The increased ionic strength can compress the electric double layers to decrease the zeta potential of particles, which affects the outer-sphere interaction (electrostatic bonding) between solute and carbon-based particles more than inner-sphere complexation (formation of covalent bonds or a coexistence of covalent and ionic bonds) (Thiel and Madey 1987). Thus, the increased ionic strength can hamper the formation of the surface activated complexes and therefore affect the oxidation efficiency, which can be used as an indicator for the formation of surface activated complexes.

Chronoamperometry is based on investigating the changes in current generation at the carbocatalyst electrode via sequential addition of persulfates and organic substrates to explore the formation of surface activated complex. The generation of a small negative current peak after the injection of persulfates may indicate an instant electron movement from carbocatalysts to persulfates and the formation of a charge-transfer carbocatalysts/persulfates complex (surface activated persulfates). Whereas the generation of a strong positive current flow after the injection of organic substrates may indicate the electron transfer from the carbocatalysts/organic substrates complex to the carbocatalysts/persulfates complex.

LSV is an electrochemical method to confirm the function of carbon matrix serving as an electron shuttle. In such case, a significant current increase toward the carbocatalyst surface can be observed only when both organic substrates and persulfates are present in the carbocatalysts/persulfates/organic substrates system (Lee et al. 2016, Lee et al. 2015b, Yun et al. 2017). Thus, whether the decomposition of persulfates depends on the coexistence of organic substrates can be used as a criterion to determine the mechanisms (formation of surface activated complex or

carbon matrix as an electron shuttle) of the non-radical processes in the carbocatalysts/persulfates/organic substrates system.

Besides, some characterization techniques (**Table 2.4**), such as SEM and TEM for morphology, Raman for defective level (I_D/I_G) and XPS for surface functionality, can be used to analyze the changes in the properties of the used carbocatalysts compared with the fresh samples. The changes may be minor in the non-radical system due to its milder redox potential compared with the radical process. The abovementioned factors collectively favor the determination of mechanisms in the carbocatalysts/persulfates/organic substrates system.

2.8 Transformation of biomass waste into carbon-based nanomaterials

2.8.1 Biomass in nature

As described in **Section 2.3**, a wide range of synthesis methods (e.g., thermal annealing with GO as the most commonly used carbon source or CVD, etc.) can be used to prepare heteroatom-doped graphene. However, most of these synthesis methods have the drawbacks with respect to the high fabrication cost, limitations to scale-up production and being unsustainable. Thus, the development of green fabrication methods (energy-saving process or employment of inexpensive starting materials) for carbocatalyst synthesis is of significant interest. In such a context, naturally abundant biomass is an ideal alternative to the conventional carbon precursor (e.g., graphene/GO/rGO) in terms of its high accessibility, low cost and recyclability.

As shown in **Figure 2.10(a)**, generally, biomass can be divided into animal wastes, municipal wastes, aquatic wastes, wood, agricultural corps and their residuals (Demirbaş 2001). Besides the conversion of biomass to biofuels (e.g., biodiesel or bioethanol), another important application of biomass is for green carbon synthesis, including AC, biochar, and nanocarbon (e.g., graphene and CNTs) (Marriott et al. 2014, Primo et al. 2012, Su 2009, Tay et al. 2009). Usually, the hierarchically intriguing nanostructure (**Figure 2.10(b) and (c)**) (Zhou et al. 2011) of the biomass can be inherited by the as-prepared carbocatalysts via the proper synthesis methods.

Figure 2.10. (a) Biomass resources in nature; (b) nanostructures of biomass; (c) bio-mimic structures of synthesized nanocarbons (right) corresponding to the original biological structure (left) (Gao et al. 2017).

2.8.2 Conversion methods for biomass-derived renewable carbon materials

Basically, the synthesis methods based on thermochemical reaction for biomass conversion into carbonaceous materials include physical activation method, chemical activation method and hydrothermal carbonization (HTC) method (Dutta et al. 2014, Titirici and Antonietti 2010, Wang and Kaskel 2012). The characteristics of each conversion method are summarized in the **Table 2.8**. Given the low porosity and SSA of the HTC-based carbon, KOH chemical activation was usually employed to introduce microporosity (Falco et al. 2013, Sevilla et al. 2011). Besides, the soft-templating approach involving amphiphilic block copolymers was used as structure-directing agents to induce micro/mesoporosity in the HTC-based carbonaceous materials (Kubo et al. 2011). Notably, as for synthesis of the heteroatom-doped carbon, HTC carbonization with soft templating at a low temperature can realize both the high contents of dopants and porous structure, which serves as a more effective approach than chemical activation. Because the chemical activation can induce the alteration of heteroatom's chemical environment and the resultant reduction in the heteroatom doping level (Titirici et al. 2012). However, how to exploit most of the

real biomass waste, shorten the reaction time and lower even more the reaction temperature with the aid of catalyst design are the potential challenges yet to address for the improved HTC carbonization (Gao et al. 2017).

Specifically, the environmentally benign preparation of graphene using the biomass waste as the starting material has been documented. Sun et al. employed chemical activation method to transform coconut shell to graphene nanosheet with ZnCl_2 as activation agent and FeCl_3 as catalyst precursor (Sun et al. 2013b). Primo et al. synthesized NG via catalyst-free pyrolysis of chitosan (obtained from crustacean skin wastes) as both the carbon precursor and nitrogen source (Primo et al. 2012). Suryawanshi et al. pyrolyzed dead neem leaves to generate porous turbostratic carbon for fabrication of graphene quantum dots (Suryawanshi et al. 2014). However, those green synthesis processes involving the biomass with the complicated chemical composition still need a further enhancement in terms of scale-up production, generation of some toxic byproducts and energy-consuming high temperature input (Deng et al. 2016b).

Table 2.8. Synthesis methods for biomass-derived carbon materials (Gao et al. 2017, Lu and Zhao 2017)

	Temperature/steps	Activating agents	Characteristics	Biomass resources
Physical activation	Step1: pyrolysis carbonization (< 1000 K) Step2: gasification (> 1150 K)	CO ₂ or H ₂ O as an activation gas	Relative higher degree of graphitization with CO ₂ as activation gas compared with chemical activation	Lignocellulosic precursors (almond shells, olive and peach stones) (Rodríguez-Reinoso and Molina-Sabio 1992). Rice husk, rice straw, corn cob, corn hulls, peanut hulls, pecan shells, coconut shells (Aworn et al. 2008, Balci et al. 1994, Daifullah et al. 2007, Ioannidou and Zabaniotou 2007)
Chemical activation	One or two steps. ~ 700 to ~ 1200 K	ZnCl ₂ , H ₃ PO ₄ , KOH, K ₂ CO ₃ (Caturla et al. 1991, Hayashi et al. 2002, Lillo-Ródenas et al. 2003, Prahas et al. 2008)	Low conversion temperature, short activation time, high carbon yield, large SSA and porosity	Corn cob, rice husks, rice straw, saw dust, nut shells, wood and barks (Hayashi et al. 2000, Ioannidou and Zabaniotou 2007, Juan and Ke-qiang 2009). Pig bone, fish scale, wheat flour, wheat straw, corncob, fungi, banana peel and pomelo peel gelatin (Huang et al. 2011c, Li et al. 2010, Liang et al. 2014, Qu et al. 2015a, Wang et al. 2014a, Wu et al. 2015c, Xu et al. 2012a, Zhao et al. 2013b, Zhu et al. 2011)
HTC	< 500 K, pure water solution and self-generated pressure (Hu et al. 2010, Titirici and Antonietti 2010)	-	Low cost, mild synthesis conditions, environmental friendliness, less pores and low SSA	Pure carbohydrates (glucose, hydroxymethylfurfural, xylose, furfural, sucrose and starch) as well as raw lignocellulosic biomass (Titirici et al. 2008)

2.8.3 Application of biomass-derived renewable carbon materials

2.8.3.1 Biochar

Biochar has the similar chemical structure to charcoal, which is used for soil amendments in terms of nutrients retention and carbon storage. Biochar can be produced from biomass via pyrolysis and HTC process. Compared with the pyrochar produced from the classical pyrolysis, HTC carbonization can directly convert wet biomass as the starting material to the relatively high-yield hydrochar without energy-consuming drying process (Titirici et al. 2012). It has been reported that the hydrochar from swine manure with the alkyl moieties as the main component. By contrast, the swine-manure pyrochar was dominantly comprised of aromatics with the larger aromatic cluster size and deeper carbonization (Cao et al. 2011). Similar report has been made by Fuertes et al., whereby corn stover-derived pyrochar had more recovered aromatic carbon than stover-derived hydrochar. However, the stover-derived hydrochar exhibited higher oxygen and hydrogen atomic ratios (Fuertes et al. 2010). That corresponds to the oxygen-rich nature of the HTC carbon, which is conducive to further functionalization and high hydrophilicity for easier dispersion in water (Gao et al. 2017). The chemical composition of biochar affects soil improvement significantly. Yeast-derived HTC hydrochar facilitated the growth of fungi in the soil, whereas the D-glucose-based HTC hydrochar promoted the Gram-negative bacteria (Steinbeiss et al. 2009). Beet root chips-based hydrochar was detrimental to the *Taraxacum* plant growth (10 vol% addition) while conducive to the fungal symbiont (20 vol% addition) (Rillig et al. 2010). Further investigation is entailed for the relationship between biochar properties and soil amendments.

2.8.3.2 Energy storage devices

The application of biomass-derived carbon as the electrode material in the energy storage devices (e.g., lithium ion battery, supercapacitor) has been extensively researched. Lithium–sulfur battery with high energy density (2600 Wh kg⁻¹) is of paramount significance toward applications such as grid power or electricmobile. However, its obstacles for the practical application originating from the sulfur

cathode include sulfur insulation, dissolution of polysulfides, and volumetric change during the electrochemical reaction between sulfur and sulfide (Manthiram et al. 2014). The biomass-derived carbon/sulfur composite serves as a promising cathode material to tackle those drawbacks, which can be explained as follows:

1) The biomass-derived carbon has the hierarchical porous structure, which can facilitate the ion and electron transfer and accommodate the large volumetric variation (Xu et al. 2016).

2) The biomass-derived carbon has rich nitrogen and oxygenated functionalities, which can immobilize polysulfides via potent chemical bonding. Most of the biomass has the rich protein contents, which can serve as the dopant source to induce the nitrogen and oxygenated functional groups via self-doping (Li et al. 2014, Qu et al. 2015b, Yang et al. 2014a, Yang et al. 2015).

A wide spectrum of biomass has been reported for improving the lithium–sulfur battery, such as bark of plane trees (carbonization) (Xu et al. 2016), banana peels (KOH activation) (Lotfabad et al. 2014), pomelo peels (KOH activation) (Zhang et al. 2014a) and shrimp shell (KOH activation) (Qu et al. 2016). Further efforts can be focused on the fundamental investigation (the relationship between the textural, compositional and structural properties of biomass-derived carbon materials and their electrochemical performance) and qualification of sustainability (in terms of the energy consumption, toxicity of byproduct, and CO₂ emission, etc.).

2.8.3.3 Environmental applications

Adsorption for water purification

Compared with the highly porous structure of the AC, the numerous oxygenated functionalities on the surface HTC-derived carbonaceous material (albeit with low porosity) mainly account for its excellent heavy metal removal from the aqueous environment. It has been reported that functionalizing the D-glucose-based HTC carbonaceous material with vinyl organic monomers can facilitate the formation of the ample amount of the C=O group and macroporosity, which contributed to its outstanding removal efficiencies for Pb(II) (351.4 mg g⁻¹) and Cd(II) (88.8 mg g⁻¹) in the aqueous environment (Demir-Cakan et al. 2009). In addition, comparison was made in the adsorption capability between pyrochar and HTC hydrochar produced

from poultry litter. The adsorption efficiency of HTC hydrochar outperformed pyrochar towards a wide range of organic pollutants (polar or non-polar), such as BPA, phenanthrene and 17 α -ethinyl estradiol (Sun et al. 2011).

Other applications

Furfural-derived HTC carbon doped TiO₂ with enhanced visible light absorption was reported to serve as photocatalyst for the degradation of methyl orange, Acid Orange 7 and 2,4-dichlorophenol via both the carbon sensitization and dye sensitization (Zhao et al. 2010b, Zhong et al. 2010). So far, there is limited research on biomass-derived carbonaceous materials employed as persulfate activators for organic pollutants removal in the aqueous environment. It has been reported that human-hair-derived N, S-co-doped porous carbon (NSC, synthesized via KOH activation) (Ma et al. 2019) and spent coffee grounds-derived carbocatalyst (pyrolysis) (Oh et al. 2018) were employed as excellent PMS activators for aqueous BPA degradation. ¹O₂ was claimed to be the main ROS in both abovementioned carbocatalysts/PMS/BPA system. These findings enable the biomass-derived carbonaceous materials to hold great promise for environmental remediation.

CHAPTER 3: ENHANCING SULFACETAMIDE DEGRADATION BY PEROXYMONOSULFATE ACTIVATION WITH N-DOPED GRAPHENE

3.1 Introduction

As described in **Chapters 1 and 2**, carbocatalysts have emerged as the metal-free, environmentally friendly and biocompatible alternatives to activate PMS during the past few years. N doping has been proposed as one of the most promising methods to tailor the properties of pristine graphene with chemical inertness due to (1) the production of modified functional groups and more defective sites; (2) the enhanced electron mobility resulting from the activated π -electrons in sp^2 carbon via sp^2 conjugation; and (3) the modification of electron density of the local carbon atom neighboring the N dopants (Nicholls et al. 2013, Xiang et al. 2012). Therefore, NG as a PMS activator was investigated for SAM degradation in this chapter.

The synthesis temperature plays a crucial role in the N doping content and configuration in carbon allotropes (Bai et al. 2016). Besides, N sources and synthesis conditions (ambient or inert) can also affect N bonding configurations. As described in **Section 2.3.2**, compared with melamine and NH_4NO_3 , urea can act as a better N source to enhance the catalytic ability of NG for PMS activation. In previous studies, the influence of synthesis temperature has been explored on the NG fabricated with nitrogen sources different from urea, such as melamine (Duan et al. 2015b) and NH_4NO_3 (Indrawirawan et al. 2015a), or on other types of catalysts, such as nitrogen-doped carbon nanotube (Duan et al. 2015h) and CuO (Zhang et al. 2014c) for pollutant degradation via PS/PMS activation.

Moreover, as described in **Section 2.5.2.2**, the possible mechanisms in the NG/PMS system include radical pathway involving $SO_4^{\cdot-}$ and $HO^{\cdot}$ (Duan et al. 2015b) and non-radical pathway involving surface activated species (Li et al. 2017a), surface-bound $SO_4^{\cdot-}$ (Chen and Carroll 2016, Wang et al. 2015) and 1O_2 (Liang et al. 2017). Thus, there is a discrepancy in the catalytic mechanism of PMS activation by NG. As such, we formulate our hypotheses: (1) the concentration of reactive N functional groups can be tuned through the controlled synthesis temperature and

choice of N source; and (2) different N functional groups will therefore endow different NGs with different performances in terms of catalytic efficiency, pollutant degradation mechanism, and catalyst reusability. To the best of our knowledge, limited studies have been conducted about the effect of thermal annealing temperature on N bonding configurations of NG synthesized with urea as a nitrogen source and the catalytic performance of the as-prepared NG for pollutant degradation via PMS activation.

Therefore, the objectives of this research are as follows: (1) to develop NGs with different N doping levels and N bonding configurations using urea as a nitrogen source through the controlled thermal annealing temperature (400, 500, 600, 700 and 800°C); (2) to investigate the variation of the intrinsic properties (e.g., N doping level, N bonding configuration) and extrinsic properties (e.g., SSA) of NGs with the thermal annealing temperature; (3) to probe the catalytic performances of NGs for SAM degradation via PMS activation; and (4) to compare the NG endowed with the most optimum N bonding configurations in this research with NGs prepared via other optimized synthesis methods found in the literature, and probe the relationship between their properties and their catalytic performances for SAM degradation via PMS activation.

3.2 Experimental

3.2.1 Chemicals

All the chemicals were of analytical grade and used without further purification. Natural graphite powder with 325 mesh (> 99.9%), hydrogen peroxide (35% w/w), Oxone (2KHSO₅·KHSO₄·K₂SO₄) were obtained from Alfa Aesar, concentrated sulfuric acid (98%), potassium permanganate (99%), sodium nitrate (99%), hydrochloric acid (37%), urea (99.0-100.5%), melamine (≥ 99%), ammonium nitrate (≥ 98%), sulfacetamide (SAM) (≥ 98%), sulfanilamide (SNM) (≥ 98%), sulfamethoxazole (SMX) (≥ 98%), and sulfathiazole (STZ) (≥ 98%), nitrobenzene (≥ 99%), humic acid and 5,5-dimethylpyrroline-oxide (DMPO) were obtained from Sigma-Aldrich, absolute ethanol (99.9%, Fisher chemical), methanol (HPLC grade, VWR), sodium hydroxide (pellet, Schedelco), sodium chloride (99.5-100.5%,

Merck) were used in the study of this chapter. Milli-Q ultrapure water (18.2 M Ω .cm at 25°C) was used for all the experiments.

3.2.2 Synthesis of N-doped graphene

GO was prepared via the modified Hummers' method (Hummers Jr and Offeman 1958) (**Appendix 1**). Exactly 200 mg of GO was dispersed in 100-mL water in a 250-mL beaker and sonicated for 30 min, followed by adding 1 g urea and the mixture was stirred at 500 rpm for 30 min for urea dissolution. Then the temperature of the mixture was increased to 55°C while stirring using a hotplate to evaporate water. The resulted dried GO/urea mixture was grinded and calcined at 400, 500, 600, 700 and 800°C in a N₂ atmosphere for 30 min in the tubular furnace with the ramping rate of 5°C min⁻¹, respectively. The final products were grinded, filtered and washed by a large amount of water and absolute ethanol in sequence and then dried at 60°C overnight in a vacuum oven. The N-doped products were denoted as NG400, NG500, NG600, NG700 and NG800, respectively. rGO was produced by the same procedure but without adding urea and calcined at 600°C in a N₂ atmosphere. The resulted product was denoted as rGO600. For comparison, NG was also prepared via other optimized synthesis methods found in the literature (NG-melamine-N₂ via thermal annealing method (Duan et al. 2015b), NG-urea-HT via hydrothermal method (Tai et al. 2014) and NG-NH₄NO₃-air via low temperature combustion methods (Sun et al. 2013a)) (**Appendix 1**).

3.2.3 Characterization

The crystal structure was investigated by X-ray diffraction (XRD, Bruker D8 Advance) with Cu-K α ($\lambda = 1.5418$ Å) operated at 40 kV and 40 mA in a 2 θ range of 5-80° with a scan rate of 0.02° s⁻¹. The morphology and structure analysis were conducted on field emission scanning electron microscopy (FESEM, JEOL JSM-7600F) and transmission electron microscopy (TEM, JEOL JEM-2010). EDX maps were taken on the FESEM with an EDX spectrometer. TGA was performed by the thermogravimetric analyzer (PerkinElmer, TGA-4000) with a heating rate of 10°C min⁻¹ under air atmosphere. The Brunauer-Emmet-Teller (BET) model and Barrett-Joyner-Halenda (BJH) method relating to the N₂ adsorption-desorption isotherm

were used to analyze the SSA and the pore size distribution, respectively, on Quantachrome Autosorb-1 analyzer (77 K). FTIR were recorded on a PerkinElmer GX FTIR system. XPS studies were carried out using a Kratos Axis Supra spectrophotometer with a dual anode monochromatic $K\alpha$ excitation source. All binding energies for carbon, nitrogen and oxygen elements were corrected against an adventitious carbon C1s core level at 284.8 eV. All XPS peaks were fitted using Shirley background together with Gaussian-Lorentzian function using CASA XPS software. The elemental composition was analyzed on a PerkinElmer Series II 2400 CHNS/O analyzer. Raman spectra were collected on a LabRAM ARAMIS Horiba Jobin Yvon instrument with a 532-nm wavelength laser.

3.2.4 Adsorption and catalysis evaluation

The catalytic performance of NG via PMS activation was evaluated through SAM degradation. The reaction took place in a 100-mL beaker with 50 mL SAM solution (10 mg L^{-1}), catalyst loading (0.2 g L^{-1}) and PMS dosage (0.5 mM PMS, which is commercially available as Oxone) and pH in the NG/PMS system was adjusted to 7 with 1 M NaOH . 0.5 mL of the aliquot was withdrawn at the designated time intervals, filtered through $0.45 \mu\text{m}$ membrane, and injected into a vial, followed by adding 0.5 mL methanol as a quenching agent. Then the SAM concentration was measured by HPLC (PerkinElmer) with mobile phase of 60% methanol: 40% deionized water at a flow rate of 0.6 mL min^{-1} in an isocratic condition. Reverse phase column (Hypersil Gold, $150 \text{ mm} \times 4.6 \text{ mm} \times 5 \mu\text{m}$) was employed. UV detector was used at $\lambda_{\text{max}} = 256 \text{ nm}$. The adsorption experiment was conducted following the same procedure as catalytic evaluation without adding PMS. Both the residual PMS and total organic carbon (TOC) were measured within 60 min. PMS concentration was determined by iodometric method (Oh et al. 2014). Specifically, 5 mL sample was mixed with 1 g KI , and then capped and aged for 30 min after vigorously shaking. The concentration of I_3^- formed which has a strong positive correlation with PMS concentration can be measured with UV-Vis spectrometer at $\lambda_{\text{max}} = 352 \text{ nm}$. TOC analysis was conducted on a Shimadzu TOC-vcph analyzer.

The effect of catalyst loading ($[\text{catalyst}] = 0.1, 0.2 \text{ and } 0.3 \text{ g L}^{-1}$, $[\text{PMS}] = 0.5 \text{ mM}$, $[\text{SAM}] = 10 \text{ mg L}^{-1}$, $\text{pH} = 7$), PMS dosage ($[\text{PMS}] = 0.2, 0.5 \text{ and } 0.9 \text{ mM}$,

[catalyst] = 0.2 g L⁻¹, [SAM] = 10 mg L⁻¹, pH = 7) and common matrix species ([Cl⁻] = 100 mg L⁻¹, [NO₃⁻] = 10 mg L⁻¹, [humic acid] = 5 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, pH = 7) on the SAM catalytic degradation in the NG/PMS system was investigated. Ethanol and NB were selected as quenching agents for possible catalytic mechanisms in NG/PMS/SAM system. The EPR study was conducted using a Bruker Biospin ELEXSYS II E500 EPR spectrometer in continuous wave X-band mode (modulation amplitude = 1.0 G, sweep width = 100 G, center field = 3490 G, and microwave power = 0.2 mW). A spin trapping agent DMPO was employed for the analysis of the generated ROS in the NG/PMS/SAM system. The EPR spectra were analyzed by the spin-fitting package of Bruker Xeon software. The simulated spectrum was based on hyperfine coupling constants of $\alpha_N = 7.23$ G, $\alpha_H^\beta = \alpha_H^{\gamma1} = 4.00$ G.

The major SAM intermediates produced in the NG600/PMS/SAM system were investigated on a 6460C Triple Quadrupole liquid chromatography tandem mass spectrometry (LC-MS/MS, Agilent) with an Agilent Zorbax Eclipse Plus C18 column (2.1 × 50 mm, 1.8 μm particle size). The gradient mobile phase was water (0.1% (v/v) formic acid) (A)/acetonitrile (0.1% (v/v) formic acid) (B) at a flow rate of 0.2 mL min⁻¹. The gradient elution conditions were presented as follows: 90% A kept for 0-1.0 min, 90% A decreased linearly to 10% A in 1.0-5.0 min and kept for 5.0-6.0 min; 10% A increased linearly to 90% A in 6.0-6.5 min and kept for 6.5-9.0 min. Mass spectral analysis was performed with the negative electrospray ionization (ESI) mode over a mass range of 50-500 mass-to-charge ratio (m/z). The p*H*_{pzc} of NG600 was analyzed by pH drift method. Specifically, 30 mg catalyst was added into 30 mL water in a 50 mL centrifuge tube. NaCl (0.01 M) was used to adjust ionic strength. The initial pH of as-prepared dispersion in each 50 mL centrifuge tube was adjusted between 1-9 with 1 M NaOH and 0.1 M HCl. After shaking for two days, the final pH of each tube was measured, and the pH point whereby the difference between final pH and initial pH was zero is the p*H*_{pzc} of catalyst. All the catalyst experiments were performed in triplicate. Error bars shown in the figures represent the standard deviation.

3.2.5 Reusability

After adsorption and degradation of SAM in the NG/PMS/SAM system, the catalyst was collected by vacuum filtration using 0.45 μm membrane, washed by methanol and water to neutral pH, and then re-dispersed in the fresh SAM solution. After three consecutive cycles, the catalyst was collected, washed and dried in the freeze dryer for further characterization.

3.2.6 Computational methods

The DFT calculations were performed by using Gaussian 09 program package. The rB3LYP functional was used to describe the exchange-correlation effects. All calculations were carried out with the 6-31G* basis sets. In the simulation, nonperiodic graphene cluster was employed and graphitic N was created by replacing one C atom in the graphene, consistent with the model proposed by Duan et al (Duan et al. 2015c). The convergence tolerance of 10^{-6} Hartree (1 Hartree = 27.21 eV) energy change was applied in all cases.

3.3 Results and discussion

3.3.1 Characteristics of NGs

3.3.1.1 NGs prepared at different temperatures

Figure 3.1 shows the FESEM images of GO, rGO600 and NG600, indicating that the thermal annealing process increases the folding and exfoliation of GO (which has a smooth and wave-like structure). By contrast, NG600 was found to be more exfoliated and crumpled at the edge of the doped graphitic sheets probably derived from the defective sites caused by N doping. The TEM images reveal that NG600 still maintained the characteristic two-dimensional planar structure of graphene after N doping, albeit with more wrinkles at the edge of graphitic sheets. The EDX elemental mappings of carbon, oxygen, nitrogen in NG600 are shown in **Figure 3.2**. The doped nitrogen is uniformly distributed over the graphene sheet of NG600.

Figure 3.1. FESEM images of GO (a), rGO600 (b) and NG600 (c). TEM images of GO (d), rGO600 (e) and NG600 (f).

Figure 3.2. EDX maps of (b) C, (c) N and (d) O elements for NG600 according to the corresponding FESEM image (a).

The XRD patterns of GO, rGO600 and NGs are shown in **Figure 3.3(a)**. It was observed that the GO had a strong peak at $2\theta = 11^\circ$, corresponding to the (002) crystalline plane, which indicates a well-ordered and layered structure. This is commensurate with a c-axis interlayer spacing of 0.8 nm. After reduction, rGO600 had a strong peak at $2\theta = 26^\circ$, corresponding to the interlayer spacing of 0.3 nm. The decrease in the interlayer spacing of rGO is attributed to the removal of oxygen-containing functional groups and restoration of graphene network during annealing. After N doping, the strong peak at $2\theta = 11^\circ$ of GO disappeared in the XRD spectra of NGs and a new strong peak at around $2\theta = 26^\circ$ emerged. It is worth noting that NG400 still had a small peak at $2\theta = 11^\circ$, which might be due to the formation of carbon nitride from urea during NG400 synthesis process (Dong et al. 2011)

(corresponding to tri-s-triazine unit peak with a relatively high intensity found in NG400 FTIR spectrum (**Figure 3.8(a)**). Besides, compared with the peak of GO at $2\theta = 42.3^\circ$, which relates to (100) reflection, all the NGs had an upshifted 2θ degrees (42.4° - 43.2°), which indicates deoxygenation due to the elimination of oxygen-containing functional groups and successful N doping.

Figure 3.3. XRD patterns of (a) GO, rGO600 and NG400-NG800, and (b) GO, NG600, NG-melamine- N_2 , NG-urea-HT and NG- NH_4NO_3 -air.

The chemical compositions of GO, rGO600 and NGs are shown in **Table 3.1** and **Figure 3.4(a)**. From NG400 to NG800, the O/C atomic ratio decreased as the thermal

annealing temperature increased, which suggests an enhancement of reduction level due to more oxygen-containing functional groups being eliminated at higher thermal annealing temperatures. Meanwhile, NG400 with the lowest thermal stability among all the NGs had the relatively high weight loss between 400-500°C due to the deoxygenation (**Figure 3.5(a)**), further substantiating the relationship between thermal annealing temperature and the reducibility of NG. A decreasing trend of N/C atomic ratio was observed as the thermal annealing temperature increased from 400°C to 800°C, owing to the scission of C-N bond at the higher thermal annealing temperature or the desorption of amine and amide from NG (Indrawirawan et al. 2015a).

Figure 3.4. Variation of nitrogen and oxygen contents (a) and variation of total N, pyridinic N, pyrrolic N, graphitic N and nitric oxide contents (b) of NG400-NG800 with thermal annealing temperature.

Table 3.1. Structure and chemical information of GO, rGO600 and NGs

	N wt%	O/C at. %	N/C at. %	I _D /I _G	pyridinic N N _{pyridinic N} /N _{total} (%)	pyrrolic N N _{pyrrolic N} /N _{total} (%)	graphitic N N _{graphitic N} /N _{total} (%)	nitric oxide N _{nitric oxide} /N _{total} (%)	C=O O _{C=O} /O _{total} (%)
GO	-	76.1	-	0.91	-	-	-	-	17.9
rGO600	-	11.1	-	0.94	-	-	-	-	23.0
NG400	30.2	12.5	44.6	1.10	54.5	43.6	1.85	-	44.9
NG500	24.2	9.80	31.7	1.11	49.2	42.6	8.27	-	44.9
NG600	16.0	8.00	18.3	1.12	38.4	31.8	25.9	3.94	43.7
NG700	13.7	7.20	15.0	1.09	33.6	21.2	37.5	7.71	43.6
NG800	11.6	6.60	12.4	1.10	32.8	21.1	36.5	9.60	41.8
NG-melamine-N₂	19.3	8.80	23.1	1.04	52.8	34.5	12.8	-	38.4
NG-urea-HT	10.6	21.8	13.7	1.07	69.2	25.6	5.18	-	39.4
NG-NH₄NO₃-air	4.82	48.0	7.7	1.01	31.0	63.6	5.45	-	47.5

Weight percentages of carbon, nitrogen and oxygen were analyzed by CHNS/O analyzer. Atomic percentages of pyridinic N, pyrrolic N, graphitic N, nitric oxide and C=O were analyzed by XPS.

Figure 3.5. TGA curves of (a) GO, rGO600 and NG400-NG800; and (b) GO, NG600, NG-melamine-N₂, NG-urea-HT and NG-NH₄NO₃-air.

The thermal stability of GO, rGO600 and NGs can be investigated by TGA. As shown in **Figure 3.5**, the weight loss of GO between 30-105°C can be attributed to the physically absorbed moisture and residual organic solvents on the GO surface. The quick weight loss between 105-500°C can be ascribed to the decomposition of oxygen functional groups on the GO surface. The weight loss after 500°C is due to the breakup of the carbon skeleton. When the temperature reached 730°C, the aromatic rings of carbon skeleton was completely decomposed (Hu et al. 2015). After N doping, the thermal stabilities of all the NGs were enhanced compared with GO

and rGO600, especially at the higher annealing temperatures. It was reported that the -COOH group can be eliminated at 300°C, whereas the C=O and phenol groups were decomposed above 500°C (Kinoshita 1988). The relatively high weight loss of NG400 between 400-500°C is attributed to the deoxygenation, suggesting the lowest reducibility of NG400 among NG400-NG800 and thermal annealing temperature of 400°C is not conducive to the formation of a reductive carbon network and N doping (tri-s-triazine formed according to FTIR result as discussed later in FTIR analysis).

The high-resolution N1s XPS spectra (in a narrow range of 394-407 eV) were obtained for all NGs (**Figure 3.6**). The N signals can be deconvoluted into four types of N bonding configurations: pyridinic N (397.6 eV), pyrrolic N (399.2 eV), graphitic N (400.9 eV) and nitric oxide (N-O, 402.7 eV). As shown in **Table 3.1** and **Figure 3.4(b)**, all four types of N bonding configurations were detected in the NGs prepared at $T \geq 600^\circ\text{C}$, while the NGs prepared at $T \leq 500^\circ\text{C}$ possessed only three types of N bonding configurations (pyridinic N, pyrrolic N and graphitic N). More graphitic N was doped in the graphitic carbon network, increasing from 1.85 to 36.5%N ($N_{\text{graphitic}}/N_{\text{total}}$ (%)), as the annealing temperature increased from 400 to 800°C. More nitric oxide (N-O) was also incorporated into the graphitic platelets, increasing from 3.94 to 9.60%N ($N_{\text{nitric oxide}}/N_{\text{total}}$ (%)), as the annealing temperature increased from 600 to 800°C. These phenomena could be attributed to the higher thermal stability of graphitic N and nitric oxide than pyrrolic N. The increase in annealing temperature also resulted in the decrease of the O/C atomic ratio (**Table 3.1**) suggesting that simultaneous N doping and reduction occurred during the thermal annealing process. Meanwhile, the defective sites in the NG interlayer can be occupied by excess oxygen-containing functional groups via a stereo-hindrance effect (Duan et al. 2016c). Thus, a minor amount of oxygen-containing functional groups such as the C=O group can also activate PMS. In this study, the content of C=O group gradually decreased from 44.9 to 41.8%O ($O_{\text{C=O}}/O_{\text{total}}$ (%)) with the increasing annealing temperature from 400 to 800°C (**Table 3.1** and **Figure A1(III), Appendix**). Hence, the N doping level and reactive functional groups (e.g., pyridinic N, pyrrolic N, graphitic N and C=O) were successfully tailored by varying the thermal annealing temperature.

Figure 3.6. N1s scans of NG400 (a), NG500 (b), NG600 (c), NG700 (d) and NG800 (e).

The degree of graphitization and doping status of graphene can be investigated by Raman spectra. As described in the **Section 2.4.2**, the ratio of I_D/I_G reveals the defective degree of carbon materials. As shown in **Table 3.1** and **Figure 3.7(a)**, all the NGs had higher ratios of I_D/I_G (1.09-1.12) than those of GO (0.91) and rGO600 (0.94), indicating more defective sites and sp^3 C atoms generated, which might be ascribed to the introduction of N dopant, the loss of C atoms owing to the elimination of oxygen-containing functional groups, and the creation of smaller-sized nanocrystalline graphitic domains (Stankovich et al. 2007). The discrepancy in the

position of G band has been reported. Lin et al. (2012b) reported a downshift of G peak after N doping. Pyridinic N and pyrrolic N, which introduce p-type doping, lead to an upshift of G peak. In contrast, graphitic N, which introduces n-type doping, downshifts the G peak. Li et al. (2012b) proposed an upshift of G peak after N doping. In this study, an upshift of G peak after N doping was observed. And this upshift at the low thermal annealing temperature can be mainly ascribed to the higher N content in NG, while the constricted C-C bond and increased bond vibration frequency due to the introduced defects can account for the upshift of G peak at the higher thermal annealing temperature (Park et al. 2011).

Figure 3.7. Raman spectra of (a) GO, rGO600 and NG400-NG800, and (b) GO, NG600, NG-melamine-N₂, NG-urea-HT and NG-NH₄NO₃-air.

The functional groups of GO, rGO600 and NGs were analyzed by FTIR. As

displayed in **Figure 3.8(a)**, GO showed characteristic peaks at 1740 cm^{-1} (C=O (COOH) stretching vibration), 1620 cm^{-1} (C=C), 1403 cm^{-1} (tertiary alcoholic C-OH bending), 1223 cm^{-1} (C-O (epoxy)), 1091 cm^{-1} (C-O (alkoxy) stretching vibration) and a broad peak at 3413 cm^{-1} (the vibration of O-H or water molecules). After N doping, the dramatic reduction in the intensities of C=O and C-O groups indicates the intensive deoxygenation due to the removal of surface oxygen-containing functional groups, which is consistent with the O/C atomic ratio analysis and substantiated by the reduction in the thickness of NG (**Figure 3.9**). The broad peak at 3413 cm^{-1} disappeared, suggesting an increment in hydrophobicity of NG. The C=C bond of NG shifted to a lower wavenumber (1553 cm^{-1}). A new peak at 1175 cm^{-1} emerged due to the formation of C-N bond and the residual C-O bond (Lin et al. 2012b). It is worth noting that a small peak at 785 cm^{-1} appeared at the FTIR spectra of NG400 and NG500 (NG500 had a lower peak intensity than NG400) which might be ascribed to the formation of tri-s-triazine (a type of nitrogen-containing heterocycle that is not conducive to PMS activation) (Costa and Camino 1988).

Figure 3.8. FTIR transmittance spectra of (a) GO, rGO600 and NG400-NG800, and (b) GO, NG600, NG-melamine- N_2 , NG-urea-HT and NG- NH_4NO_3 -air.

Figure 3.9. AFM images of sheets of GO (a) and NG600 (b) deposited on a freshly cleaved mica and their corresponding line scans.

The thickness and the estimation of layer number can be revealed by AFM. As shown in **Figure 3.9(a)**, the thickness of GO layer in this study was found to be of ca. 1.1 ± 0.2 nm, which is consistent with the thickness of GO monolayer documented (Gómez-Navarro et al. 2007, Huang et al. 2011b, Wang et al. 2012a, Zhao et al. 2010a). As shown in **Figure 3.9(b)**, NG600 had a thickness of ca. 0.4-0.6 nm, indicating it is a monolayer of graphene.

The SSA, pore volume and pore size distribution of GO, rGO600 and NGs are shown in **Table 3.2** and **Figure 3.10(a)** and **(b)**. GO possessed a low SSA ($26 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.017 \text{ cm}^3 \text{ g}^{-1}$) probably due to the severe stacking effect resulted from the strong hydrogen bonding formed between oxygen-containing functional groups on the GO layers. Thermal annealing can not only reduce the oxygen-containing functional groups, but also result in thermal expansion. Thus, rGO600 had the highest SSA ($452 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.441 \text{ cm}^3 \text{ g}^{-1}$). The SSA of NG400-NG800 increased from 25 to $140 \text{ m}^2 \text{ g}^{-1}$ with the same mean pore size as the thermal annealing temperature increases, indicating the enhanced exfoliation of GO under a higher thermal annealing temperature to reduce its severe stacking effect.

Figure 3.10. (a) N_2 sorption isotherm and (b) pore size distributions of GO, rGO600 and NG400-800. (c) N_2 sorption isotherm and (d) pore size distributions of NG600, NG-melamine- N_2 , NG-urea-HT and NG- NH_4NO_3 -air.

Table 3.2. SSA, pore volume and pore size information of GO, rGO600 and NGs

Catalyst	BET SSA (m ² g ⁻¹)	Average pore volume ^a (cm ³ g ⁻¹)	Average pore size ^b (nm)
GO	26	0.017	2.03
rGO600	452	0.441	2.02
NG400	25	0.060	2.03
NG500	24	0.056	2.03
NG600	74	0.164	2.02
NG700	131	0.238	2.01
NG800	140	0.243	2.03
NG-melamine-N₂	8	0.0168	2.03
NG-urea-HT	515	0.385	2.02
NG-NH₄NO₃-air	93	0.191	2.03

^a BJH method cumulative desorption pore volume.^b BJH method desorption pore radius (Mode D_v(r)).

3.3.1.2 NGs prepared with different synthesis routes

For comparison, NGs were also prepared using various synthesis methods found in the literature, namely NG-melamine- N_2 , NG-urea-HT and NG- NH_4NO_3 -air. The morphologies of NGs were analyzed by FESEM (**Figure 3.11**). More exfoliation of NGs was formed after N doping for all the NGs. As shown in **Table 3.1**, the O/C atomic ratios followed the order of NG600 < NG-melamine- N_2 < NG-urea-HT < NG- NH_4NO_3 -air, indicating a higher reducibility caused by thermal annealing at a higher temperature under an inert condition with urea as a nitrogen source than hydrothermal and low temperature combustion methods (with mild synthesis condition) or thermal annealing with melamine as a nitrogen source. NG600 had the highest content of graphitic N. Thermal annealing at a high temperature can induce more graphitic N ($N_{\text{graphitic N}}/N_{\text{total}}$ (%)) with the higher thermal stability in the carbon network (25.9%N of NG600 and 12.8%N of NG-melamine- N_2 , respectively) than that of NG-urea-HT and NG- NH_4NO_3 -air (5.18 and 5.45%N, respectively) (**Figure A1(II), Appendix**). Milder synthesis methods or adoption of melamine as a nitrogen source are inefficacious to produce the desirable N bonding configurations.

Figure 3.11. FESEM images of NG600 (a), NG-melamine- N_2 (b), NG-urea-HT (c) and NG- NH_4NO_3 -air (d).

The XRD spectra are shown in **Figure 3.3(b)**. The higher intensity of the characteristic GO peak at $2\theta = 42^\circ$ reflects the restoration of a well-ordered sp^2 hybridized carbon network, which can be interrupted by the formation of sp^3 hybridized C such as C-O bond (Hasan et al. 2012). The NG-NH₄NO₃-air having the lowest reducibility (the highest O/C atomic ratio) among NGs might account for its lowest peak intensity at $2\theta = 42^\circ$. The FTIR spectra are shown in **Figure 3.8(b)**. It is worth noting that NG-NH₄NO₃-air still had a weak peak at 1740 cm^{-1} attributable to C=O, which is commensurate with NG-NH₄NO₃-air having the lowest reducibility among NGs. A small peak at 785 cm^{-1} appeared at the FTIR spectrum of NG-melamine-N₂ which might be ascribed to the formation of tri-s-triazine. As shown in **Table 3.2** and **Figure 3.10(c) and (d)**, hydrothermal method can increase the SSA dramatically, resulting in NG-urea-HT with a higher SSA and pore volume than thermal annealing and low temperature combustion methods.

3.3.2 Catalytic performance of NGs

The performance of NG as a PMS activator for SAM degradation was evaluated in the aqueous solution at pH 7 (close to the pH value of real water matrix). In general, for GO and NGs, about 20% of SAM removal was due to the adsorption process (**Figure 3.12(a)** and **Figure 3.15(a)**). The rGO600 exhibited the highest adsorption ability with 34% SAM removal efficiency, probably due to its relatively higher SSA ($452\text{ m}^2\text{ g}^{-1}$) and favorable surface functional groups for adsorption process. Compared to the rGO600 (without N surface functionalization), the N doping process in the NG can induce reduction as well as the incorporation of N atoms which reduces the π - π stacking interaction between NG and SAM, leading to the poor adsorption performance of NG-urea-HT, albeit with a comparable high SSA ($515\text{ m}^2\text{ g}^{-1}$). Besides, the performance of adsorption depends on solution pH, pK_a of pollutant, and pH_{pzc} of catalyst. SAM has $pK_{a1} = 1.8$ and $pK_{a2} = 5.4$. The pH_{pzc} of NG600 is 6.1 (**Figure A2(a)**). Under the solution pH = 7, SAM was negatively charged. NG600 was negatively charged. Therefore, the electrostatic repulsion between the negatively charged SAM and the negatively charged NG600 also partially account for the poor adsorption performance of NG600.

Figure 3.12. Adsorption performances (a) and catalytic performances (b) of catalysts prepared at different thermal annealing temperatures. TOC removal and PMS consumption in the NG600/PMS/SAM system (c) (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7).

3.3.2.1 Catalytic performance of NGs prepared at different temperatures

Figure 3.12(b) shows the catalytic activity of NGs fabricated at different synthesis temperatures. Direct PMS oxidation contributed to ~ 40% SAM removal efficiency within 60 min. The apparent first order reaction rate constant (k_{app}) of SAM degradation *via* PMS activation by GO, rGO600 and NGs was estimated using the pseudo first-order kinetics as shown below:

$$\ln \left(\frac{C}{C_o} \right) = -k_{app} t \quad (3.3.2.1.1)$$

where C_o is the initial SAM concentration and C is the SAM concentration at time t . The SAM degradation rate by direct PMS oxidation (0.0095 min^{-1}), GO/PMS (0.0086 min^{-1}) and NG400/PMS (0.0081 min^{-1}) (**Table A1, Appendix**) were comparable, indicating that GO and NG400 can hardly activate PMS for SAM degradation. Meanwhile, rGO600 (0.019 min^{-1}) exhibited 75% removal efficiency within 60 min, mainly due to its relatively higher adsorption efficiency. On the other hand, NG500, NG600, NG700 and NG800 exhibited catalytic activities for PMS activation. The performance of NGs prepared at different temperatures was in the following order: NG400 < NG500 < NG700 < NG800 < NG600. The poorer performance of NG400 (no significant catalytic activity) and NG500 (with 85% removal efficiency within 60 min) to activate PMS might be ascribed to: (1) the formation of tri-s-triazine (a type of nitrogen-containing heterocycle that is not conducive to PMS activation, which can be verified by the experiment for the comparison between g-C₃N₄ (**Appendix 1**) and NG600 in activating PMS for SAM degradation, as shown in **Figure 3.13**); (2) the relatively lower amount of graphitic N; and (3) the relatively small SSA (25 and 24 m² g⁻¹ for NG400 and NG500, respectively). The NG600 exhibited the highest catalytic activity with 100% SAM removal efficiency, 58% TOC removal, and 74% PMS consumption within 60 min (**Figure 3.12(c)**). The SAM degradation by NG600/PMS is 5 and 10 times faster than that of rGO/PMS and GO/PMS, respectively, indicating the catalytic activity of NG could be attributed to the N functional groups developed during N doping process. During NG synthesis, amino groups in the urea reacted with oxygen-containing functionalities on the GO surface (e.g., -OH and C=O). N atom was incorporated into the edges of carbon lattice to form pyridinic N and pyrrolic N first. As the thermal annealing temperature increased,

pyridinic N and pyrrolic N could be transformed into graphitic N (Seredych et al. 2008). Meanwhile, NH_3 and CO_2 would be released from the decomposition of urea to produce porous structure as well as N-doping. Urea was reported to yield low carbon nitride during pyrolysis (Schaber et al. 2004b) and a slow ramping rate (5°C min^{-1}) adopted in this study suppressed the formation of carbon nitride at thermal annealing temperature of $\geq 600^\circ\text{C}$ (Liao et al. 2012). Meanwhile, the N doping level and reactive functional groups to activate PMS can be tailored by changing the thermal annealing temperature. Therefore, NG600 possesses a higher N doping level (16.0 wt%) and an optimal amount of pyridinic N (38.4%N), pyrrolic N (31.8%N), graphitic N (25.9%N) and C=O groups (43.7%O) (**Table 3.1**), inducing SAM degradation via the best combination of radical and non-radical pathways. These factors contribute to the outstanding catalytic performance of NG600/PMS. The degradation of other antibiotics, namely SNM, SMX, and STZ in the NG600/PMS system were also investigated (**Figure 3.14**). The NG600/PMS system can remove these pollutants ($> 95\%$ removal efficiency) within 60 min, indicating that the NG600 is a promising carbocatalyst for sulfonamide antibiotics removal.

Figure 3.13. Catalytic performances of g-C₃N₄ and NG600 for SAM degradation via PMS activation (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7).

Figure 3.14. Performance of NG600 as PMS activator treating SAM, SNM, SMX and STZ (Condition: [PMS] = 0.5 mM, [pollutant] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7).

3.3.2.2 Catalytic performance of NGs prepared with different synthesis routes

Figure 3.15(b) compares the catalytic activities of NGs fabricated by different synthesis methods. The performance of the NGs (SAM removal efficiency, k_{app}) was in the order of NG600 (100%, 0.090 min⁻¹) > NG-NH₄NO₃-air (88%, 0.032 min⁻¹) > NG-urea-HT (65%, 0.017 min⁻¹) > NG-melamine-N₂ (59%, 0.014 min⁻¹). Thermal annealing temperature of > 600°C is required for the decomposition of carbon nitride formed during NG-melamine-N₂ synthesis process, and the following incorporation of N atom into the graphitic sheets by the interaction between the formed N species during carbon nitride decomposition and active sites on GO (Li et al. 2013). Thus, the thermal annealing temperature of 600°C adopted in the present study is not high enough to decompose carbon nitride. Besides, the SSA of NG-melamine-N₂ (8 m² g⁻¹) (**Table 3.2** and **Figure 3.10(c)**) is too small to provide necessary active sites for PMS activation. These two factors may mainly account for the poorest PMS activation performance of NG-melamine-N₂ for SAM degradation even with the highest N doping level (19.3 wt%) (**Table 3.1**), which can be substantiated by the tri-s-triazine peak detected in the FTIR spectra (**Figure 3.8(b)**).

Figure 3.15. Adsorption performances (a) and catalytic performances (b) of catalysts prepared via different synthesis methods (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7).

The NG-NH₄NO₃-air with the lowest N doping level of 4.82 wt% exhibited superior catalytic performance, i.e., ~ 2 times better than that of NG-melamine-N₂ or NG-urea-HT. The decomposition of NH₄NO₃ during synthesis released NH₃ which acts as a doping agent together with other gases like N₂ or N₂O, resulting in the NG with a porous structure and a large SSA (93 m² g⁻¹) (Table 3.2 and Figure 3.10(c)). As shown in Table 3.1, NG-NH₄NO₃-air possessed higher densities of pyrrolic N and pyridinic N than that of graphitic N. It was reported that the abundant free-flowing π -electrons from sp² graphitic plane can be activated through conjugating with the lone-pair electrons of N dopants to induce PMS activation and production of free radicals, and N functionalities at the edge (rather than graphitic N) improved the catalytic ability via PMS activation (Sun et al. 2013a).

The best SAM degradation performance of NG600 among the NGs might be due to reasons: 1) NG600 had a higher N doping level and an optimal amount of reactive functional groups (pyridinic N, pyrrolic N, graphitic N and C=O group) effective for the best combination of radical and non-radical pathways (**Table 3.1**); 2) NG600 had the highest I_D/I_G value (1.12) and lower O/C atomic ratio (8.00%) (**Table 3.1 and Figure 3.7(b)**), indicating more defective sites have been created for PMS activation due to N doping and removal of oxygen-containing functional groups; and 3) NG600 had a relative high SSA ($74 \text{ m}^2 \text{ g}^{-1}$) (**Table 3.2 and Figure 3.10(c)**) to provide a higher density of active sites for PMS activation. However, the SSA contributes less significantly than N doping to the degradation performance. The highest SSA of NG-urea-HT ($515 \text{ m}^2 \text{ g}^{-1}$) (**Table 3.2 and Figure 3.10(c)**) does not endow it with the best catalytic performance for SAM degradation via PMS activation. Therefore, the NG600 synthesis method adopted in this research makes an improvement in controlling N bonding configurations and is superior in producing a good PMS activator over other optimized methods found in the literature.

3.3.3 Effects of PMS dosage, catalyst loading and common matrix species

Since NG600 showed the best catalytic performance to activate PMS for SAM degradation, NG600 is selected for further kinetics study. To investigate the effect of PMS dosage on the catalytic performance of NG via PMS activation, 0.2, 0.5 and 0.9 mM PMS dosages were used and the corresponding molar ratios of PMS: SAM were 3.5:1, 10:1 and 20:1, respectively. **Figure 3.16(a)** shows that the SAM degradation rate of NG600 increases linearly from $k_{app} = 0.020$ to 0.19 min^{-1} with the increasing PMS dosage from 0.20 to 0.90 mM. The better catalytic performance at the higher PMS dosage can be attributed to increased interaction between PMS and catalysts, which is conducive to SAM degradation via both radical generation and non-radical pathways.

Figure 3.16. The effect of (a) PMS dosage, (b) catalyst loading and (c) common matrix species on the SAM degradation by NG600 via PMS activation (Condition: $[\text{PMS}] = 0.2, 0.5, 0.9 \text{ mM}$, $[\text{SAM}] = 10 \text{ mg L}^{-1}$, $[\text{catalyst}] = 0.1, 0.2, 0.3 \text{ g L}^{-1}$, $[\text{Cl}^-] = 100 \text{ mg L}^{-1}$, $[\text{NO}_3^-] = 10 \text{ mg L}^{-1}$, $[\text{humic acid}] = 5 \text{ mg L}^{-1}$, $\text{pH} = 7$). Inset of (a) and (b): the relationship between SAM degradation rate and PMS dosage (a) and catalyst loading (b).

Figure 3.16(b) reveals that the catalytic activity of NG600 increases linearly from 0.015 to 0.020 min⁻¹ with the increasing catalyst loading from 0.1 to 0.3 g L⁻¹. A higher catalyst loading can provide more active sites for PMS activation, thus elevating the SAM degradation rate. The slopes of the linear plots in insets of **Figure 3.16(a)** and **Figure 3.16(b)** demonstrate that an increase in the catalyst loading improves SAM degradation 4 times more than an increase in the PMS dosage. Given it is easier to recover and recycle NG than PMS, it is operationally more economical to improve the SAM degradation by increasing catalyst loading than PMS dosage in the NG/PMS system.

Figure 3.16(c) presents the effects of several common matrix species. The actual wastewater usually contains inorganic ions (e.g., Cl⁻, SO₄²⁻, Mg²⁺, and Na⁺, etc.) and organics. Especially, humic acid (soluble in alkaline media and insoluble at pH 1) is the principal component of humic substances which account for 50-80% of dissolved organic matters (DOM) in natural waters with respect to dissolved organic carbon (Hertkorn et al. 2002, Janoš 2003). Some of the common aqueous matrix species serve as the quenching agents to diminish the catalytic performance in the NG600/PMS/SAM system. Background matters such as Cl⁻, NO₃⁻ and humic acid were selected in this study and their concentrations were set according to the real secondary wastewater effluent (Oh et al. 2015). While NO₃⁻ exhibited a negligible effect (< 5%) on SAM degradation in the NG600/PMS/SAM system, Cl⁻ and humic acid both affected the SAM degradation negatively, leading to 25% and 43% decreases in the k_{app} values, respectively. The Cl⁻ is a relatively strong SO₄^{•-} scavenger with pseudo-second order rate constant of $k_{SO_4^{\bullet-}+Cl^-} = 3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Anipsitakis et al. 2006, Lutze et al. 2015b). This suppression caused by humic acid can be attributed to the competition for ROS between SAM and humic acid (comprising organics with carbon and oxygen-based moieties, such as carboxylate, carbonyl and phenolic groups with high reactivity (Bai et al. 2008)) in the NG600/PMS/SAM system.

3.3.4 Mechanism of PMS activation by NG

3.3.4.1 Quenching experiments and electron paramagnetic resonance analysis

As described in **Section 2.5.2.1**, radical pathway can be triggered by delocalized π electrons from vacancies, zigzag/armchair edges, Lewis basic sites with lone-pair electrons, and conjugation between lone-pair electrons of N dopants and the abundant free-flowing π -electrons from sp^2 carbons of graphene. These factors can function as electron donors, which transfer electrons to activate PMS by O-O bond cleavage and thereby produce $SO_4^{\bullet-}$ and $HO^{\bullet}$. Then pollutants (electron donor) can be oxidized into CO_2 and H_2O by $SO_4^{\bullet-}$ and $HO^{\bullet}$ (electron acceptor). Non-radical pathway refers to the degradation of the organic pollutants via the direct electron transfer without production of radicals. For the NG/PMS system, non-radical pathway can work through forming outer-sphere complexes between NG and PMS to facilitate pollutant degradation. The surface activated PMS (electron acceptor) can readily react with the adsorbed organic pollutant (electron donor) resulting in PMS consumption. The formation of surface activated PMS can be significantly hampered by the increase in the ionic strength of the reaction system (Zhang et al. 2014c).

To investigate the possible PMS activation mechanism in the NG600/PMS/SAM system, chemical scavenger (with ethanol and NB as ROS scavengers) and EPR were employed to determine the dominant pathway contributing to SAM degradation. In the radical scavenger method, ethanol can be used to scavenge both $SO_4^{\bullet-}$ and $HO^{\bullet}$ ($k_{SO_4^{\bullet-}+ethanol} = 10^7 \text{ M}^{-1} \text{ s}^{-1}$, $k_{HO^{\bullet}+ethanol} = 10^9 \text{ M}^{-1} \text{ s}^{-1}$). NB can serve as a quenching agent for $HO^{\bullet}$ ($k_{HO^{\bullet}+NB} (3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}) \gg k_{SO_4^{\bullet-}+NB} (< 10^6 \text{ M}^{-1} \text{ s}^{-1})$) (**Table 2.7**) (Chen et al. 2018b).

As shown in **Figure 3.17**, in the NG600/PMS/SAM system, 1.5 M ethanol led to 20% reduction in k_{app} , while 25 mg L^{-1} NB did not exert significant influence in the SAM degradation (11% reduction in k_{app}). Furthermore, the results of the EPR study are presented in **Figure 3.18**. There were no obvious characteristic signals present in the EPR spectra of experiments conducted with (i) DMPO and (ii) PMS + SAM +DMPO systems, respectively. However, in the NG600/PMS/SAM system, the characteristic signals of DMPOX (which were formed by the oxidation of DMPO)

with heptet were detected, instead of DMPO- $\text{SO}_4^{\cdot-}$ or DMPO- $\text{HO}^{\cdot}$ adducts. Based on the results of the chemical scavengers and EPR studies, it can be construed that the non-radical pathway is the key contributor to SAM degradation compared with radicals (such as $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$) in the NG600/PMS/SAM system.

Figure 3.17. The effect of ethanol and NB as quenching agents on the SAM removal and SAM degradation rate (inset) in the NG600/PMS/SAM (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7, [ethanol] = 1.5 M, [NB] = 25 mg L⁻¹).

Figure 3.18. EPR spectra detection in (i) DMPO, (ii) PMS + SAM + DMPO, and (iii) NG600 + PMS + SAM + DMPO. (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7, [DMPO] = 11.5 mM).

3.3.4.2 Density Functional Theory calculation

The DFT calculations were adopted to give further insights into the PMS activation process on NG. **Figure 3.19** presents structural information of adsorbed and free PMS based on DFT calculation. As shown in **Figure 3.19**, after PMS being adsorbed on the graphitic N area of NG, the position of the peroxide O-O bond changed slightly, much closer to the graphitic sheet of NG. The E_{ads} between PMS and NG was calculated by $E_{\text{ads}} = E_{\text{graphene} + \text{PMS}} - E_{\text{graphene}} - E_{\text{PMS}}$, where $E_{\text{graphene} + \text{PMS}}$, E_{graphene} , E_{PMS} are total energies of graphene with PMS adsorption, graphene alone, and free PMS molecule, respectively. DFT calculation results for PMS activation on graphitic N are $E_{\text{ads}} = -2.78 \text{ eV}$ and $Q = -0.908 \text{ e}$ (where Q is the number of electrons transferred between PMS and NG), which indicates a high E_{ads} of PMS on the graphitic N area of NG and significant electron transfer from NG to PMS. Therefore, the graphitic N can activate PMS through enhancing adsorption of PMS on NG and transferring electrons from the sp^2 carbon network of NG to PMS to form surface activated PMS with a slight change in the position of O-O bond, resulting in the slight rearrangement of electron structure of PMS. Collaboratively, results of the radical quenching experiment, EPR and DFT substantiated that non-radical pathway with surface activated PMS as the main ROS is the dominant pathway compared with radical pathway in the NG600/PMS/SAM system. The proposed mechanism of PMS activation and SAM degradation on the NG is shown in **Figure 3.20** and Eqs 3.3.4.2.1 - 3.3.4.2.6 as follows:

Figure 3.19. Structural information of adsorbed and free PMS based on DFT calculation.

Figure 3.20. Mechanism of PMS activation and SAM degradation on NG600.

3.3.5 Proposed major sulfacetamide degradation pathway

Figure 3.21 presents the main SAM degradation pathways in the NG600/PMS/SAM system while the mass spectra of the detected intermediates are presented in **Figure A3 (Appendix)**. A total of 5 intermediates were detected from the mass spectra. Based on the detected intermediates, the main SAM degradation

pathways are proposed. The first reaction step for SAM degradation involves electron transfer reaction between ROS (e.g., surface activated PMS, $\text{SO}_4^{\cdot-}$, $\text{HO}^{\cdot}$, etc.) and the aromatic amino group of SAM to form nitroso-substitutional SAM (A, m/z (-) 227.1), which can be further oxidized into nitro-substitutional SAM (B, m/z (-) 243.1) (Ji et al. 2015, Mahdi Ahmed et al. 2012). The nitro-substitutional sulfonamides have been documented to be detected in the ESI negative mode (Bao et al. 2019). Considering that the aromatic amino group is an important bioactive functional group of sulfonamide antibiotics, oxidation of the aromatic amino group can effectively remove the bioactivity of SAM (Corcoran 1975). Afterwards, the electrophilic C1-attack mediated by $\text{HO}^{\cdot}$ may lead to the formation of 4-nitrophenol (C, m/z (-) 138.1) (Ge et al. 2018). It has been reported that 4-nitrophenol can be detected in the ESI negative mode (Guan et al. 2019, Souza et al. 2016, Yang et al. 2019). The other possible degradation pathway is that nitroso-substitutional SAM (A, m/z (-) 227.1) can directly go through electrophilic C1-attack to form 4-nitrosophenol (D, m/z (-) 122.0). The intermediate E with m/z (-) = 305.2 could be assigned to the polymerized SAM byproduct. Subsequently, the ring opening reaction takes place and the SAM intermediates are further degraded to mineral acids, inorganic anions, CO_2 and H_2O . The mineralization of SAM is further evidenced by the results of TOC removal efficiency of 58% (at $t = 60$ min, $[\text{PMS}] = 0.5$ mM, $[\text{SAM}] = 10$ mg L^{-1} , $[\text{NG600}] = 0.2$ g L^{-1} , $\text{pH} = 7$).

Figure 3.21. The main SAM degradation pathways in the NG600/PMS/SAM system (Condition: $[\text{PMS}] = 0.5$ mM, $[\text{SAM}] = 10$ mg L^{-1} , $[\text{catalyst}] = 0.2$ g L^{-1} , $\text{pH} = 7$).

3.3.6 Reusability

The reusability of NG600 is shown in **Figure 3.22**. Compared with 1st run (100% SAM removal within 50 min, 0.090 min⁻¹), the SAM degradation efficiency decreased to 92% (0.021 min⁻¹) and 58% (0.007 min⁻¹) within 120 min in the 2nd and 3rd run, respectively. To gain insights into the reusability of NG600, the N bonding configuration was analyzed by XPS (**Figure 3.23**). As shown in **Table 3.3**, the contents of graphitic N (from 25.9%N to 11.9%N), pyridinic N (from 38.4%N to 32.2%N) and nitric oxide (from 3.94%N to 3.34%N) all decreased, whereas pyrrolic N increased from 31.8%N to 52.2%N. Overall, the total N content of the NG600 remained unchanged (5% reduction after 3rd run), indicating that dopant reconstruction occurred in the graphene network during PMS activation process, and graphitic N, pyridinic N and nitric oxide were converted to pyrrolic N (Eq 3.3.6.1).

$$\text{pyridinic N / graphitic N} \rightarrow \text{pyrrolic N} \quad (3.3.6.1)$$

The deactivation of NG600 are mainly due to the occupation of active sites by the SAM intermediates adsorbed and the change in the N bonding configuration, inhibiting outer-sphere interaction and the radical production. It was reported that in terms of formation energies of the three N types, pyrrolic N and pyridinic N are significantly more stable than graphitic N by about 110 kJ/mol. Pyrrolic N is slightly more stable than the pyridinic N (Tian et al. 2015). In an oxidative environment of NG600/PMS system, the reconstruction of N dopants could occur due to the attack of ROS (e.g. surface activated PMS, SO₄^{•-} and HO[•]) on pyridinic N and graphitic N (cannibalistic reaction), resulting in the conversion of pyridinic N / graphitic N to a more stable pyrrolic N. To recover the catalytic activity of NG, the heat treatment can be employed for the passivated NG (Guo et al. 2018), because high thermal annealing temperature favors the formation of graphitic N and can remove the adsorbed intermediates. Given the relationship between the cannibalistic reaction and N dopants reconstruction is not clear enough, further investigation is needed to probe this relationship and develop more efficient and robust carbocatalysts with certain structures, such as the core-shell structure with excellent tunability and stability (Li et al. 2017b) or with some specifically engineered reactive functional groups that can withstand harsh oxidative environment (Oh et al. 2016).

Figure 3.22. Reusability of NG600 (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7).

Figure 3.23. N1s scans of the fresh NG600 (a) and used NG600 after three consecutive cycles (b).

Table 3.3. Chemical composition of the fresh NG600 and used NG600

	N	O/C	N/C	pyridinic N	pyrrolic N	graphitic N	nitric oxide
	wt%	at.%	at.%	N_{pyridinic N}/N_{total} (%)	N_{pyrrolic N}/N_{total} (%)	N_{graphitic N}/N_{total} (%)	N_{nitric oxide}/N_{total} (%)
NG600	16.0	8.00	18.3	38.4	31.8	25.9	3.94
NG600 3rd run	15.2	10.0	17.6	32.2	52.5	11.9	3.34

Weight percentages of carbon, nitrogen and oxygen were analyzed by CHNS/O analyzer. Atomic percentages of pyridinic N, pyrrolic N, graphitic N, nitric oxide and C=O were analyzed by XPS.

3.4 Conclusion

The XPS results demonstrated that four N bonding configurations, namely, pyridinic N, pyrrolic N, graphitic N and nitric oxide, can occur on the doped graphene. Due to their different thermal stabilities and catalytic activities, the contents of different N species and the catalytic performance of NGs can be well controlled by the thermal annealing temperature. The N doping level and the contents of pyridinic N, pyrrolic N and C=O groups of NG400-NG800 manifested a negative correlation with the thermal annealing temperature. The contents of graphitic N and nitric oxide correlated positively with the thermal annealing temperature. The NG endowed with catalytic activity should be synthesized at thermal annealing temperatures of $\geq 500^{\circ}\text{C}$. The NG600 with a higher N doping level (16.0 wt%) and an optimal amount of pyridinic N (38.4%N), pyrrolic N (31.8%N), graphitic N (25.9%N) and C=O groups (43.7%O) exhibited the best performance for SAM decomposition via PMS activation. NG600 was superior as a good PMS activator over NGs prepared via other optimized methods found in the literature. Milder synthesis methods or adoption of melamine as a nitrogen source were inefficacious to produce the desirable N bonding configurations. The efficiency of SAM degradation followed the order of NG600 > NG-NH₄NO₃-air > NG-urea-HT > NG-melamine-N₂. The SSA contributed less significantly than N doping to the SAM degradation performance. It was operationally more economical to improve the SAM degradation by increasing catalyst loading than PMS dosage in the NG/PMS/SAM system. Non-radical pathway contributed more to SAM degradation than radical pathway. Surface activated PMS was the key reactive species for the SAM degradation in the NG/PMS/SAM system. The conversion of graphitic N and pyridinic N to pyrrolic N partially contributed to the deactivation of NG600. Further efforts can be put in improving the stability of carbocatalysts. This study gives a further insight into the role of different surface N functional groups in the PMS activation, facilitating the future development in carbocatalysts engineering via chemical functionalization with the specific reactive groups.

CHAPTER 4: NITROGEN AND BORON-CO-DOPED GRAPHENE FOR PEROXYMONOSULFATE ACTIVATION

4.1 Introduction

In **Chapter 3**, NG fabricated via thermal annealing method with urea as a nitrogen source demonstrated the outstanding catalytic activity to activate PMS for SAM degradation. N bonding configuration can be effectively tuned by adjusting the synthesis temperature. In contrast, it has been reported that BG, PG or SG exhibit limited catalytic activity toward PMS activation for phenol degradation (Duan et al. 2015e, Duan et al. 2015f). Hence, it comes naturally to a question whether co-doping could further improve the catalytic performance of carbocatalyst as PMS activator. As described in the **Section 2.5.2.2.2**, co-doping with P or I is not effective in enhancing the catalytic activity of NG for phenol degradation via PMS activation at the current state of knowledge (Sun et al. 2013a). However, NSG exhibited a remarkably enhanced catalytic performance to activate PMS for degradation of phenol and BPA (Duan et al. 2015f, Ma et al. 2019).

As highlighted in **Section 2.3.3**, N and B atoms are promising candidates for co-doping graphene. The bonding configuration of N and B atoms in the graphitic framework of NBG is a pivotal factor affecting the catalytic activity of NBG. The B-C-N heteroring (especially B atom is meta to N atom) in the NBG fabricated by a two-step synthesis method has been reported to exhibit synergistic effect that renders NBG a superior electrocatalyst over NG or BG (Tai et al. 2014). On the other hand, hexagonal boron nitride (h-BN) has been reported to form during the one-step NBG synthesis, which exhibited chemical inertness and hampered oxygen reduction reaction (ORR) catalyzed by NBG (Wang et al. 2012c, Zheng et al. 2013). However, h-BN has also been claimed to play a key role in nitroarenes reduction catalyzed by NBG (Yang et al. 2018a) and serve as adsorbent for organic contaminants (Jia et al. 2016, Lei et al. 2013). Thus, the formation of N-B bonding configuration is closely associated with synthesis method and it remains disputable in terms of the catalytic activity of different N-B bonding configurations toward PMS activation.

So far, most research about NBG as carbocatalyst is related to ORR (Tabassum et al. 2016, Tai et al. 2014, Wang et al. 2012c, Zheng et al. 2013), triiodide reduction (Yu et al. 2016), and nitroarenes reduction (Yang et al. 2018a). To the best of our knowledge, limited research has focused on NBG acting as a carbocatalyst to activate PMS for degradation of aqueous organic contaminants. As highlighted in the **Section 2.5.2.2.2**, Sun et al. (Sun et al. 2013a) claimed that NBG (0.1 wt% B₂O₃) prepared by one-step thermal annealing (GO + NH₄NO₃ + H₈B₁₀N₂O₁₆·8H₂O) outperformed NG as PMS activator to degrade phenol, whereas Duan et al. (Duan et al. 2015e) reported the reverse scenario and proposed the formation of h-BN as a reason for the deteriorated catalysis (**Table 2.3**). Thus, it is still debatable in terms of the catalytic activity of NBG for PMS activation to degrade the aqueous organic contaminants. Besides, the reactive N-B bonding configurations in carbocatalysis need to be identified.

Herein, in the study of this chapter, the hypotheses are proposed as follows: 1) NBG dominated by h-BN or B-C-N heteroring can be realized by deliberately designed synthesis methods (thermal annealing with common C (GO), N (urea) and B (H₃BO₃) precursors under different sequences: one step or two steps); 2) the concentration of different N-B bonding configurations can be tuned by adjusting the synthesis conditions (e.g., synthesis temperature); and 3) NBG with different N-B bonding configurations will demonstrate different catalytic activities to activate PMS for degradation of aqueous organic contaminants in terms of degradation kinetics, catalytic mechanism and reusability.

Thus, the objectives of the study in this chapter are as follows: 1) to synthesize 2sNBG free of h-BN via the deliberately designed two-step thermal annealing, whereby NG was first synthesized via thermal annealing, followed by incorporation of B atoms via second-step thermal annealing; 2) to synthesize 1sNBG containing h-BN via the deliberately designed one-step thermal annealing, whereby the mixture of GO, urea and H₃BO₃ was calcined in one-pot mode; 3) to fabricate 2sNBGs possessing different doping levels of N and B atoms as well as N-B bonding configurations through tuning the thermal annealing temperature (T_a) (600, 700, 800 and 900°C); 4) to investigate the effect of T_a on the structural and compositional properties (e.g., SSA, doping levels of N and B atoms, N-B bonding configuration,

etc.) of 2sNBGs; 5) to explore catalytic capabilities of 2sNBGs via PMS activation for degradation of SAM in the aqueous environment, the catalytic mechanism of PMS activation, degradation pathway and reusability; and 6) to fabricate 1sNBGs under selected T_a (600, 700, 800 and 900°C) and compare the compositional and structural properties as well as catalytic performances between 1sNBG and 2sNBG.

4.2 Experimental

4.2.1 Chemicals

The chemicals employed in the study of this chapter include graphite powder (> 99.9%, Alfa Aesar), hydrogen peroxide (30%, Alfa Aesar), concentrated sulfuric acid (98%, Sigma-Aldrich), potassium permanganate (99%, Sigma-Aldrich), sodium nitrate (99%, Sigma-Aldrich), hydrochloric acid (37%, Sigma-Aldrich), peroxymonosulfate (PMS, commercially available as Oxone (2KHSO₅.KHSO₄.K₂SO₄), Alfa Aesar), urea (99.0-100.5%, Sigma-Aldrich), boric acid ($\geq$ 99%, Sigma-Aldrich), sulfacetamide (SAM) ($\geq$ 98%, Sigma-Aldrich), sulfanilamide (SNM) ($\geq$ 98%, Sigma-Aldrich), sulfamethoxazole (SMX) ($\geq$ 98%, Sigma-Aldrich), sulfathiazole (STZ) ($\geq$ 98%, Sigma-Aldrich), nitrobenzene (NB) ($\geq$ 99%, Sigma-Aldrich), humic acid (technical grade, Merck), absolute ethanol ($\geq$ 99.5%, Merck), methanol ($\geq$ 99.9%, Sigma-Aldrich), sodium hydroxide ($\geq$ 98%, Sigma-Aldrich), sodium chloride ($\geq$ 99.5%, Alfa Aesar). All the chemicals were used without further purification. Milli-Q ultrapure water with a resistivity of 18.2 M Ω .cm (25°C) was used for all the experiments.

4.2.2 Two-step synthesis

Step 1: NG600 synthesis

NG600 was prepared using a thermal annealing method as described in **Section 3.2.2** (NG800 was also synthesized as described in **Section 3.2.2** as a control group).

Step 2: 2sNBG synthesis

Exactly 100 mg of NG600 was put into 50 mL water and sonicated for 30 min. Then 500 mg of H₃BO₃ was added into the NG600 suspension and sonicated for another 30 min for H₃BO₃ dissolution. The mixture was then heated to 55°C

(magnetically stirred, 500 rpm) for water evaporation. After grinding, the dried NG600/H₃BO₃ mixture was transferred to a quartz boat and then into the tubular furnace operated under N₂ atmosphere. The furnace was progressively heated at a ramping rate of 10°C min⁻¹ to the desired T_a (600, 700, 800 and 900°C) and maintained for 30 min. The products were then ground and put into the 80°C Milli-Q ultrapure water (magnetically stirred, 500 rpm) to dissolve the impurities (such as the residual B₂O₃). Afterwards, the products were filtered and washed several times with absolute ethanol and water, and then dried in an oven at 60°C. The final products prepared via the two-step approach were designated as 2sNBG600, 2sNBG700, 2sNBG800 and 2sNBG900, respectively.

4.2.3 One-step synthesis

For comparison, NBG was also synthesized via one-step thermal annealing method. GO (200 mg) was dissolved in 100-mL water and sonicated for 30 min. Then 1 g of urea and 500 mg of H₃BO₃ were added and sonicated for another 30 min for dissolution of urea and H₃BO₃. Then the mixture was heated to 55°C (magnetically stirred, 500 rpm) for water evaporation. After grinding, the dried GO/urea/H₃BO₃ mixture was transferred to a quartz boat and then into the tubular furnace operated under N₂ atmosphere. The furnace was progressively heated at a ramping rate of 10°C min⁻¹ to the desired T_a (600, 700, 800 and 900°C) and maintained for 30 min. The products were then ground and put into the 80°C Milli-Q ultrapure water (magnetically stirred, 500 rpm) to dissolve impurities (such as the residual B₂O₃). Afterwards, the products were filtered and washed several times with absolute ethanol and water, and then dried in an oven at 60°C. The final products prepared via the one-step approach were denoted as 1sNBG600, 1sNBG700, 1sNBG800 and 1sNBG900, respectively.

rGO800 was synthesized as follows: exactly 200 mg of GO was ground and calcined at 800°C in a N₂ atmosphere for 30 min in the tubular furnace with the ramping rate of 5°C min⁻¹. Afterwards, the product was ground, filtered and washed by a large amount of water and absolute ethanol in sequence and then dried at 60°C overnight in an oven. The final product was denoted as rGO800.

BG800 was synthesized as follows: exactly 200 mg of GO was dispersed in 100-mL water in a 250-mL beaker and sonicated for 30 min, followed by adding 500 mg H_3BO_3 . The mixture was sonicated for 30 min for H_3BO_3 dissolution. Then the temperature of the mixture was increased to 55°C while stirring using a hotplate to evaporate water. The resulted dried GO/ H_3BO_3 mixture was ground and calcined at 800°C in a N_2 atmosphere for 30 min in the tubular furnace with the ramping rate of $10^\circ\text{C min}^{-1}$. The product was then ground and put into the 80°C Milli-Q ultrapure water while stirring using a hotplate to dissolve impurities (such as the residual B_2O_3). Afterwards, the product was filtered and washed by a large amount of water and absolute ethanol in sequence and then dried at 60°C overnight in an oven. The final product was denoted as BG800.

4.2.4 Characterization

The characterization techniques used for studying the characteristics of NBGs were presented in **Section 3.2.3**.

4.2.5 Evaluation of sulfacetamide catalytic oxidation

The performance of NBG was evaluated as PMS activator to degrade aqueous SAM. A 50-mL solution containing 10 mg L^{-1} SAM and 0.5 mM PMS was prepared in a 100-mL beaker, followed by the addition of carbocatalyst (0.2 g L^{-1}) into the solution ($\text{pH}_{\text{initial}} = 7$). The suspension was magnetically stirred at 600 rpm to initiate the catalytic oxidation. Solution sample (0.5 mL) was taken and filtered ($0.45 \mu\text{m}$ hydrophilic polyethersulfone membrane) at designated time intervals, and then immediately quenched with 0.5 mL methanol. Then the SAM concentration in the filter solution was determined by a HPLC as described in **Section 3.2.4**. The adsorption experiment was similar to the catalytic experiment except the addition of PMS and methanol as quenching agent.

The effect of catalyst loading (0.1 , 0.2 and 0.3 g L^{-1}), PMS dosage (0.2 , 0.5 and 0.9 mM), and common matrix species ($[\text{Cl}^-] = 100 \text{ mg L}^{-1}$, $[\text{NO}_3^-] = 10 \text{ mg L}^{-1}$, [humic acid] = 5 mg L^{-1}) on the SAM removal in the 2sNBG/PMS/SAM system was probed. The possible ROS in the 2sNBG/PMS/SAM system was explored using ethanol and NB as radical scavengers. The measurement of TOC, the main intermediates of SAM

generated in the 2sNBG/PMS/SAM system, and the pH_{pzc} of 2sNBG800 was same as described in **Section 3.2.4**. Each of the experiments was carried out in triplicate. Error bars represent the standard deviation.

4.2.6 Reusability

2sNBG800 reusability experiment was similar to that described in **Section 3.2.5**. The analyses of XPS, FTIR and TGA were conducted for the 2sNBG 3rd run (the used 2sNBG after three consecutive cycles). The concentration of B element in the solution after each run was analyzed on the ICP Mass spectrometer (PerkinElmer SCIEX, ELAN DRC-e).

4.2.7 Theoretical methodology for Density Functional Theory calculation

The spin-polarized DFT calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) code with projected augmented wave (PAW) approach for calculation of energies (Kresse and Furthmüller 1996, Kresse and Furthmüller 1996, Kresse and Hafner 1993, 1994). The exchange-correlation interactions were treated with the GGA parameterized by Perdew-Burke-Ernzerhof (PBE) function (Perdew et al. 1996). The cutoff energy of plane-wave basis was set to 400 eV. The atomic positions were fully relaxed with convergence tolerance for energy and force were set to be 10^{-4} eV and 0.03 eV/Å, respectively. The gamma point was used for sampling the Brillouin zone for all the calculations within a vacuum box of $30\text{Å} \times 30\text{Å} \times 20\text{Å}$ to avoid the interaction between the nonperiodic graphene clusters. The carbon atoms at the open ends of the graphene slabs were saturated by hydrogen atoms to alleviate the dangling-bond effect. The DFT-D3 exchange functionals have been applied for corrections of the van der Waals (vdW) interactions (Klimeš et al. 2011). The charge density analysis and electron transfer were analyzed by the Bader code (Bader 1994, Tang et al. 2009). The E_{ads} (Zheng et al. 2014) of PMS onto different graphene substrates can be defined as

$$E_{\text{ads}} = E_{\text{graphene+PMS}} - E_{\text{graphene}} - E_{\text{PMS}} \quad (4.2.7.1)$$

where $E_{\text{graphene+PMS}}$, E_{graphene} and E_{PMS} represent for the total energy of the PMS adsorbed graphene composite, free graphene and PMS molecule, respectively.

4.3 Results and discussion

4.3.1 Characterization of carbocatalysts

4.3.1.1 2sNBGs fabricated under selected thermal annealing temperatures

Morphologies of 2sNBGs were investigated through FESEM and TEM. As shown in FESEM images (**Figure 4.1(a)-(b)** and **(g)-(l)**), compared with GO with a silk veil-like structure, after thermal annealing and doping process, more exfoliation and wrinkles were created. The incorporation of N atoms induced more exfoliation and crumples than that of B atoms. The 2sNBG800 was found to be most exfoliated. The higher degree of exfoliation provides more active sites exposed for carbocatalysis. The partially aggregated and corrugated structure was obtained at the boundaries of the carbon network of 2sNBG800, originating from the structural distortion and the created defective sites after N, B-co-doping. Furthermore, the TEM images (**Figure 4.1(d)-(e)** and **(m)-(n)**) reveal that the characteristic 2D planar-like structure of graphene was still maintained after thermal annealing and doping. 2sNBG800 possessed more wrinkles and folding at the edges of graphitic sheets. The EDX elemental mappings of 2sNBG800 show the homogeneous distribution of the doped N and B atoms over the carbon network of 2sNBG800 (**Figure 4.2(a)-(e)**).

Figure 4.1. FESEM images of NG600 (a), 2sNBG800 (b), 1sNBG800 (c), GO (g), rGO800 (h), BG800 (i), 2sNBG600 (j), 2sNBG700 (k) and 2sNBG900 (l). TEM images of NG600 (d), 2sNBG800 (e), 1sNBG800 (f), GO (m) and rGO800 (n).

Figure 4.2. EDX maps of (b) C, (c) O, (d) N and (e) B elements for 2sNBG800 according to the corresponding FESEM image (a). EDX maps of (g) C, (h) O, (i) N and (j) B elements for 1sNBG800 according to the corresponding FESEM image (f).

The XRD patterns of 2sNBGs are shown in **Figure 4.3**. After thermal annealing and doping, the characteristic strong (002) peak at $2\theta = 10^\circ$ (the corresponding interlayer spacing = 0.854 nm) in the XRD pattern of GO completely disappeared, whereas a new broad peak at $\sim 26^\circ$ (graphene (002) crystal plane) appeared in the XRD patterns of rGO800, NG600, BG800 and 2sNBGs, which suggests the exfoliation and reduction (removal of oxygen-containing functional groups) of GO. Negligible influence on the crystalline structure of graphene was caused by the doping treatment (Yuan et al. 2016). Compared with rGO800 (25.9° , 0.335 nm) and BG800 (26.0° , 0.334 nm), the peaks of NG600 (26.7° , 0.325 nm) and 2sNBGs ($\sim 26.3^\circ$, 0.330 nm) shifted to a higher 2θ degree, which indicates that more reduction and exfoliation can be induced by N doping using urea as a nitrogen source, whereby urea can act as an expansion-reduction agent (Wakeland et al. 2010).

Figure 4.3. XRD patterns of GO, rGO800, BG800, NG600 and 2sNBGs.

Raman spectra can provide further information on the structure of 2sNBGs. Two remarkable peaks at $\sim 1350\text{ cm}^{-1}$ (D-band) and $\sim 1580\text{ cm}^{-1}$ (G-band) correspond to the disorder content and graphitic symmetry, respectively, were observed in all the Raman spectra. The intensity ratio of D- to G-band (I_D/I_G) is closely related to the level of disorder of carbocatalysts. **Figure 4.4 and Table 4.1(a)** show thermal annealing (I_D/I_G of rGO800: 0.99) and doping processes can increase the defective degree of GO (I_D/I_G of GO: 0.96). Compared with single N doping (1.02) or B doping (1.02), N, B-co-doping (2sNBGs: 1.02-1.04), especially at a high T_a , can further increase the I_D/I_G ratio, which can be explained as follows: 1) the difference in the bond distance between C-N/C-B and C-C enhanced the asymmetry of electron distribution in the graphitic domain, further indicating the successful incorporation of N and B heteroatoms (Zheng et al. 2013); 2) more defective sites (e.g., zigzag/armchair edges and vacancies) were generated by reduction and doping; and 3) smaller-size graphitic nanosheets were created (Stankovich et al. 2007). 2sNBG800 had the highest defective level ($I_D/I_G = 1.04$).

Figure 4.4. Raman spectra of GO, rGO800, BG800, NG600 and 2sNBGs.

FTIR can be employed to study the functional groups of 2sNBGs. As shown in **Figure 4.5**, after thermal reduction and doping, the peak of C=C bond shifted from 1620 cm^{-1} of GO to 1553 cm^{-1} of rGO800, NG600, BG800 and 2sNBGs. Besides, a new broad peak centered at $\sim 1175\text{ cm}^{-1}$ was found in the FTIR spectra of rGO800, NG600, BG800 and 2sNBGs, which is ascribed to C-N/C-B/B-O/residue C-O bonds (Lee et al. 2015a, Lin et al. 2012b, Xu et al. 2014). Notably, BG800 still maintained the broad peak centered at 3413 cm^{-1} (associated with the H_2O adsorption or O-H stretching), which implies that B doping can improve the hydrophilicity of rGO.

Figure 4.5. FTIR spectra of GO, rGO800, BG800, NG600 and 2sNBGs.

TGA can be used to explore the thermal stability of 2sNBGs. As shown in **Figure 4.6**, all the carbocatalysts (rGO800, NG600, BG800 and 2sNBGs) processed by thermal annealing and doping demonstrated enhanced thermo-oxidative stability of up to 500°C in air, which suggests the existence of the well-ordered graphitic carbon framework in those carbocatalysts (Jung et al. 2014). After N, B-co-doping, the thermal stability of all the 2sNBGs was improved in comparison to that of rGO800, NG600 and BG800, especially at the high T_a . The substituted B atoms in the graphitic carbon framework (BC3) has been documented to be capable of promoting the graphitization and suppressing the oxidation (Serp and Machado 2015). Hence, the formation of BC3 can reinforce the sp^2 graphitic carbon framework, which is commensurate with the following XPS analysis of 2sNBG800 with the highest level of BC3 (43.4 at.%, B_{BC3}/B_{total}) (**Table 4.1(b)** and **Figure 4.7(b)**) and the resultant high thermal stability of 2sNBG800. Notably, ~ 15 wt% residual can be detected in the BG800 TGA curve after combustion at 900°C in air. It has been reported that the combustion sites can be blocked by B doping, which retards the oxidation of graphitic carbons even at the elevated T_a (Jones and Thrower 1987, Lee and Radovic 2003, McKee 1991). Compared with rGO800, the relatively higher initial weight loss of BG800 can be attributed to the evaporation of absorbed water, which is commensurate with the obvious broad peak detected at $\sim 3413\text{ cm}^{-1}$ in the FTIR spectrum of BG800 (**Figure 4.5**) and further confirms the B doping can promote the hydrophilicity of rGO (Yuan et al. 2016).

Figure 4.6. TGA curves of GO, rGO800, BG800, NG600 and 2sNBGs.

Table 4.1(a). Structural and chemical information of GO, rGO, NG, NBGs and BG

	C at. %	O at. %	N at. %	B at. %	O/C	N/C	B/C	N/B	I_b/I_G
GO	53.2	42.8	-	-	0.80	-	-	-	0.96
rGO800	88.5	11.5	-	-	0.13	-	-	-	0.99
NG600	77.9	11.6	10.4	-	0.15	0.13	-	-	1.02
2sNBG600	80.4	7.8	10.2	1.6	0.10	0.13	0.02	6.38	1.02
2sNBG700	72.6	9.9	11.0	6.5	0.14	0.15	0.09	1.70	1.03
2sNBG800	56.6	13.2	13.8	16.3	0.23	0.24	0.29	0.84	1.04
2sNBG900	58.7	13.7	12.5	15.1	0.23	0.21	0.26	0.83	1.03
1sNBG800	53.2	15.9	13.3	17.6	0.30	0.25	0.33	0.76	1.12
BG800	84.9	11.6	-	3.4	0.14	-	0.04	-	1.02

Atomic percentages of C, O, N and B were analyzed by XPS.

Table 4.1(b). XPS deconvolution information of NG, NBGs and BG

	pyridinic N	pyrrolic N	graphitic N	N of h-NB	BC3	BC2O/BCO2	B-O	B of h-NB
	N _{pyridinic-N} /N _{total} (%)	N _{pyrrolic-N} /N _{total} (%)	N _{graphitic-N} /N _{total} (%)	N _{h-NB} /N _{total} (%)	B _{BC3} /B _{total} (%)	B _{BC2O or BCO2} /B _{total} (%)	B _{B-O} /B _{total} (%)	B _{h-NB} /B _{total} (%)
NG600 ^a	34.5	21.7	30.8	-	-	-	-	-
2sNBG600	28.5	39.7	31.7	-	7.0	57.8 (BC2O)/35.2(BCO2)	-	-
2sNBG700	55.6	16.4	28.0	-	25.6	41.4(BC2O) /33.0(BCO2)	-	-
2sNBG800	73.4	23.2	3.4	-	43.4	56.6(BC2O)	-	-
2sNBG900	64.0	30.2	5.8	-	34.9	65.1(BC2O)	-	-
1sNBG800	43.4	18.4	7.8	30.4	17.2	29.0(BC2O) /20.9(BCO2)	-	32.8
BG800	-	-	-	-	21.1	-	78.9	-

Atomic percentages of pyridinic N, pyrrolic N, graphitic N, h-NB, BC3, BC2O/BCO2 and B-O were analyzed by XPS.

^a NG600 still contained nitric oxide (13.0 at.%) (N_{nitric oxide}/N_{total}) apart from pyridinic N, pyrrolic N and graphitic N, while other carbocatalysts in the Table 1(b) just contained pyridinic N, pyrrolic N and graphitic N in the high resolution N1s spectrum.

The chemical compositions of 2sNBGs were acquired from XPS analysis (**Figure A4(m), Appendix**). The detailed information is shown in **Table 4.1(a)**. After incorporation of B atoms into NG600, the atomic ratio of N/C of 2sNBGs increased from 0.13 to 0.24 with an increase in T_a from 600 to 800°C, then slightly decreased at 900°C (N/C = 0.21). The atomic ratio of B/C of 2sNBGs raised from 0.02 to 0.29 with the elevated T_a from 600 to 800°C, whereas the atomic ratio of B/C of 2sNBG900 was slightly reduced to 0.26, exhibiting the similar trend to that of N/C. The reduction of the atomic ratios of N/C and B/C in 2sNBG900 results from the breakup of C-N and C-B bond at a high T_a (Tabassum et al. 2016). The raised T_a induces a relatively greater increase in B/C ($\Delta = 0.27$) than that of N/C ($\Delta = 0.11$), which implies that the higher T_a facilitates B doping into NG. Among all the 2sNBGs, 2sNBG800 had the highest level of N (13.8 at.%) and B (16.3 at.%).

The XPS N1s fitting (394-407 eV) was obtained for all 2sNBGs (**Figure A4(a)(c)(e)(g), Appendix**). The detailed information is shown in **Table 4.1(b) and Figure 4.7(a)**. The most common N bonding configurations include pyrrolic N (N in a 5-membered heteroring, 398.76-400.3 eV), pyridinic N (N in a 6-membered heteroring on the edges, 397.95-399 eV) and graphitic N (sp^2 hybridized N adjacent to three sp^2 C atoms, 400.9-401.7 eV) (Tai et al. 2014). All three categories of N species were identified in the 2sNBGs. However, the typical N (397.6-397.9 eV) in h-BN (Lin et al. 2012a, Tabassum et al. 2016, Young et al. 2007) was not detected. As described in **Chapter 3**, with the elevated T_a , the content of pyridinic N and pyrrolic N of NG would decrease in NG, while the content of graphitic N would increase due to the better thermal stability (Chen et al. 2018a). However, a different scenario occurs for two-step N, B-co-doping. The content of pyridinic N increased from 28.5 to 73.4 at.% ($N_{\text{pyridinic-N}}/N_{\text{total}}$) with an increase in T_a from 600 to 800°C, whereas 2sNBG900 had a slightly reduced pyridinic N content of 64.0 at.% ($N_{\text{pyridinic-N}}/N_{\text{total}}$). By contrast, the content of graphitic N decreased from 31.7 to 3.4 at.% ($N_{\text{graphitic-N}}/N_{\text{total}}$) with the elevated T_a from 600 to 800°C, while 2sNBG900 had a slightly increased graphitic N content of 5.8 at.% ($N_{\text{graphitic-N}}/N_{\text{total}}$), which suggests that the sequential incorporation of B atoms can induce the conversion of N bonding configurations in NG (Yang et al. 2018a, Yu et al. 2016). 2sNBG800 had the highest level of pyridinic N (73.4 at.%, $N_{\text{pyridinic-N}}/N_{\text{total}}$).

Figure 4.7. The doing level and the concentration of bonding configuration of N dopant (a) and B dopant (b) in 2sNBGs, 1sNBG800, NG600 and BG800, and their influence on k_{app} (catalytic activity) of the carbocatalysts.

The XPS B1s fitting (184-200 eV) was obtained for all 2sNBGs (**Figure A4 (b)(d)(f)(h), Appendix**). The detailed information is displayed in **Table 4.1(b)** and **Figure 4.7(b)**. The B signals can be deconvoluted into BC3 (189-190 eV), B of h-

BN (190.6-191 eV), B-C-O (BC₂O/BCO₂) (191-192 eV) and B-O (192-193 eV) (Tai et al. 2014, Young et al. 2007, Zhao et al. 2013c, Zheng et al. 2013). BC₃ and BC₂O/BCO₂ were detected for all the 2sNBGs. The B in h-BN was barely detected. The content of BC₃ increased from 7.0 to 43.4 at.% (B_{BC3}/B_{total}) with the elevated T_a from 600 to 800°C, and decreased slightly to 34.9 at.% (B_{BC3}/B_{total}) at 900°C, which follows the similar trend to that of pyridinic N and implies that the high T_a can facilitate the substitutional doping of B. 2sNBG800 had the highest level of BC₃ (43.4 at.%, B_{BC3}/B_{total}). No B-O bond was detected for all the 2sNBGs, whereas 78.9 at.% (B_{B-O}/B_{total}) of B-O existed in BG800, which is ascribed to the large amount of oxygen functional groups in GO and the high T_a (Chen et al. 2015, Tai et al. 2014, Zheng et al. 2013).

Table 4.2 and **Figure 4.8(a) and (b)** show the textural properties of 2sNBGs. Similarly, as described in the **Section 3.3.1.1**, GO had the lowest SSA (26 m² g⁻¹). However, SSA can be dramatically increased after the thermal annealing, leading to the highest SSA value (450 m² g⁻¹) of rGO800. The incorporation of N or B atoms can reduce the SSA from 450 m² g⁻¹ of rGO to 51-84 m² g⁻¹ of N, B single/co-doped graphene, which can be associated with the disorientation and corrugation of graphitic basal planes due to the introduction of dopants (Qu et al. 2010). The elevated T_a slightly increases the SSA value of 2sNBGs from 51 to 62 m² g⁻¹. 2sNBG800 possessed the highest SSA value of 62 m² g⁻¹ among all the 2sNBGs. All the carbocatalysts in this study are mainly comprised of mesopores (distribution of pore radius mainly centered at ~ 2 nm).

Figure 4.8. (a) N₂ sorption isotherm and (b) pore size distributions of GO, rGO800, NG600, BG800, 2sNBGs and 1sNBG800.

Table 4.2. SSA, pore volume and pore size information of GO, rGO, NG, NBGs and BG

Catalyst	BET SSA (m ² g ⁻¹)	Average pore volume ^a (cm ³ g ⁻¹)	Average pore size ^b (nm)
GO	26	0.017	2.03
rGO800	450	0.439	2.02
NG600	51	0.102	2.01
2sNBG600	51	0.110	2.03
2sNBG700	55	0.116	2.03
2sNBG800	62	0.122	2.02
2sNBG900	61	0.109	2.02
1sNBG800	30	0.048	2.02
BG800	84	0.104	2.02

^a BJH method cumulative desorption pore volume.^b BJH method desorption pore radius (Mode D_v(r)).

4.3.1.2 Comparison between 1sNBG and 2sNBG

Compared with 2sNBG800, FESEM (**Figure 4.1(c)**) and TEM (**Figure 4.1(f)**) images of 1sNBG800 both demonstrate 1sNBG800 still maintained the planar 2D structure of graphene. However, 1sNBG800 was less wrinkled albeit with more random aggregation of layers, which has been documented in the case of h-BN nanosheets (Bhimanapati et al. 2014) and is related to the relatively lower SSA of 1sNBG800 ($30 \text{ m}^2 \text{ g}^{-1}$) (**Table 4.2**). EDX elemental mappings of 1sNBG800 (**Figure 4.2(f)-(j)**) demonstrate that N and B heteroatoms were uniformly distributed across the sheets of 1sNBG.

As shown in **Table 4.1(a)**, in comparison to 2sNBG800 (the atomic ratio of N/C: 0.24, B/C: 0.29 and O/C: 0.23), 1sNBG800 had a relatively higher level of N (N/C: 0.25), B (B/C: 0.33) and O (O/C: 0.30) in its XPS spectrum (**Figure A4(m)**, **Appendix**). **Table 4.1(b)**, **Figure 4.7** and **Figure A4(k)** and **(l)** (**Appendix**) show that 30.4 at.% N of h-BN ($N_{\text{h-BN}}/N_{\text{total}}$) can be detected apart from pyridinic N (43.4 at.%, $N_{\text{pyridinic-N}}/N_{\text{total}}$), pyrrolic N (18.4 at.%, $N_{\text{pyrrolic-N}}/N_{\text{total}}$) and graphitic N (7.8 at.%, $N_{\text{graphitic-N}}/N_{\text{total}}$) in 1sNBG800. By contrast, 2sNBG800 had a higher level of pyridinic N (73.4 at.%, $N_{\text{pyridinic-N}}/N_{\text{total}}$) and none of N of h-BN. Similarly, 32.8 at.% B of h-BN ($B_{\text{h-BN}}/B_{\text{total}}$) can be detected besides BC3 (17.2 at.%, $B_{\text{BC3}}/B_{\text{total}}$) and BC2O (29.0 at.%) / BCO2 (20.9 at.%) ($B_{\text{BC2O or BCO2}}/B_{\text{total}}$) in 1sNBG800. By contrast, 2sNBG800 had a higher BC3 (43.4 at.%, $B_{\text{BC3}}/B_{\text{total}}$) content and none of B of h-BN.

As shown in **Figure 4.9(a)**, the XRD pattern of 1sNBG800 is similar to that of 2sNBG800 ($2\theta = 26.3^\circ$, 0.330 nm) with a strong peak at $2\theta = 26.8^\circ$ (0.324 nm), which cannot exclude the existence of h-BN in 1sNBG800. This is because the (002) orientation of h-BN nanosheets corresponds to the characteristic peak at $2\theta = 26.8^\circ$ (Bhimanapati et al. 2014, Ma et al. 2011) and the crystalline h-BN is less likely to form at 800°C (Oh et al. 2019). As shown in **Figure 4.9(b)** and **Table 4.1(a)**, 1sNBG800 exhibited the highest $I_{\text{D}}/I_{\text{G}}$ ratio (1.12) among all the carbocatalysts in this study with a wider D band, which indicates the formation of h-BN (Zheng et al. 2013). It has been reported that the two characteristic FTIR peaks of h-BN are $\sim 1390 \text{ cm}^{-1}$ (in-plane bending) and $\sim 780 \text{ cm}^{-1}$ (out-of-plane stretching). Thus, the two strong peaks (1375 and 755 cm^{-1}) in the FTIR spectrum of 1sNBG800 (**Figure 4.9(c)**)

further confirm the formation of h-BN/NBG hybrid. TGA curve of 1sNBG800 (**Figure 4.9(d)**) exhibits that, among all the carbocatalysts in this study, the oxidation of 1sNBG800 was significantly retarded (46 wt% residual after combustion at 900°C in air), which is associated with the high thermal stability of h-BN (up to 2950°C) (Bhimanapati et al. 2014, Ma et al. 2011) and commensurate with the FTIR result. Around 30 wt% weight loss of 1sNBG800 below 600°C can be attributed to the desorption of absorbed water in the interspace between h-BN and graphene sheets (Ma et al. 2011). As shown in **Table 4.2** and **Figure 4.8**, 1sNBG800 had a lower SSA ($30 \text{ m}^2 \text{ g}^{-1}$) and mediocre pore volume ($0.048 \text{ cm}^3 \text{ g}^{-1}$) in comparison to those of 2sNBG800 ($62 \text{ m}^2 \text{ g}^{-1}$ and $0.122 \text{ cm}^3 \text{ g}^{-1}$), which can be associated with the formation of h-BN.

Figure 4.9. Comparison between 1sNBG800 and 2sNBG800 in (a) XRD patterns, (b) Raman spectra, (c) FTIR spectra and (d) TGA curves.

Thus, results of the above characterization of 1sNBG800 and 2sNBG indicate that one-step thermal annealing (simultaneous incorporation of N and B heteroatoms) leads to the formation of h-BN (byproduct)/NBG hybrid (the structure shown in the inset of **Figure A4(k), Appendix**). However, two-step thermal annealing (sequential incorporation of N and B) results in the h-BN-free NBG. From the thermodynamic perspective, there is a tendency for the separation of C-rich domain and BN-rich domain (Blase et al. 1999). However, the kinetics of a specific synthesis method usually controls the formation of N-B bonding configurations, leading to the possible existence of B-C-N heteroring (Golberg et al. 2002). The kinetics of a specific synthesis are comprehensively determined by the synthesis parameters (e.g.,

precursor, temperature, flow rate, in situ generated gas, etc.) (Golberg et al. 2004), which account for the differences in the N-B bonding configurations caused by one-step and two-step thermal annealing methods used in this study. Besides, in one-pot synthesis, the direct interaction between urea and H_3BO_3 can also induce the formation of h-BN. Further efforts can be dedicated to the role of those abovementioned synthesis parameters in formation of N-B bonding structures.

4.3.2 Catalytic performance of NBGs

The catalytic activity of NBGs was evaluated in the catalytic activation of PMS to degrade aqueous SAM. Generally, less than 10% of SAM could be adsorbed within 60 min by the carbocatalysts except for rGO800 (**Table A2, Appendix** and **Figure 4.10(a)**). rGO800 can adsorb 35% SAM within 60 min, which is associated with its high SSA value of $450 \text{ m}^2 \text{ g}^{-1}$ (**Table 4.2** and **Figure 4.8**) and surface functionalities conducive to adsorption. The SSA of NG600, BG800 and 2sNBGs are in the same range from 51 to $84 \text{ m}^2 \text{ g}^{-1}$, whereas 1sNBG800 had the relatively low SSA of $30 \text{ m}^2 \text{ g}^{-1}$ (**Table 4.2** and **Figure 4.8**). The poor adsorption capacity of the doped graphene is associated with their relatively low SSA and reduced π - π interactions with SAM, attributed to the alteration of surface chemistry and lattice distortion by the incorporation of the dopants. Besides, the pH_{pzc} of 2sNBG800 is 6.2 (**Figure A2(b)**). Under the solution $\text{pH} = 7$, SAM was negatively charged. 2sNBG800 was negatively charged. Therefore, the electrostatic repulsion between the negatively charged SAM and the negatively charged 2sNBG800 also partially account for the poor adsorption performance of 2sNBG800.

Figure 4.10. (a) Adsorption performances of all the carbocatalysts prepared in this study. Catalytic performances of (b) 2sNBGs and (c) 1sNBGs to activate PMS for SAM degradation (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7).

4.3.2.1 PMS-activating ability of 2sNBGs

The catalytic activities of 2sNBGs prepared under selected T_a are shown in **Figure 4.10(b)**. The pseudo first-order kinetics was used to estimate k_{app} of SAM removal on carbocatalysts through PMS activation as described in **Section 3.3.2.1**. GO (0.009 min^{-1}) and BG800 (0.009 min^{-1}) can hardly activate PMS with only $\sim 40\%$ SAM removal within 60 min (**Table A2, Appendix**). It has been reported that substitutional B atoms (BC3) (21.1 at.%, B_{BC3}/B_{total} in BG800) (**Table 4.1(b)** and **Figure 4.7(b)**) tend to lower the electron density of the graphitic nanocarbon network (Wu and Radovic 2005). Besides, the inactivity of B-O bond (78.9 at.%, B_{B-O}/B_{total} in BG800) (**Table 4.1(b)** and **Figure 4.7(b)**) has been documented (Tai et al. 2014). Thus, B doping (BG800) resulted in a suppression of PMS activation. rGO800 exhibited 76% SAM removal within 60 min (0.020 min^{-1}), primarily attributed to its outstanding adsorption ability (**Figure 4.10 (b)** and **Table A2, Appendix**). NG600 achieved 100% removal of SAM within 50 min (the catalytic activity of NG800 (0.071 min^{-1}) was lower than that of NG600 (0.090 min^{-1})) (**Chapter 3, Figure 4.11 and Table A2, Appendix**). However, all the 2sNBGs outperformed NG600 in terms of catalytic activity and followed the order of 2sNBG800 (0.182 min^{-1}) > 2sNBG900 (0.161 min^{-1}) > 2sNBG700 (0.133 min^{-1}) > 2sNBG600 (0.110 min^{-1}) > NG600 (0.090 min^{-1}) (**Table A2, Appendix**). Given that the SSA of 2sNBGs is in the same range of $51\text{-}61 \text{ m}^2 \text{ g}^{-1}$ (**Table 4.2** and **Figure 4.8**), the catalytic performance of 2sNBGs is probably dominated by active sites rather than SSA. 2sNBG800 performed best to activate PMS for SAM degradation, inducing 20-, 9- and 2-fold improvements over GO, rGO800 and NG600, respectively. The order of catalytic capability of 2sNBGs followed the similar trend of the changes in the contents of pyridinic N and BC3 of 2sNBGs with the elevated T_a (**Figure 4.7**).

Figure 4.11. Catalytic performance of NG600, NG800, 2sNBG800 and 1sNBG800 (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7).

The best catalytic performance of 2sNBG800 can be explained as follows:

1) As described in the **Chapter 3**, the separated N atoms (not linked to B) can boost the catalytic activity of 2sNBG800 as they did in NG600 mainly through the non-radical pathway to form surface activated species (Chen et al. 2018a, Li et al. 2017a).

2) Compared with single N doping, the synergistic coupling effect between N and B atoms, especially synergy between pyridinic N and BC3, can contribute to the enhanced catalytic activity of 2sNBG (**Section 4.3.3**). Besides, the inactivity of B-C-O bond (BC2O/BCO2) has been reported in oxygen reduction (Zheng et al. 2013). 2sNBG800 possessed the highest levels of N (13.8 at.%) and B (16.3 at.%), the highest contents of pyridinic N (73.4 at.%, $N_{\text{pyridinic-N}}/N_{\text{total}}$) and BC3 (43.4 at.%, $B_{\text{BC3}}/B_{\text{total}}$), the lowest B-C-O content (56.6 at.% BC2O, $B_{\text{BC2O}}/B_{\text{total}}$), and none of h-BN (**Table 4.1** and **Figure 4.7**). The optimal surface chemistry secures its highest catalytic activity for PMS activation to degrade SAM.

3) 2sNBG800 had the highest I_D/I_G ratio of 1.04 (**Figure 4.4** and **Table 4.1(a)**) among all the 2sNBGs, indicating that rich defective sites have been created in 2sNBG800. As described in the **Section 2.4.2**, the zigzag/armchair edges can activate PMS by cleaving the peroxide O-O bond for the generation of $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$, whereas the vacancies are more capable of adsorbing PMS to form a surface complex with fewer transfer electrons from graphitic lattice to PMS to coordinate the non-radical

oxidation (Duan et al. 2016c).

An increase in PMS dosage (leading to enhanced interactions between PMS and 2sNBG800) or catalyst loading of 2sNBG800 (more active sites brought in for PMS activation) can further enhance the SAM degradation in the 2sNBG800/PMS/SAM system (**Figure 4.12(a) and (b)**). However, comparing the slopes of the linear plots (the insets of **Figure 4.12(a) and (b)**), the enhancement in SAM degradation efficiency caused by increasing catalyst loading is ~ 3 times higher than that caused by increasing PMS dosage. Given that recovering and recycling 2sNBG is easier than that of PMS, the increase in the catalyst loading operationally outperforms that of PMS dosage for the enhanced SAM degradation. Meanwhile, the downstream impact of residual PMS can be reduced. The catalytic activity of 2sNBG800 was also investigated for the degradation of other antibiotics (e.g., SNM, SMX and STZ) (**Figure 4.12(c)**). These pollutants can be eliminated within 30 min by 2sNBG800/PMS, which suggests that 2sNBG can be used as a promising carbocatalyst to remove sulfonamides.

Figure 4.12. The effect of (a) PMS dosage and (b) catalyst loading on the SAM degradation by 2sNBG800 via PMS activation (Condition: [PMS] = 0.2, 0.5, 0.9 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.1, 0.2, 0.3 g L⁻¹, pH = 7). Insets of (a) and (b): the relationship between SAM degradation rate and PMS dosage (a) and catalyst loading (b). (c) Removal of SAM, SNM, SMX and STZ in the 2sNBG800/PMS system. (Condition: [PMS] = 0.5 mM, [pollutant] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7).

4.3.2.2 Comparison in catalytic performance between 1sNBGs and 2sNBGs

Figure 4.10(c) demonstrates the catalytic performance of 1sNBG600, 1sNBG700, 1sNBG800 and 1sNBG900 as compared to that of 2sNBG800, NG600, rGO800 and GO. The SAM removal efficiency and *k_{app}* in 1sNBGs/PMS/SAM system fall between 54-60% within 60 min and 0.013-0.014 min⁻¹ (Table A2, Appendix), respectively. Therefore, the elevated *T_a* did not induce a great difference in the catalytic activity of 1sNBGs. All the 1sNBGs performed worse than NG600

with 100% SAM removal (reaction time = 50 min, $k_{app} = 0.090 \text{ min}^{-1}$) (**Table A2, Appendix**). The catalytic performance of all the doped carbocatalysts employed in this study follows the order of 2sNBGs > NG600 > 1sNBGs > BG800. The poor catalytic performance of 1sNBG800 can be explained as follows: 1) 1sNBG800 has been demonstrated to be a h-BN/graphene hybrid according to its characterization analysis in this study. h-BN has been reported to be chemically inert (Ma et al. 2011), which is caused by the neutralization between the bonded N and B atoms. Specifically, the vacant orbital of B atom can be significantly neutralized by the lone-pair electrons of the adjacent N atom, which leads to looser electron density to conjugate with the free-flowing π -electrons from sp^2 carbons in graphene (Zhao et al. 2013c); and 2) the relatively lower SSA of 1sNBG800 ($30 \text{ m}^2 \text{ g}^{-1}$) (**Table 4.2 and Figure 4.8**) results in limited access to active sites for PMS activation. Therefore, the two-step strategy in this study successfully limited the formation of h-BN, giving rise to maneuvered and favorable N-B bonding configurations (especially pyridinic N and BC3) for PMS activation.

4.3.3 Mechanism of PMS activation in the 2sNBG800/PMS/SAM system

4.3.3.1 Quenching experiments

As described in **Section 3.3.4.1**, non-radical oxidation with surface activated PMS as the main ROS is the dominant pathway over radical oxidation in the NG600/PMS/SAM system. For comparison, 1.5 M ethanol and 25 mg L^{-1} NB have also been selected to probe the possible catalytic mechanism of PMS activation in the 2sNBG800/PMS/SAM systems.

As shown in **Figure 4.13**, in the NG600/PMS/SAM system, 1.5 M ethanol led to 20% reduction in k_{app} , while 25 mg L^{-1} NB did not exert significant influence in the SAM degradation (11% reduction in k_{app}). By contrast, in the 2sNBG800/PMS/SAM system, 45% and 24% decreases in k_{app} were induced by 1.5 M ethanol and 25 mg L^{-1} NB, respectively. 1.5 M ethanol (molar ratio of ethanol: PMS = 3000 : 1) can effectively quench radicals produced in the Co^{2+} /PMS/SAM system (87% reduction in k_{app}) (**Figure 4.14**), which is well known as a pure radical based system (Ghanbari and Moradi 2017). Thus, it indicates that NG600/PMS/SAM is a non-radical-

dominated system and the incorporation of B atoms into NG facilitates the shift of non-radical oxidation to radical oxidation in the 2sNBG800/PMS/SAM system. Both $\text{HO}^\bullet$ and $\text{SO}_4^{\bullet-}$ partially contributed to the SAM oxidation in the 2sNBG800/PMS/SAM system.

Figure 4.13. The effect of ethanol and NB as quenching agents on the SAM removal (a) and SAM degradation rate (b) in the NG600/PMS/SAM and 2sNBG800/PMS/SAM systems (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7, [ethanol] = 1.5 M, [NB] = 25 mg L⁻¹).

Figure 4.14. The effect of ethanol as quenching agent on the SAM degradation in the Co²⁺/PMS/SAM system (Condition: [PMS] = 1 mM, [SAM] = 10 mg L⁻¹, [Co²⁺] = 0.2 mM, [ethanol] = 0.5 and 1.5 M).

4.3.3.2 Density Functional Theory calculation

DFT calculation was conducted to further elucidate the catalytic mechanism in the single-doped graphene (NG or BG) and co-doped graphene (NBG) for PMS activation. PMS activation process on different atomic structures of graphene before and after doping is shown in **Figure 4.15**. The E_{ads} of PMS onto different graphene substrates, length of O-O bond (l_{O-O}) and electron transfer (Q) from carbon to PMS were calculated for different graphene structures before and after doping (**Figure 4.16 - Figure 4.20, Table 4.3 - Table 4.7**). As shown in the summary of **Table 4.8**, as for single doping and pristine graphene (G), the enhancement in the E_{ads} , l_{O-O} , and Q follows the order of graphitic N-doped graphene (NG-g) > BG > G > pyridinic N-doped graphene (NG-pd) $\approx$ pyrrolic N-doped graphene (NG-pl). As for N, B-co-doping models, the enhancement order is pyridinic N and B-co-doped graphene (NBG-pd) > graphitic N and B-co-doped graphene (NBG-g) > pyrrolic N and B-co-doped graphene (NBG-pl).

The NG-g manifests the longest l_{O-O} (1.475 Å) and most electron transfer (0.959 e), suggesting that PMS can be effectively activated. The strongest adsorption energy ($E_{ads} = -2.468$ eV) implies that the activated PMS molecule will be intimately

confined on the carbon surface to form surface reactive species (non-radical pathway) rather than releasing $\text{SO}_4^{\bullet-}$.

NBG-pd-4 (4 indicates bonding configuration of B-C-C-C-pyridinic N, as shown in **Figure 4.15(g)** and **Figure 4.19**) also manifests a great performance for PMS activation with a prolonged peroxide O-O bond (1.470 Å vs 1.332 Å of free PMS) and a great electron transfer of 0.813 e from carbon to PMS. However, the E_{ads} is much smaller compared with NG-g, which indicates the potential to generate free radicals after the cleavage of peroxide O-O bonds (the radical pathway).

Figure 4.15. Atomic structures of graphene before and after doping: (a) pure graphene, (b) pyridinic N-doped graphene (NG-pd), (c) pyrrolic N-doped graphene (NG-pl), (d) graphitic N-doped graphene (NG-g), (e) BG, (f) graphitic N and B-co-doped graphene (NBG-g), (g) pyridinic N and B-co-doped graphene (NBG-pd) and (h) pyrrolic N and B-co-doped graphene (NBG-pl). Color codes: the gray, white, blue and pink are carbon, hydrogen, nitrogen and boron atoms, respectively. The number indicates the possible arrangement of dopants.

Figure 4.16. Illustrations of PMS adsorption on different graphene slabs: (a) pure graphene (G), (b) NG-pyridinic (NG-pd), (c) NG-pyrrolic (NG-pl), and (d) NG-graphitic (NG-g). Color codes: the gray, white and blue are carbon, hydrogen and nitrogen atoms, respectively.

Table 4.3. Theoretical computations of PMS adsorption onto pure graphene and different NG models, where l_{O-O} represents for the length (Å) of O-O bond, Q represents for the electron transfer (e) from carbon to PMS, and E_{ads} represents for the adsorption energy (eV)

Configuration	l_{O-O} (Å)	$Q(e)$	E_{ads} (eV)
Free PMS	1.332	-	-
G	1.420	0.617	-0.909
NG-pd	1.414	0.573	-0.847
NG-pl	1.416	0.582	-0.836
NG-g	1.475	0.959	-2.468

Figure 4.17. Illustrations of single BG slabs at different doping positions. Color codes: the gray, white and pink are carbon, hydrogen and boron atoms, respectively. The number indicates the possible arrangement of dopants.

Table 4.4. Theoretical computations of PMS adsorption onto different BG models

Configuration	lo-o (Å)	Q(e)	E _{ads} (eV)
BG-1	1.419	0.590	-0.819
BG-2	1.416	0.581	-0.827
BG-3	1.417	0.584	-0.816
BG-4	1.428	0.632	-0.867

Figure 4.18. Illustrations of PMS adsorption on different NBG-g slabs. Color codes: the gray, white, blue and pink are carbon, hydrogen, nitrogen and boron atoms, respectively. The number indicates the possible arrangement of dopants.

Table 4.5. PMS adsorption onto different NBG-g models

Configuration	lo-o (Å)	Q(e)	E _{ads} (eV)
NBG-g-1	1.427	0.656	-1.016
NBG-g-2	1.435	0.682	-1.074
NBG-g-3	1.437	0.683	-1.052
NBG-g-4	1.451	0.765	-1.220

Figure 4.19. Illustrations of PMS adsorption on different NBG-pd slabs. Color codes: the gray, white, blue and pink are carbon, hydrogen, nitrogen and boron atoms, respectively. The number indicates the possible arrangement of dopants.

Table 4.6. PMS adsorption onto different NBG-pd models

Configuration	lo-o (Å)	Q(e)	E _{ads} (eV)
NBG-pd-1	1.417	0.588	-0.926
NBG-pd-2	1.470	0.816	-1.701
NBG-pd-3	1.408	0.558	-0.749
NBG-pd-4	1.470	0.813	-1.721

Figure 4.20. Illustrations of PMS adsorption on different NBG-pl slabs. Color codes: the gray, white, blue and pink are carbon, hydrogen, nitrogen and boron atoms, respectively. The number indicates the possible arrangement of dopants.

Table 4.7. PMS adsorption onto different NBG-pl models

Configuration	lo-o (Å)	Q(e)	E _{ads} (eV)
NBG-pl-1	1.427	0.620	-0.922
NBG-pl-2	1.413	0.590	-0.800

Table 4.8. PMS adsorption onto different models of graphene before and after doping

Configuration	lo-o (Å)	Q(e)	E _{ads} (eV)
Free PMS	1.332	-	-
G	1.420	0.617	-0.909
BG	1.428	0.632	-0.867
NG-pd	1.414	0.573	-0.847
NG-pl	1.416	0.582	-0.836
NG-g	1.475	0.959	-2.468
^a NBG-pd-4	1.470	0.813	-1.721
^b NBG-pl-1	1.427	0.620	-0.922
^c NBG-g-4	1.451	0.765	-1.220

^a NBG-pd-4 refers to the B-C-C-C-pyridinic N structure (Figure 4.15(g) and Figure 4.19).

^b NBG-pl-1 refers to the B-pyrrolic N structure (Figure 4.15(h) and Figure 4.20).

^c NBG-g-4 refers to the B-C-C-C-graphitic N structure (Figure 4.15(f) and Figure 4.18).

Figure 4.22. Illustrations of charge density on BG slab. Color codes: the red number is negative charge and the blue number is positive charge. The gray, white and pink atoms are carbon, hydrogen and boron atoms, respectively.

Figure 4.23. Illustrations of charge density on slabs of (a) NBG-g-1, (b) NBG-g-2, (c) NBG-g-3 and (d) NBG-g-4. Number 1-4 indicate different B doping positions relative to graphitic N. Color codes: the red number is negative charge and the blue number is positive charge. The gray, white, blue and pink atoms are carbon, hydrogen, nitrogen and boron atoms, respectively.

Figure 4.24. Illustrations of charge density on slabs of (a) NBG-pd-1, (b) NBG-pd-2, (c) NBG-pd-3 and (d) NBG-pd-4. Number 1-4 indicate different B doping positions relative to pyridinic N. Color codes: the red number is negative charge and the blue number is positive charge. The gray, white, blue and pink atoms are carbon, hydrogen, nitrogen and boron atoms, respectively.

Figure 4.25. Illustrations of charge density on slabs of (a) NBG-pl-1 and (b) NBG-pl-2. Number 1 and 2 indicate different B doping positions relative to pyrrolic N. Color codes: the red number is negative charge and the blue number is positive charge. The gray, white, blue and pink atoms are carbon, hydrogen, nitrogen and boron atoms, respectively.

Figure 4.26. Molecular model of NBG-pd-4 (4 indicates bonding configuration of B-C-C-C-pyridinic N). Color codes: the gray, white, blue and pink are carbon, hydrogen, nitrogen and boron atoms, respectively.

Table 4.9. Charge density of atoms in the graphitic sheet

Atom number	Graphene	^a BG-4	^b NG-pd	^c NBG-pd-4
N	-	-	-0.854	-0.854
B	-	-1.045	-	-1.106
C1	-0.040	0.114	0.406	0.536
C2	-0.113	0.101	0.592	0.558
C3	-0.039	0.454	0.177	0.408
C4	0.124	0.222	-0.110	0.247
C5	0.186	0.235	0.142	0.276

^a BG-4 refers to B-doped graphene. 4 indicates the position of B atom in the graphitic sheet (**Figure 4.15(e)** and **Figure 4.17**).

^b NG-pd refers to pyridinic N-doped graphene (**Figure 4.15(b)** and **Figure 4.16**).

^c NBG-pd-4 refers to pyridinic N and B-co-doped graphene. 4 indicates the bonding configuration of B-C-C-C-pyridinic N (**Figure 4.15(g)** and **Figure 4.19**).

In regard to the better experimental performance of 2sNBG compared with NG, the phenomenon can be explained in two aspects. Firstly, as aforementioned, the 2sNBG contains both sole N sites and N, B-co-doped domains, which will simultaneously induce radical and non-radical pathways which have already been evidenced by the radical quenching tests (45% radical oxidation). The radical pathway is a homogeneous reaction which further accelerates the oxidation. More importantly, the N, B-co-doping can bring in more positively charged carbons in the graphene lattice, suggesting that more catalytic centers are generated for binding with the negatively charged oxygen atoms in PMS.

In addition, as shown in **Figure 4.27**, the two most reactive N dopants (pyridinic N and graphitic N) and their distances with B atom can induce different functions. Pyridinic N interacting with B in the position 2 (B meta to N, B-C-pyridinic N, $E_{\text{ads}} = -1.701$ eV) or 4 (B-C-C-C-pyridinic N, $E_{\text{ads}} = -1.721$ eV) demonstrate a higher E_{ads} , whereas the lower E_{ads} ($-0.926 \sim -1.016$ eV) was found when B is in position 1 (B ortho to N, B-N) for both pyridinic N and graphitic N. This DFT result explained the experimental phenomenon that the existence of h-BN deteriorated the performance of 1sNBG catalyzed PMS activation.

Figure 4.27. The effect of position of B relative to N on the E_{ads} of NBG. Position 1, position 2, position 3 and position 4 refer to bonding configurations of B-N, B-C-N, B-C-C-N and B-C-C-C-N, respectively.

In summary, DFT results theoretically verifies the experiment-derived order of catalytic activities: 2sNBGs > NG600 > 1sNBGs > BG800. The N, B-co-doping is highly reactive for PMS activation with a moderate adsorption energy, which is different from the single-graphitic N doping with strong adsorption. This suggests that intermediate of NBG/PMS is prone to be detached to induce a radical process ($\text{SO}_4^{\cdot-}$ or $\text{HO}^{\cdot}$). Types of N dopant and distance between N and B atoms significantly influence the charge density distribution of the carbon lattice, and therefore the catalytic activity of NBG. The synergistic coupling effect between pyridinic N and BC3 in the bonding configuration of B-C-C-C-pyridinic N can induce more positively charged carbon atoms as active sites, which boost the catalytic activity of 2sNBG for PMS activation. However, the neutralization between bonded N and B atoms (B ortho to N, B-N bond) results in the poorer performance of SAM degradation by 1sNBG (h-BN/NBG hybrid)/PMS. The proposed catalytic mechanism on different sites of 2sNBG800 for PMS activation is illustrated in **Figure 4.28**.

Figure 4.28. Mechanism of PMS activation and SAM degradation on 2sNBG800.

4.3.4 Proposed major sulfacetamide degradation pathway and ecotoxicity of products

The intermediates in the 2sNBG800/PMS/SAM system were analyzed by LC-

MS/MS. Generally, three main types of intermediates were generated in the 2sNBG800/PMS/SAM system: 1) nitroso- and nitro- derivatives, which can relate to the inclination of $\text{SO}_4^{\cdot-}$ to attack $-\text{NH}_2$ group; 2) hydroxylated products, which can relate to the reaction between SAM and $\text{HO}^{\cdot}$; and 3) dimeric products, which can relate to the recombination of N-centered radicals caused by $\text{SO}_4^{\cdot-}$ (Luo et al. 2017, Yang et al. 2017). Based on the seven intermediates identified in the mass spectra (**Figure A5, Appendix**), the four possible pathways for SAM degradation are profiled in **Figure 4.29**. The first two SAM degradation pathway is similar to that in the NG600/PMS/SAM system as described in the **Section 3.3.5**. The amino group connected with benzene ring can be oxidized to nitroso and nitro groups by ROS to form nitroso- (A, m/z (-) 227.1) and nitro-substitutional SAM (B, m/z (-) 243.1). Afterwards, the formation of 4-nitrophenol (C, m/z (-) 138.1) and 4-nitrosophenol (D, m/z (-) 122.0) may be induced through the electrophilic C1-attack mediated by $\text{HO}^{\cdot}$ in the 2sNBG800/PMS/SAM system. The third SAM degradation pathway can be initiated by direct removal of the amine group on the benzene ring of SAM to generate the intermediate E (m/z (-) 198.1). In the fourth SAM degradation pathway, the nitroso-substitutional SAM (A) can be polymerized with another benzene ring to produce intermediate F (m/z (-) 303.1). Another polymerized intermediate G (m/z (-) 477.2) has also been detected. Then, the intermediates can proceed to be degraded via ring opening and formation of small molecular derivatives (e.g. alcohols and acids), and finally be mineralized into SO_4^{2-} , NO_3^- , CO_3^{2-} , CO_2 and H_2O . Significant mineralization occurred in the 2sNBG800/PMS/SAM system, which can be observed from the 84% TOC removal efficiency (reaction time = 60 min) (**Figure 4.30**). From the results, it can be concluded that the transformation of amine groups and subsequent mineralization can effectively reduce the harmful effect of sulfonamides to the environment. 2sNBG fabricated by the two-step synthesis method in this study is effective in mineralizing the recalcitrant pollutant via PMS activation.

Figure 4.29. The main SAM degradation pathways in the 2sNBG800/PMS/SAM system (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7).

Figure 4.30. TOC removal in the 2sNBG800/PMS/SAM system.

4.3.5 Practical applications

4.3.5.1 Effect of common matrix species

As mentioned in **Section 3.3.3**, the quenching effect of Cl^- , NO_3^- and humic acid on the SAM degradation performance in the 2sNBG800/PMS/SAM system was investigated. As shown in **Fig. 12**, NO_3^- exerted a negligible influence (< 5%

reduction in k_{app}) on the PMS activation by 2sNBG800 to degrade SAM. By contrast, Cl^- and humic acid caused 33% and 64% reduction in k_{app} , respectively, suggesting more induced inhibition in the 2sNBG800/PMS/SAM system compared with that in the NG/PMS/SAM system (25% and 43%, respectively). That is associated with more radical oxidation (45%) induced in the 2sNBG800/PMS/SAM system, which is more susceptible to the quenching effect caused by Cl^- and humic acid.

Figure 4.31. The effect of common matrix species on the SAM degradation by 2sNBG800/PMS (Condition: $[\text{PMS}] = 0.5 \text{ mM}$, $[\text{SAM}] = 10 \text{ mg L}^{-1}$, $[\text{catalyst}] = 0.2 \text{ g L}^{-1}$, $[\text{Cl}^-] = 100 \text{ mg L}^{-1}$, $[\text{NO}_3^-] = 10 \text{ mg L}^{-1}$, $[\text{humic acid}] = 5 \text{ mg L}^{-1}$, $\text{pH} = 7$).

4.3.5.2 Reusability

Figure 4.32(a) demonstrates the stability of 2sNBG800. In comparison to 100% SAM removal within 20 min (0.182 min^{-1}) by the fresh 2sNBG800 in the 1st run, to achieve 100% SAM removal entailed 40 and 60 min in the 2nd (0.093 min^{-1}) and 3rd run (0.061 min^{-1}), respectively (**Table 4.10**). The chemical composition of the 2sNBG800 3rd run (2sNBG800 used after 3 consecutive cycles) was analyzed by XPS (**Table 4.11** and **Figure 4.33**). Compared with the fresh 2sNBG800, the N/C ratio of 2sNBG800 3rd run showed negligible change albeit with 41% and 22% declines in B/C and O/C ratios, respectively (**Table 4.11(a)**). The reduction of B/C and O/C ratios mainly correspond to the leaching of B element from B_2O_3 . Any other possible

reasons for the loss of B element in the catalysis process may involve the cannibalistic oxidation, whereby the generated ROS can attack the active sites in the carbocatalyst besides pollutant to deactivate the carbocatalyst (Oh et al. 2016). However, we tested the leaching B element in the solution collected after each run reaction and in the control experiment (2sNBG800 stirred in the Milli-Q at pH = 7 within 60 min) by ICP-MS. The leaching B element (0.024-0.140 mg L⁻¹) was detected in the solution collected after each run reaction by ICP-MS (**Table 4.10**), whereas 0.170 mg L⁻¹ B leaching can also be detected in the control experiment with 2sNBG800 stirred in the Milli-Q at pH = 7 within 60 min, which indicates the residual B₂O₃ (it is difficult to completely remove B₂O₃ despite the vigorous washing) is the dominant reason for the loss of B element over cannibalistic oxidation during catalytic process. Meanwhile, the content of pyridinic N and BC3 in 2sNBG800 3rd run demonstrated an insignificant change (< 10% reduction) in comparison to that of the fresh 2sNBG800 (**Table 4.11(b)**), suggesting that the catalytic sites are considerably stable for PMS activation.

Table 4.10. The performance of 2sNBG800 after each run

	SAM Degradation Efficiency (%)	<i>k_{app}</i> (min⁻¹)	^bElement B (mg L⁻¹)
^a1st run	100 (20 min)	0.182	0.140
^a2nd run	100 (40 min)	0.093	0.032
^a3rd run	100 (60 min)	0.061	0.024

^aCondition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7.

^bThe concentration of element B in the solution after each run detected by ICP-MS spectrometer.

Figure 4.32. (a) Reusability of 2sNBG800 (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L^{-1} , [catalyst] = 0.2 g L^{-1} , pH = 7). FTIR spectrum (b) and TGA curve (c) of the 2sNBG800 3rd run.

Figure 4.33. N1s scan (a) and B1s scan (b) of the fresh 2sNBG800. N1s scan (c) and B1s scan (d) of the 2sNBG800 3rd run. Survey scans (e) of the fresh 2sNBG800 and 2sNBG800 3rd run.

Table 4.11(a). Chemical composition of the fresh 2sNBG800 and used 2sNBG800

	C	O	N	B	O/C	N/C	B/C	N/B
	at. %	at. %	at. %	at. %				
Fresh 2sNBG800	56.6	13.2	13.8	16.3	0.23	0.24	0.29	0.84
2sNBG800 3rd run	64.5	11.7	12.3	11.2	0.18	0.19	0.17	1.09

Atomic percentages of C, O, N and B were analyzed by XPS.

Table 4.11(b). XPS deconvolution information of the fresh 2sNBG800 and 2sNBG800 3rd run

	pyridinic N	pyrrolic N	graphitic N	BC3	BC2O/BCO2
	N_{pyridinic-N}/N_{total} (%)	N_{pyrrolic-N}/N_{total} (%)	N_{graphitic-N}/N_{total} (%)	B_{BC3}/B_{total} (%)	B_{BC2O or BCO2}/B_{total} (%)
Fresh 2sNBG800	73.4	23.2	3.4	42.4	56.6 (BC2O)
2sNBG800 3rd run	66.0	26.4	7.6	41.0	59.0 (BC2O)

Atomic percentages of pyridinic N, pyrrolic N, graphitic N, BC3 and BC2O/BCO2 were analyzed by XPS.

FTIR analysis was conducted for 2sNBG800 3rd run. As shown in **Figure 4.32(b)**, the intensities of the peaks centered at $\sim 1350\text{ cm}^{-1}$ and $\sim 3400\text{ cm}^{-1}$ increased, which is associated with the adsorption of SAM degradation intermediates. It has been reported that the asymmetric stretch of S=O bond in sulfonamides is at 1325 cm^{-1} , the symmetric stretch of the aromatic nitro group is at $1355\text{-}1315\text{ cm}^{-1}$, and NH₂ stretch in sulfonamides is at $3350\text{-}3250\text{ cm}^{-1}$ (Pavia et al. 2015). In addition, the rapid weight loss can be observed in the TGA curve of the 2sNBG800 3rd run (**Figure 4.32(c)**), which suggests the existence of the adsorbed intermediates and corresponds to the FTIR result. Thus, the main reason for the deactivation of 2sNBG800 is the adsorbed intermediates occupying the active sites on the 2sNBG800 surface. Thermal regeneration (annealing at 350°C under N₂ atmosphere for 2 h with the heating rate of 5°C min^{-1}) was applied to burn the adsorbed intermediates covering the active sites of 2sNBG800 3rd run. The catalytic activity was recovered with 100% removal of SAM within 30 min ($k_{app} = 0.102\text{ min}^{-1}$) compared with 2sNBG800 3rd run (100% removal of SAM within 60 min, $k_{app} = 0.061\text{ min}^{-1}$) (**Figure 4.32(a)**).

4.4 Conclusion

In summary, this study carried out a two-step thermal annealing approach to produce 2sNBG without h-BN. The concentration of N and B dopants and the content of pyridinic N and BC3 of 2sNBGs showed a similar trend with elevated T_a (increasing from $600\text{-}800^\circ\text{C}$ and decreasing at 900°C). 2sNBG800 exhibited the best catalytic activity for PMS activation to degrade SAM. In contrast, the one-step thermal annealing would lead to the formation of a h-BN/NBG hybrid (1sNBG). The elevated T_a induced an insignificant difference in the catalytic activity of 1sNBGs. Two-step thermal annealing was superior in generating an ideal PMS activator for SAM degradation over one-step thermal annealing. The catalytic performance of the doped carbocatalysts followed the order of $2\text{sNBG}800 > 2\text{sNBG}900 > 2\text{sNBG}700 > 2\text{sNBG}600 > \text{NG}600 > 1\text{sNBGs} > \text{BG}800$. Both experimental results and DFT calculation collectively unveiled the mechanism for the remarkable catalytic efficiency of 2sNBG800. The reasons can be described as below: 1) both radical and non-radical oxidative reaction existed in the 2sNBG/PMS system, while NG/PMS

was a non-radical-dominated system; and 2) the synergistic coupling effect between pyridinic N and BC₃ (B-C-C-C-pyridinic N) brought in more positively charged carbon atoms as active sites for PMS activation. The neutralization effect in the B-N bond resulted in the poor performance of SAM degradation by 1sNBG (h-BN/NBG hybrid)/PMS. The transformation of the amine group and subsequent mineralization can effectively reduce the hazardous effect of sulfonamides to the environment. The presence of Cl⁻ and humic acid can more adversely affected the SAM removal in 2sNBG/PMS/SAM system compared with that in the NG600/PMS/SAM system. The occupation of active sites on the surface of 2sNBG by the adsorbed intermediates was the major reason for the deactivation of 2sNBG. Further efforts can be carried out to investigate the role of synthesis parameters in formation of N-B bonding configurations and develop more robust carbocatalysts engineered with rational functionalities toward practical application. This study contributes to a deeper insight into the functions of different N-B bonding configurations in carbocatalysts for PMS activation and provides an advanced strategy for fabricating high-performance carbocatalysts in environmental remediation.

CHAPTER 5: NITROGEN-DOPED CHITOSAN-DERIVED CARBON NANOSHEETS AS HIGHLY EFFECTIVE PEROXYMONOSULFATE ACTIVATOR

5.1 Introduction

As described in **Chapters 1** and **2**, biomass is an ideal alternative to conventional nanocarbons (e.g., graphene) as carbon precursor for carbocatalyst fabrication due to being cheap, sustainable and easily accessible. Particularly, chitosan with a similar chemical structure to glucose is the abundant N-containing biomass (containing large quantities of amino groups) in nature. Chitosan has garnered increasing interest because 1) a large amount of chitosan can be reclaimed from the crustacean skin waste (Chitichigrovsky et al. 2009, Primo and Quignard 2010); 2) carbonization of chitosan can lead to high carbon yield (~ 50 wt%) (Matei Ghimbeu and Luchnikov 2018); and 3) chitosan can serve as the carbon and nitrogen precursors simultaneously, resulting in nitrogen self-doping. NG has been reported to be synthesized from chitosan film via pyrolysis at 800°C under nitrogen atmosphere (Primo et al. 2012). However, the low nitrogen content in chitosan is prejudicial to nitrogen-doped carbocatalyst synthesized via high-temperature carbonization (Wu et al. 2015b). As highlighted in the **Chapter 3**, urea was a better nitrogen precursor to enhance the catalytic activity of graphene for decomposition of aqueous organic pollutants via PMS activation in comparison to melamine and NH_4NO_3 . Moreover, urea is the cheapest structure-directing agent (Liu et al. 2014, Wakeland et al. 2010). Basically, the g- C_3N_4 with the sp^2 C-N nanosheet structure can be formed upon the decomposition of urea at 500°C, which facilitates the evolution of graphene-like nanosheets with advantages such as excellent electric conductivity and high SSA (Lee et al. 2017).

To achieve the ample pore structure with high SSA and pore volume, the synthesis of biomass-derived nanocarbons usually involves some harsh treatments such as HF washing for etching elimination of hard template (Liu et al. 2010, Mane et al. 2012, Vinu et al. 2005) or KOH activation (Li et al. 2016, Lillo-Ródenas et al. 2003, Vilaplana-Ortego et al. 2009). By contrast, sodium bicarbonate (NaHCO_3) with

pore-forming ability is a green and scalable porogen, given that water washing can effortlessly eliminate sodium carbonate formed upon NaHCO_3 decomposition (Tian et al. 2016, Tian et al. 2017). To date, chitosan-derived nanocarbons have been reported to be prepared through complicated synthesis methods involving two-step procedures with hydrothermal methods followed by pyrolysis (Wu et al. 2015b), using liquid nitrogen and freeze drying before thermal treatment (Matei Ghimbeu and Luchnikov 2018), and employing metal ions during fabrication of chitosan-based nanocarbons and tailoring its electrochemical activity through adjusting the chitosan/metal ratio (Wang et al. 2010). Besides, most research on the chitosan-based nanocarbons has been focused on ORR (Liu et al. 2014, Rybarczyk et al. 2015), formic acid dehydrogenation catalysis (Lee et al. 2017), supercapacitor (Ba et al. 2018), Na-ion battery (Conder et al. 2019), and lindane dehydrochlorination (Yang et al. 2018b). By contrast, reports on the chitosan-derived carbocatalyst as PMS activator for the removal of recalcitrant organic pollutants have been rather limited so far.

In this study, to address the abovementioned gap, nitrogen-doped chitosan-derived graphene-like carbocatalyst was synthesized via one-pot pyrolysis of chitosan/urea/ NaHCO_3 mixture (denoted as CNU), which was facile, cheap, ecofriendly and scalable. Chitosan acted as a nitrogen-containing carbon precursor. Urea served as a graphene-like structure-directing agent and nitrogen source. NaHCO_3 acted as a green porogen to enhance SSA and pore volume. In addition, CNUs in this study were engineered by controlling pyrolysis temperature (T_p) to tailor their catalytic activities for PMS activation. The effect of T_p on the compositional and textural features (e.g., N dopant concentration, N species, SSA and pore volume, etc.) of CNUs was investigated. The catalytic activities of CNUs prepared at different T_p were evaluated in the SAM degradation via PMS activation with respect to catalytic mechanism, degradation kinetics and pathway, and reusability. To explore the role of each agent involved during synthesis, comparison was also made between CNU and carbocatalysts synthesized with chitosan/ NaHCO_3 mixture (denoted as CN) and chitosan/urea mixture (denoted as CU) with respect to the compositional and textural properties together with PMS-activating activity.

5.2 Experimental

5.2.1 Chemicals

The chemicals used in the study of this chapter were chitosan (molecular weight: 100000-300000, ACROS Organics), urea ($\text{CH}_4\text{N}_2\text{O}$, Merck), sodium bicarbonate (NaHCO_3 , Merck), Oxone ($2\text{KHSO}_5\cdot\text{KHSO}_4\cdot\text{K}_2\text{SO}_4$, the trade name of PMS, Merck), sulfacetamide (SAM) ($\text{C}_8\text{H}_{10}\text{N}_2\text{O}_3\text{S}$, Sigma-Aldrich), methanol (CH_3OH , Merck), nitrobenzene (NB) ($\text{C}_6\text{H}_5\text{NO}_2$, Sigma-Aldrich), absolute ethanol ($\text{C}_2\text{H}_6\text{O}$, Merck), sodium azide (NaN_3 , Sigma-Aldrich), *p*-benzoquinone ($\text{C}_6\text{H}_4\text{O}_2$, Sigma-Aldrich), 2,2,6,6-tetramethyl-4-piperidone (TEMP, Merck), 5-tert-butoxycarbonyl-5-methyl-1-pyrroline-N-oxide (BMPO, Cayman chemical), sodium hydroxide (NaOH , Merck), sodium nitrate (NaNO_3 , Merck), sodium chloride (NaCl , Merck), humic acid (Merck), nitric acid (HNO_3 , Merck). All the chemicals were employed as obtained without being additionally purified. Milli-Q ultrapure water ($18.2\text{ M}\Omega\cdot\text{cm}$ at 25°C) was used in this study.

5.2.2 Synthesis of CNUs

CNU was synthesized via one-pot pyrolysis of chitosan/urea/ NaHCO_3 mixture. Typically, chitosan (400 mg), urea (2 g) and NaHCO_3 (1.2 g) was mixed and uniformly grinded in an agate mortar (10 min). Afterwards, the mixed powder was loaded into a quartz boat with a cover and then moved to the tubular furnace for pyrolysis with ramping rate of 5°C min^{-1} under N_2 atmosphere for 2 h ($T_p = 600, 700$ and 800°C). Then the product was grinded and washed several times with water and absolute ethanol, and dried at 60°C in an oven. The final product was denoted as CNU600, CNU700, and CNU800, respectively. For comparison, chitosan (simplified as Chi) was directly pyrolyzed at 600, 700 and 800°C following the abovementioned procedure without addition of both urea and NaHCO_3 (denoted as Chi600, Chi700 and Chi800, respectively). CN and CU were fabricated through pyrolysis of chitosan/ NaHCO_3 mixture and chitosan/urea mixture, respectively, at 700°C (denoted as CN700 and CU700, respectively), which is because $T_p = 700^\circ\text{C}$ is the critical temperature, whereby g- C_3N_4 started to decompose and the graphitization of infiltrated amorphous chitosan-derived carbon was initialized. Comparison between

CNU700, CN700, CU700 and Chi700 was used to explore the role of urea/ NaHCO_3 in the compositional and structural properties, and the PMS-activating activity of chitosan-derived carbocatalysts. Besides, CN800 was also synthesized for comparison in the SAM degradation performance between CN800/PMS/SAM and CNU800/PMS/SAM systems to further investigate the effect of urea/ NaHCO_3 on the catalytic activity of chitosan-derived carbocatalysts. The synthesis procedure for bulk g- C_3N_4 is shown in **Appendix 1**, which is for the comparison in the characterization **Section 5.3.1.1**.

5.2.3 Characterization

The characterization techniques used for studying the characteristics of CNUs were presented in **Section 3.2.3**. Specially, the surface functionalities of carbocatalysts were analyzed on a PerkinElmer attenuated total reflectance Fourier transform infra-red (ATR-FTIR) system. As for the measurement of the textural properties, t-plot method was used for micropore surface area ($\text{SSA}_{\text{micro}}$) and micropore volume (V_{micro}). BJH method was employed for mesopore distribution. DFT method was adopted for mesopore and micropore distribution.

5.2.4 Catalytic oxidation of sulfacetamide

All the experiments were carried out in a 100-mL beaker. The target pollutant employed in this study was SAM. 0.3 g L^{-1} of carbocatalyst was added into the 50-mL SAM solution (initial pH = 7, 10 mg L^{-1}), followed by the addition of PMS (0.5 mM) into the SAM solution to start the oxidation reaction (stirred at 600 rpm). At a designated reaction time, 0.5 mL of solution was withdrawn, filtered with $0.45 \mu\text{m}$ hydrophilic polyethersulfone membrane with addition of 0.5 mL methanol as quenching agent. The SAM concentration was analyzed on a PerkinElmer HPLC as described in **Section 3.2.4**. The adsorption experiment followed the similar procedure without the addition of PMS.

The SAM removal via PMS activation by CNU was evaluated under different operational conditions in terms of PMS dosage (0.2-0.9 mM), catalyst loading ($0.1\text{-}0.3 \text{ g L}^{-1}$) and common aqueous matrix species ($[\text{humic acid}] = 5 \text{ mg L}^{-1}$, $[\text{NO}_3^-] = 10 \text{ mg L}^{-1}$, $[\text{Cl}^-] = 100, 200 \text{ and } 500 \text{ mg L}^{-1}$). The main ROS produced via PMS activation

by CNU were investigated through quenching experiment (employing NB, ethanol, NaN_3 and *p*-BQ as quenchers) and EPR (as described in **Section 3.2.4**). The spin-trapping reagents employed included BMPO (for $\text{SO}_4^{\cdot-}$, $\text{HO}^{\cdot}$ and $\text{O}_2^{\cdot-}$) and TEMP (for $^1\text{O}_2$). The measurement of TOC, the SAM intermediates formed via PMS activation by CNU, and the pH_{pzc} of carbocatalysts was same as described in **Section 3.2.4**. All the experiments were conducted in triplicate. Error bars represent the standard deviation.

5.2.5 Reusability

CNU800 reusability experiment was similar to that described in **Section 3.2.5**. XPS analysis was conducted for the used CNU800 of the 3rd run.

5.3 Results and discussion

5.3.1 CNUs fabricated under selected pyrolysis temperatures

5.3.1.1 Characterization of CNUs

FESEM and TEM were used to explore the morphologies of CNUs. As displayed in FESEM images, chitosan had a featureless slab-like structure (**Figure 5.1(a)**). Chi800 possessed a limited porous structure on the smooth surface of chitosan (**Figure 5.1(b)**). By contrast, after pyrolysis and doping process with the aid of NaHCO_3 as porogen, more exfoliation and pores were found in CNU600, CNU700 and CNU800 with increasing T_p (**Figure 5.1(c)-(e)**). CNU800 possessed the 3D porous structure, facilitating mass transfer, adsorption and exposure of more active sites for carbocatalysis. The inset of **Figure 5.1(e)** shows that nanoflakes with relatively smooth surface were found in CNU800 and interstitial voids were formed between nanoflakes, which corresponds to the existence of mesopores in CNU800 (as discussed later). TEM images of CNU800 (**Figure 5.1(f)-(h)**) also substantiated the porous graphene-like structure in CNU800. As revealed in the EDX elemental mappings of CNU800, the N dopant was homogeneously distributed over the porous nanocarbon network of CNU800 (**Figure 5.2**).

Figure 5.1. FESEM images of chitosan (a), Chi800 (b), CNU600 (c), CNU700 (d) and CNU800 (e). (b), (c) and (d) were TEM images of CNU800.

Figure 5.2. EDX maps of (b) C, (c) N and (d) O elements for CNU800 according to the corresponding FESEM image (a).

The functional groups of CNUs were probed via FTIR. As demonstrated in **Figure 5.3(a)**, in the FTIR spectrum of chitosan, several detected peaks were 3325 (stretching vibration of O-H bond overlapped to the symmetric stretching vibration of N-H bond), 2877 (symmetric stretching vibration of C-H bond), 1649 (C=O

stretching of amide I band), 1588 (bending vibrations of N-H (N-acetylated residues, amide II band)), 1425 and 1373 (C-H bending), 1155 (symmetric stretching of C-O-C bridge), 1063 and 1023 (skeletal vibration involving C-O stretching) cm^{-1} (Silva et al. 2012). After pyrolysis and nitrogen doping with the aid of NaHCO_3 , two new peaks centered around 1545 and 1232 cm^{-1} appeared in the spectra of CNU600, CNU700 and CNU800, which can be ascribed to the stretching modes of C-N heterocycles in g- C_3N_4 (Liao et al. 2014). Moreover, the intensities of these two peaks exhibited a descending trend with the increasing T_p from 600-800°C, which can be attributable to g- C_3N_4 starting decomposition when heating up to 700°C (Zhu et al. 2014).

Figure 5.3(b) reflects the XRD patterns of CNUs. The well-known partly crystalline peak at $\sim 20^\circ$ for pure chitosan was detected in the XRD pattern of chitosan (Singh et al. 2010). Two typical peaks at 27.2° ((002) facet of g- C_3N_4) and 13.1° ((100) facet of g- C_3N_4) were detected in the XRD pattern of g- C_3N_4 , which indicates the easy formation of g- C_3N_4 from thermal treatment of urea at 500°C (Liu et al. 2011). Only one sharp peak centered at $\sim 26^\circ$ appeared in the XRD pattern of CNU600 (26.8° , interlayer distance = 0.324 nm), CNU700 (26.5° , 0.327 nm) and CNU800 (25.8° , 0.335 nm). As T_p increased from 600-800°C, the XRD peak intensities of CNUs decreased and the XRD peak positions of CNUs downshifted, which implies 1) the existence of g- C_3N_4 in the CNU600, CNU700 and CNU800, and 2) the decomposition of g- C_3N_4 started at $T_p = 700^\circ\text{C}$ (commensurate with FTIR result). The chitosan-derived carbon infiltrated between the g- C_3N_4 sheets, leading to the graphene-like (**Figure 5.1(f)-(h)** and **Figure 5.6(k)-(m)**) structure of CNU with a larger interlayer distance at a higher T_p (Liu et al. 2014).

The structural properties of CNUs were investigated via Raman spectra (**Figure 5.3(c)**). All the samples displayed the distinctive D band ($\sim 1350 \text{ cm}^{-1}$) and G band ($\sim 1580 \text{ cm}^{-1}$). D band relates to lattice defects and disordered carbon atoms. G band relates to sp^2 hybridized carbon atoms. The intensity ratio of D- to G-band (I_D/I_G) is in inverse proportion to the graphitization degree (Ferrari and Robertson 2000). Compared with Chi800 ($I_D/I_G = 1.02$), all the CNUs had higher I_D/I_G values (1.07-1.05) (**Table 5.1**), which suggests more defects created in CNUs. Furthermore, the I_D/I_G values of CNUs slightly decreased from 1.07 to 1.05 with the increasing T_p from

600–800°C, which suggests graphitization degree was moderately enhanced with the increasing T_p . It has been reported that a high temperature ($\geq 700^\circ\text{C}$) facilitates the transformation of small amorphous carbon clusters into graphitic patches (Barreiro et al. 2013, Westenfelder et al. 2011). The relatively higher graphitization degree of CNU800 (1.05) (**Table 5.1**) is conducive to the enhanced electrical conductivity of its carbon nanosheet framework, which might partially account for the enhanced PMS-activating capability of CNU800 for SAM degradation (**Section 5.3.1.2**).

The thermal stability of CNUs was investigated by TGA. As shown in TGA curve of chitosan in **Figure 5.3(d)**, the weight loss of $\sim 10\%$ in the first stage below 100°C was ascribed to the evaporation of the adsorbed water in chitosan. The weight loss of $\sim 40\%$ in the second stage from $\sim 250^\circ\text{C}$ – 350°C was attributed to the depolymerization of chitosan chains, decomposition of pyranose rings through dehydration and deamination, and finally ring-opening reaction (Bengisu and Yilmaz 2002). The weight loss of $\sim 50\%$ in the third stage of $\sim 350^\circ\text{C}$ – 600°C was associated with chitosan chain cleavage with the generation of volatile degradation products (Zawadzki and Kaczmarek 2010). By contrast, all the CNU600, CNU700, CNU800 and Chi800 exhibited an improved thermal stability (up to 500°C) under air atmosphere, which implies the removal of the surface functional groups in chitosan and the well-oriented graphitic nanocarbon domain formed in the carbocatalysts (Wakeland et al. 2010). T_p exerted an insignificant influence on the thermal stability of the resulted CNUs.

Figure 5.3. (a) FTIR spectra, (b) XRD patterns, (c) Raman spectra and (d) TGA curves of Chi, Chi800 and CNUs. (e) N₂ sorption isotherm and (f) pore size distribution of CNUs.

XPS analysis was carried out for the chemical compositions of CNUs (**Figure A6, Appendix**). As shown in **Table 5.1**, chitosan possessed a high O content (O/C (%) = 44.6%) and low N content (N/C (%) = 10.2%). After pyrolysis at 800°C, C atoms gained on the content at the expense of O and N atoms in Chi800 (O/C (%) = 10.4%, N/C (%) = 6.1%) due to carbonization and reduction at a high T_p . The N/C (%) content of CNUs decreased (32.9%-24.3%) with the increasing T_p from 600°C to 800°C, which can be explained by 1) when $T_p = 600^\circ\text{C}$, the chitosan can be carbonized into amorphous carbon and infiltrated between g-C₃N₄ nanosheets (formed by the condensation of urea at $T_p \geq 500^\circ\text{C}$) (Liu et al. 2011, Xu et al. 2013). Besides, the decomposition of urea can lead to the formation of NH₃ for N doping on the chitosan-derived carbon nanosheets (Ruiz-Hitzky et al. 2011); and 2) when $T_p \geq 700^\circ\text{C}$, the graphitization of infiltrated amorphous carbon was initialized (Westenfelder et al. 2011). In addition, the reactive template g-C₃N₄ started to

decompose to release N-containing vapor (e.g., NH_3 , C_3N_3^+ , C_2N_2^+) as nitrogen source for doping (Holst and Gillan 2008, Jun et al. 2009, Schaber et al. 2004a), corresponding to the decreasing FTIR and XRD intensities from CNU600 to CNU800 (**Figure 5.3(a) and (b)**).

Table 5.1. Structural and chemical information of Chi, Chi800, CNUs, Chi700, CN700 and CU700

	C at. %	O at. %	N at. %	O/C %	N/C %	pyridinic N N_{pyridinic-N}/N_{total} (%)	pyrrolic N N_{pyrrolic-N}/N_{total} (%)	graphitic N N_{graphitic-N}/N_{total} (%)	C=O C_{C=O}/C_{total} (%)	I_D/I_G
Chi	64.6	28.8	6.6	44.6	10.2	-	-	-	-	-
Chi800	85.9	8.9	5.2	10.4	6.1	41.0	59.0	ND*	ND	1.02
CNU600	68.4	9.1	22.5	13.3	32.9	42.1	44.3	13.6	ND	1.07
CNU700	70.9	9.7	19.4	13.7	27.4	47.0	37.8	15.2	17.6	1.06
CNU800	76.9	4.4	18.7	5.7	24.3	43.5	36.9	19.6	23.7	1.05
Chi700	80.7	14.7	4.6	18.2	5.7	38.3	61.7	ND	ND	0.97
CN700	76.6	4.8	18.6	6.2	24.3	44.3	34.6	21.1	27.3	1.00
CU700	67.0	9.2	23.8	13.7	35.5	47.1	43.7	9.2	ND	1.03

Atomic percentages of C, O and N were analyzed by XPS.

* ND refers to non-detected.

The XPS N1s deconvolution (394-408 eV) for all the CNUs was acquired. All the CNUs exhibited three intense peaks at ~ 398 , ~ 400 and ~ 401 eV (**Table 5.1** and **Figure A6(a)-(c)**, **Appendix**), which corresponds to pyridinic N, pyrrolic N and graphitic N, respectively. By contrast, only pyridinic N and pyrrolic N were detected for Chi800 (**Table 5.1** and **Figure A6(d)**, **Appendix**), which indicates the foreign nitrogen source (urea) mainly contributed to the formation of graphitic N. As shown in **Figure 5.4**, the atomic ratios (%) of pyridinic N/C (13.8%-10.6%) and pyrrolic N/C (14.6%-9.0%) decreased with the increasing T_p from 600°C to 800°C. However, CNU800 possessed a relatively higher graphitic N/C atomic ratio (%) of 4.8% than that of CNU600 (4.5%) and CNU700 (4.2%), because the graphitic N possesses a superior thermal tolerance over pyrrolic N. The C1s spectra of CNUs can be deconvoluted into four main peaks: C=C (284.6-284.7 eV), C-O/C=N (285.6 eV), C=O/C-N (286 eV) and O-C=O (288.8 eV) (**Figure A6(f)-(i)**, **Appendix**) (Ba et al. 2018, Hu et al. 2013, Sheng et al. 2011). The C=O group was detected in CNU700 and CNU800 except for CNU600 (**Table 5.1**). CNU800 possessed the highest C=O/C atomic ratio (%) of 23.7% (**Figure 5.4**) among CNUs, which has been reported to be a redox-active functional group for both radical (e.g., $\text{SO}_4^{\cdot-}$ and $\text{HO}^{\cdot}$) and non-radical (e.g., $^1\text{O}_2$) pathway during PMS activation process (Chen et al. 2018b, Duan et al. 2018a, Nie et al. 2018).

Figure 5.4. Variation of the content of N species and C=O in CNUs with pyrolysis temperature.

Table 5.2 displays the textural properties of CNUs. A higher T_p facilitated the formation

of the higher BET SSA (SSA_{BET}) and total pore volume (V_{total}). CNU800 ($943 \text{ m}^2 \text{ g}^{-1}$, $0.539 \text{ cm}^3 \text{ g}^{-1}$) had a much higher SSA_{BET} and V_{total} than CNU600 ($21 \text{ m}^2 \text{ g}^{-1}$, $0.012 \text{ cm}^3 \text{ g}^{-1}$) and CNU700 ($330 \text{ m}^2 \text{ g}^{-1}$, $0.028 \text{ cm}^3 \text{ g}^{-1}$), which positively correlates with their exfoliation and porous levels shown in **Figure 5.1**. As shown in **Figure 5.3(e)** and **(f)**, among CNUs, only CNU800 possessed a type IV isotherm with a H2 hysteresis loop in relative pressure range of 0.4-0.6, which indicates a well-developed pore system with an irregular pore size and hierarchically porous structure (Lee et al. 2017, Liu et al. 2014). The pore size distribution of CNU800 was comprised of micropore ($< 2 \text{ nm}$) and mesopores centered at 2.65 and 3.47 nm (**Table 5.2**), which indicates the formation of the hierarchically porous structure in CNU800. A higher SSA_{micro} and V_{micro} contributed to a better adsorption performance and exposure of more reactive sites for activating PMS (Matei Ghimbeu and Luchnikov 2018, Tian et al. 2016), while mesopores facilitated the mass transfer (Wu et al. 2015b). By contrast, only mesopores (centered around 4.05 nm) were found in CNU600 and CNU700 (**Table 5.2**).

Table 5.2. SSA, pore volume and pore size information of Chi800, CNUs, Chi700, CN700 and CU700

Catalyst	SSA_{BET} (m² g⁻¹)	^aSSA_{micro} (m² g⁻¹)	V_{total} (cm³ g⁻¹)	^aV_{micro} (cm³ g⁻¹)	^bV_{meso} (cm³ g⁻¹)	D_{ave} (nm)	^gD_{peak} (nm)
CNU600	21	-	0.012 ^c	-	-	4.05 ^c	4.05
CNU700	330	-	0.028 ^c	-	-	4.06 ^c	4.06
CNU800	943	178	0.539 ^d	0.091	0.448	2.65 ^f	< 2, 2.65, 3.47
CN700	953	830	0.372 ^d	0.316	0.056	0.82 ^f	0.82
CU700	107	-	0.015 ^c	-	-	4.06 ^c	4.06
Chi700	8	-	0.008 ^c	-	-	4.03 ^c	4.03
Chi800	11	-	0.010 ^c	-	-	4.03 ^c	4.03

^a Micropore surface area and micropore volume calculated from t-plot. ^b V_{meso} = V_{total} - V_{micro} ^c BJH method desorption total pore volume.

^d DFT method desorption total pore volume. ^e BJH method desorption average pore width (dV(log d)). ^f DFT method desorption average pore width (dV(log d)).

^g peak pore width.

5.3.1.2 Catalytic activity of CNUs fabricated under selected pyrolysis temperatures

SAM degradation performance via PMS activation by CNUs was used to evaluate the catalytic activity of CNUs. As shown in **Figure 5.5(a)** and **Table A3 (Appendix)**, the adsorption by Chi600, Chi800, CNU600, CNU700 and CNU800 contributed to less than 10% of SAM removal within 60 min. The poor adsorption capacity of mesoporous Chi600, Chi800, CNU600 and CNU700 relates to their relatively low SSA_{BET} and V_{total} (**Figure 5.3(e)** and **(f)**, **Figure 5.8**, **Table 5.2**) (The poor adsorption efficiency of CNU800 as discussed in **Section 5.3.2.2**).

Figure 5.5. Adsorption (a) and catalytic (b) performances of CNUs to activate PMS for SAM degradation (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.3 g L⁻¹, pH = 7).

Figure 5.5(b) reveals the PMS-activating performance of CNUs obtained at selected T_p . The kinetics of SAM degradation via PMS activation by CNUs was estimated by the initial

apparent rate constant (k_{app}) via the pseudo first-order kinetics as described in **Section 3.3.2.1**. Chi600 ($k_{app} = 0.009 \text{ min}^{-1}$), Chi800 ($k_{app} = 0.009 \text{ min}^{-1}$) and CNU600 (0.007 min^{-1}) can barely serve as PMS activators due to their low SAM removal efficiency ($\sim 40\%$ within 60 min) (**Table A3, Appendix**). CNU700 and CNU800 both demonstrated catalytic activity for PMS activation. CNU800 (0.482 min^{-1} with 100% SAM removal within 10 min) outperformed CNU700 (0.031 min^{-1} with 83% SAM removal within 60 min) as PMS activator for SAM degradation (**Table A3, Appendix**). The catalytic performance of carbocatalysts followed the order of $\text{CNU800} > \text{CNU700} > \text{CNU600} \approx \text{Chi800} \approx \text{Chi600}$. CNU800 induced 54-, 69- and 16-fold improvements of catalytic activity for PMS activation over Chi600/Chi800, CNU600 and CNU700, respectively, despite the low adsorption efficiency of CNU800 ($< 10\%$ SAM removal within 60 min) (**Figure 5.5(a)**).

Different surface functionalities on carbocatalysts can induce different oxidation pathways for PMS activation in the carbocatalyst/PMS system. Pyridinic N and pyrrolic N as Lewis basic sites with lone-pair electrons are conducive to radical pathway. By contrast, graphitic N inclines to induce the non-radical pathway through the formation of the incurred polarized and positively charged carbon region due to electronegativity difference between N and C atoms ($\chi_{\text{N}} (3.04) > \chi_{\text{C}} (2.55)$) (Duan et al. 2018b). Meanwhile, C=O has been documented to contribute to both radical (C=O as Lewis basic sites with lone-pair electrons) and non-radical (C=O favoring the formation of $^1\text{O}_2$ (Zhou et al. 2015b)) oxidation via PMS activation. The outstanding catalytic activity of CNU800 among CNUs can be explained as follows:

- 1) CNU800 possessed the higher level of C=O/C (23.7%) and graphitic N/C (4.8%) (**Figure 5.4**) compared with that of CNU600 (no C=O and 4.5% of graphitic N/C) and CNU700 (17.6% of C=O/C and 4.2% of graphitic N/C) (**Table 5.1** and **Figure 5.4**). The graphitic N and C=O group can act as the redox-active functional groups facilitating the production of ROS for degrading SAM in the CNU800/PMS/SAM system. Besides, CNU800 possessed a relatively higher graphitization degree among CNUs might partially contribute to its enhanced catalytic activity for PMS activation.

- 2) The large SSA_{BET} ($943 \text{ m}^2 \text{ g}^{-1}$) and hierarchically porous structure ($V_{\text{micro}} = 0.091 \text{ cm}^3$)

g^{-1} , mesopore volume ($V_{\text{meso}} = 0.448 \text{ cm}^3 \text{ g}^{-1}$) of CNU800 can expose more reactive sites to activate PMS (**Table 5.2**). Briefly, redox-active functionalities (e.g., graphitic N and C=O groups), graphitization degree, and SSA together with pore distribution comprehensively determine the catalytic activity of CNUs.

5.3.2 The effect of synthesis agents on the properties of the resulted carbocatalysts

5.3.2.1 Characteristics of the carbocatalysts

To investigate the role of each agent involved during synthesis, comparison was carried out among CNU700, CN700, CU700 and Chi700 ($T_p = 700^\circ\text{C}$ is the critical temperature, whereby g- C_3N_4 started to decompose and the graphitization of infiltrated amorphous chitosan-derived carbon was initialized). According to FESEM and TEM analysis (**Figure 5.6**), the introduction of NaHCO_3 as porogen during pyrolysis can convert chitosan to the carbon nanosheet with a 3D interconnected highly porous network composed of the honeycomb-like in-plane micropores distributed uniformly (**Figure 5.6(b) and (e)-(g)**). By contrast, the introduction of urea as a structure-directing agent and N source in the pyrolytic process can transform chitosan to a highly crumpled sheet-like structure with mesopores and the layered structure due to the formation of g- C_3N_4 serving as layer template (**Figure 5.6(c) and (h)-(j)**).

Figure 5.6. FESEM images of Chi700 (a), CN700 (b), CU700 (c) and CNU700 (d). (e), (f) and (g) were TEM images of CN700. (h), (i) and (j) were TEM images of CU700. (k), (l) and (m) were TEM images of CNU700.

As shown in the FTIR spectra (**Figure 5.7(a)**), compared with the NaHCO_3 alone or urea alone introduced during chitosan pyrolysis, the co-existence of NaHCO_3 and urea facilitated the formation of g- C_3N_4 (CNU700 had higher intensities of peaks at 1545 and 1232 cm^{-1}

corresponding to g-C₃N₄). That is beneficial to the generation of graphene-like structure (**Figure 5.6(k)**) with potential advantages such as a large SSA, unique electronic structure and conductivity (Rybarczyk et al. 2015). The FTIR result is commensurate with the XRD result. The co-existence of urea and NaHCO₃ resulted in an upshifted sharp peak with high intensity (26.5°, 0.327 nm) in the XRD spectrum of CNU700 (**Figure 5.7(b)**), which implies the formation of g-C₃N₄ (27.2°, 0.319 nm) is promoted by the co-existence of urea and NaHCO₃.

Figure 5.7. (a) FTIR spectra, (b) XRD patterns, (c) Raman spectra and (d) TGA curves of Chi700, CN700, CU700 and CNU700.

The Raman spectra (**Figure 5.7(c)**) reveal that the introduction of urea in the pyrolytic process of chitosan can induce a higher disorder level than that of NaHCO₃. The co-existence of urea and NaHCO₃ can further enhance the defective level of the resulted carbocatalyst, which is evidenced by the highest I_D/I_G value (1.06) of CNU700. In terms of the thermal stability of the resulted carbocatalyst, TGA curves show that NaHCO₃ might adversely affect the thermal stability in comparison to that of urea during chitosan pyrolysis, while the co-existence of urea

and NaHCO_3 can improve the thermal stability of the resulted carbocatalyst. That can be substantiated by the fact that a higher temperature was entailed for the same weight loss of CUN700 than that of CN700 and CU700 (**Figure 5.7(d)**).

Chemical composition of Chi700, CN700, CU700 and CNU700 was explored via XPS (**Figure A7, Appendix**). As revealed in **Table 5.1** and **Figure 5.8**, generally, compared with Chi700 with a low N content as well as no graphitic N and C=O groups detected, the presence of NaHCO_3 or urea during chitosan pyrolysis can dramatically increase the N/C content together with the concentration of pyridinic N/C and pyrrolic N/C. Moreover, graphitic N existed in all the CN700, CU700 and CNU700. Notably, even without the foreign nitrogen source, the addition of NaHCO_3 alone as porogen in the pyrolytic process of chitosan can induce formation of a high content of N species of N/C (%) = 24.3%, pyridinic N/C (%) = 10.8%, pyrrolic N/C (%) = 8.4%, graphitic N/C (%) = 5.1% in CN700. That is associated with the exposure of more redox-active N species by its 3D interconnected highly microporous structure (**Figure 5.6(b)**). In addition, CN700 had the higher graphitic N/C and C=O/C atomic ratio (5.1% and 27.3%, respectively) compared with CU700 (3.3%, no C=O group detected) and CNU700 (4.2%, 17.6%) (**Table 5.1** and **Figure 5.8**), which envisages the potential catalytic activity of CN700 for PMS activation (**Section 5.3.2.2**).

Figure 5.8. Variation of the content of N species and C=O in Chi700, CN700, CU700 and CNU700 with pyrolysis temperature.

As shown in **Table 5.2**, CN700 ($953 \text{ m}^2 \text{ g}^{-1}$) had a much higher SSA_{BET} than that of CU700 ($107 \text{ m}^2 \text{ g}^{-1}$) and CNU700 ($330 \text{ m}^2 \text{ g}^{-1}$). CN700 possessed a type I isotherm with no hysteresis loops and peak pore width of 0.82 nm ($< 2 \text{ nm}$) (**Figure 5.9**), which indicates that NaHCO_3 as a pore forming agent facilitated the formation of a microporous structure and corresponds to its highest $\text{SSA}_{\text{micro}}$ ($830 \text{ m}^2 \text{ g}^{-1}$) and V_{micro} ($0.316 \text{ cm}^3 \text{ g}^{-1}$) (**Table 5.2**). By contrast, only mesopores (centered at 4.06 nm) were found in the CU700 and CNU700 (**Table 5.2**), which implies the role of urea in the generation of mesopores due to the resulted crumples in the nanocarbon network (De et al. 2015, Wakeland et al. 2010).

Figure 5.9. (a) N_2 sorption isotherm and (b) pore size distributions of Chi700, Chi800, CN700, CU700 and CNU700.

5.3.2.2 Catalytic activity of the carbocatalysts

Figure 5.10(a) shows the adsorption performance of Chi700, CN700, CU700 and CNU700. The adsorption by Chi700, CU700 and CNU700 contributed to less than 10% of SAM removal within 60 min. However, CN700 exhibited a high adsorption capacity with 81% SAM removal within 60 min, which is partially ascribed to its highest SSA_{BET} ($953 \text{ m}^2 \text{ g}^{-1}$) and V_{total} ($0.372 \text{ cm}^3 \text{ g}^{-1}$) (**Table 5.2**). Besides, the pH_{pzc} of Chi700, CU700, CNU700 and CN700 are 5.2, 6.6, 6.2 and 7.5, respectively (**Figure A2(c)-(f)**). Under the solution $pH = 7$, SAM was negatively charged. Chi700, CU700 and CNU700 were negatively charged, whereas CN700 was positively charged. Therefore, the electrostatic attraction between the negatively charged SAM and the positively charged CN700 also partially promoted the enhanced adsorption performance of CN700. Generally, compared with Chi700, CU700 and CNU700, the higher adsorption efficiency of CN700 relates to the following aspects: 1) its higher SSA_{BET} and V_{total} (**Table 5.2**); 2) the electrostatic attraction between the negatively charged SAM and the positively charged CN700; and 3) its higher content of C=O group (**Table 5.1**) (as discussed later in **Section 5.3.2.2**).

The SAM degradation performance of Chi700, CN700, CU700 and CNU700 is shown in **Figure 5.10(b)**. Chi700 (0.009 min^{-1}) and CU700 (0.008 min^{-1}) were ineffective for PMS activation, reflected by their low SAM degradation efficiency ($\sim 40\%$) (**Table A3, Appendix**). CN700 and CNU700 both demonstrated catalytic activity for PMS activation. CN700 (0.541 min^{-1} with 100% SAM removal within 10 min) outperformed CNU700 (0.031 min^{-1} with 83% SAM removal within 60 min) as PMS activator for SAM degradation (**Table A3, Appendix**). The excellent SAM oxidation performance of CN700 can be explained below:

1) CN700 possessed the higher level of C=O/C (27.3%) and graphitic N/C (5.1%) (serving as the possible active sites) than that of CU700 (no C=O group and graphitic N/C (%) = 3.3%) and CNU700 (C=O/C (%) = 17.6% and graphitic N/C (%) = 4.2%) (**Figure A6(g)** and **Figure A7(f) and (g), Appendix**).

2) CN700 had a lower I_D/I_G value (1.00) compared with CU700 (1.03) and CNU700 (1.06) (**Table 1** and **Fig. S5(c)**), which indicates CN700 had a higher graphitization degree. It has

been reported that the sp^2 hybridized nanocarbons outperform sp^3 and amorphous carbon in transferring electrons, which endows the sp^2 hybridized nanocarbons with a better catalytic activity for PMS activation (Duan et al. 2015d). The conjugated π system of graphitic nanocarbon network is beneficial to electrophilic attack of the aromatic rings of organics in the non-radical process as well as the radical production via PMS activation (Chen et al. 2018b).

Figure 5.10. Adsorption (a) and catalytic (b) performances of Chi700, CN700, CU700 and CNU700 to activate PMS for SAM degradation (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.3 g L⁻¹, pH = 7).

3) The higher adsorption efficiency of CN700 can facilitate the enrichment of SAM onto the CN700 surface, which increases the proximity of SAM to active sites on CN700 to accelerate SAM degradation. Conversely, the fast degradation of the adsorbed SAM and its intermediates can release more sites on CN700 for re-adsorbing residual SAM in the solution.

Notably, although SSA_{BET} of CN700 ($953 \text{ m}^2 \text{ g}^{-1}$) was close to that of CNU800 ($943 \text{ m}^2 \text{ g}^{-1}$), CN700 (81% SAM removal within 60 min) exhibited a much higher adsorption efficiency over CNU800 (10% SAM removal within 60 min) (**Table A3, Appendix**). This can be attributed to the following aspects: i) CN700 possessed the higher level of C=O/C (27.3%) than that of CNU800 (23.7%), which contributed to the improved SAM adsorption via the formation of a donor–acceptor complex whereby C=O group served as an electron donor and the aromatic ring of SAM served as an electron acceptor (Dąbrowski et al. 2005). ii) CN700 (SSA_{micro} of $830 \text{ m}^2 \text{ g}^{-1}$) possessed much more micropores than CNU800 (SSA_{micro} of $178 \text{ m}^2 \text{ g}^{-1}$), which is beneficial to the enhanced SAM adsorption and exposure of more active sites as discussed in the **Section 5.3.1.1**. And iii) the electrostatic attraction existed between the negatively charged SAM and the positively charged CN700, whereas the electrostatic repulsion existed between the negatively charged SAM and the negatively charged CNU800 (The pH_{pzc} of CNU800 = 6.4) (**Figure A2(g)**).

The synergistic effect between adsorption and catalysis can account for the outstanding SAM degradation performance of CN700 (0.541 min^{-1}), which is even better than that of CNU800 (0.482 min^{-1}) (**Table A3, Appendix**). However, in terms of catalytic activity, a different scenario occurred. The SAM degradation performance in the carbocatalyst/PMS/SAM system is collectively affected by the PMS direct oxidation, adsorption and catalysis. 100% SAM removal can be achieved in both the CN700/PMS/SAM and CNU800/PMS/SAM system at reaction time $t = 10 \text{ min}$, nonetheless, the catalytic contribution of CNU800 (81%) surpassed that of CN700 (46%) (**Figure 5.11**), which can be ascribed to the following aspects: 1) the effective SSA for PMS activation diminished due to the blockage of active sites/pores of CN700 caused by the excessive adsorption of SAM; and 2) the SAM adsorption process also utilized the same active sites for PMS activation (e.g., C=O group) (Oh and Lim 2019). This result indicates the introduction of urea with the presence of NaHCO_3 in the pyrolytic process of chitosan can further enhance the PMS-activating activity of as-prepared carbocatalyst, which can be further substantiated by the relatively lower catalytic contribution of CN800 (45%) (**Table A3, Appendix** and **Figure 5.11**).

Figure 5.11. At reaction $t = 10$ min, the contribution of adsorption, PMS direct oxidation and catalysis to the overall SAM degradation in the CN700/PMS/SAM, CNU800/PMS/SAM and CN800/PMS/SAM ($t = 5$ min) systems.

In summary, NaHCO_3 as a porogen can effectively endow chitosan with an outstanding SAM degradation performance due to the excellent adsorption efficiency (related to its microporous structure and high content of $\text{C}=\text{O}$ group) and the mediocre PMS-activating activity (associated with the induced reactive functionalities, such as graphitic N and $\text{C}=\text{O}$ groups). Urea itself as a graphene-like structure directing agent as well as a nitrogen source in the pyrolytic process of chitosan inefficaciously contributed to an improved textural structure (leading to mesoporous carbon nanosheets with low SSA_{BET} and V_{total}) and ineffectively induced the desirable active sites (no $\text{C}=\text{O}$ group and limited graphitic N content) for PMS activation. However, by contrast, the introduction of urea with the presence of NaHCO_3 during chitosan pyrolysis can serve as a feasible approach for fabricating graphene-like carbocatalyst with hierarchically porous structure and an enhanced PMS-activating activity.

5.3.3 Effects of PMS dosage and catalyst loading on the CNU800/PMS/SAM system

The effect of catalyst loading and PMS dosage on the catalytic and adsorption performance of CNU800 (with the most outstanding catalytic performance among CNUs) was investigated for SAM removal via PMS activation. As shown in **Figure 5.12(a)**, the catalyst loading exerted an insignificant influence ($< 10\%$) on the adsorption performance of CNU800 for SAM

removal. However, as the catalyst loading of CNU800 increased from 0.1, 0.2 to 0.3 g L⁻¹, the catalytic activity of CNU800 was dramatically enhanced with the k_{app} value increasing from 0.101, 0.321 to 0.482 min⁻¹, respectively (**Table A4, Appendix**), which can be attributable to the more active sites brought in by a higher catalyst loading for PMS activation. **Figure 5.12(b)** displays the effect of PMS dosage on degrading SAM in the CNU800/PMS/SAM system. To achieve 100% SAM removal, as the PMS dosage increased from 0.2, 0.5 to 0.9 mM, the reaction time decreased from 40 (0.102 min⁻¹), 15 (0.321 min⁻¹) to 5 min, respectively. The improvement in the PMS-activating activity of CNU800 with the increasing PMS dosage can be ascribed to the enhanced interplay between carbocatalysts and PMS.

Figure 5.12. (a) The effect of catalyst loading on the adsorption (inset) and catalytic performance of CNU800 (Condition: [PMS] = 0.5 mM, [catalyst] = 0.1, 0.2 and 0.3 g L⁻¹, [SAM] = 10 mg L⁻¹, pH = 7). (b) The effect of PMS dosage on the SAM degradation in the CNU800/PMS/SAM system (Condition: [PMS] = 0.2, 0.5 and 0.9 mM, [catalyst] = 0.2 g L⁻¹, [SAM] = 10 mg L⁻¹, pH = 7).

5.3.4 Mechanism of PMS activation by CNU800

5.3.4.1 Quenching experiments

Considering the radical and non-radical pathways can occur in the CNU800/PMS/SAM system during SAM degradation, it is crucial for the identification of the major ROS and the relative oxidation pathway. Ethanol, NB, NaN₃, and *p*-BQ were employed as the quenchers to probe the possible PMS-activating mechanism by CNU800. As described in the **Section 3.3.4.1**, ethanol can act as a scavenger for both SO₄^{•-} and HO[•], while NB can be used to quench HO[•] without affecting SO₄^{•-}. *p*-BQ has been reported to be used as a quenching agent for O₂^{•-} ($k_{O_2^{\bullet-}+p-BQ} = 9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) (Ma et al. 2019, Yang et al. 2013). **Figure 5.13(a)** reveals that 1.5 M ethanol resulted in a 28% decrease in k_{app} , while 80 mg L⁻¹ NB and 2 mM *p*-BQ exerted a negligible impact on the decomposition of SAM (with a reduction of 5% and 7% in k_{app} , respectively) in the CNU800/PMS/SAM system. Since no significant inhibition was induced by ethanol, NB and *p*-BQ, it can be construed that the non-radical oxidation was the dominant pathway for the SAM decomposition over radical pathway in the CNU800/PMS/SAM system. Azide ion has been used as an effective ¹O₂ quencher (Gspomer et al. 1987). Upon addition of NaN₃, the SAM degradation was significantly inhibited. However, it is noteworthy that NaN₃ also can react with PMS, SO₄^{•-} and HO[•] (Chen et al. 2018b). Thus, NaN₃ cannot be used as an exclusive indicator for the existence of ¹O₂ in the CNU800/PMS/SAM system.

5.3.4.2 Electron paramagnetic resonance analysis

EPR was conducted to further explore the oxidation pathway and the main ROS. The spin trapping agents used in this study were BMPO (trapping SO₄^{•-}, HO[•] and O₂^{•-}) and TEMP (trapping ¹O₂). As shown in **Figure 5.13(b)**, when BMPO was added in the PMS/SAM system, the weak signals with peak intensity ratio of 1: 2: 2: 1 can be assigned to BMPO- HO[•] adduct, which indicates the existence of HO[•] in the PMS/SAM system. Similarly, upon addition of CNU800 into the PMS/SAM system, no obvious peak was detected, which indicates radicals (e.g., SO₄^{•-}, HO[•]) were unlikely to act as the major ROS produced via PMS activation by

CNU800. To investigate the possible existence of $O_2^{\cdot-}$ in the CNU800/PMS/SAM system, the $O_2^{\cdot-}$ trapping experiment (with BMPO) was carried out in the absolute ethanol due to the enhanced stability of BMPO- $O_2^{\cdot-}$ adduct in the absolute ethanol. Only weak signals attributed to $O_2^{\cdot-}$ (Buettner 1993) can be detected in the EPR spectrum, which implies that $O_2^{\cdot-}$ was improbably the major ROS produced via PMS activation by CNU800.

Figure 5.13. (a) The effect of ethanol, NB, NaN₃ and *p*-BQ as quenching agents on the SAM removal and SAM degradation rate in the CNU800/PMS/SAM system; (b) EPR spectra of PMS/CNU800 with BMPO; and (c) EPR spectra of PMS/CNU800 with TEMP (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7, [ethanol] = 1.5 M, [NB] = 80 mg L⁻¹, [NaN₃] = 20 mM, [*p*-BQ] = 2 mM, [BMPO] = 30 mM, [TEMP] = 40 mM, reaction time for (b) and (c) = 1 min).

As shown in **Figure 5.13(c)**, when TEMP was added in the PMS/SAM system, only weak signals with the triple-peak intensity ratio of 1: 1: 1 (hyperfine splitting constants of $a_N = 16$ G) appeared, which is associated with the formation of TEMPO, indicating that low quantity of ¹O₂ was produced by PMS/SAM. By contrast, upon the addition of CNU800 into the PMS/SAM system, the intensities of the triple peaks increased drastically (5 times more than that of PMS/SAM system), indicating that CNU800 mainly activated PMS to produce ¹O₂. This can be explained as follows: 1) it has been reported that the C=O group can activate PMS to produce ¹O₂ via the involvement of a dioxirane intermediate (Zhou et al. 2015b). CNU800 possessed the highest level of C=O/C (23.7%) among CNUs (**Table 5.1** and **Figure 5.4**), facilitating the formation of ¹O₂ in the CNU800/PMS/SAM system; and 2) the production of ¹O₂ can be induced by the nucleophilic addition of PMS into the active site of graphitic N (Ma et al. 2019, Oh et al. 2018). CNU800 had the highest graphitic N/C atomic ratio (%) of 4.8% among CNUs (**Figure 5.4**), conducive to ¹O₂ production in the CNU800/PMS/SAM system. According to the results of quenching experiment and EPR, it can be inferred that non-radical

Figure 5.15. The main SAM degradation pathways in the CNU800/PMS/SAM system (Condition: $[\text{PMS}] = 0.5 \text{ mM}$, $[\text{SAM}] = 10 \text{ mg L}^{-1}$, $[\text{catalyst}] = 0.2 \text{ g L}^{-1}$, $\text{pH} = 7$).

Figure 5.16. TOC removal in the CNU800/PMS/SAM system (Condition: $[\text{PMS}] = 0.5 \text{ mM}$, $[\text{SAM}] = 10 \text{ mg L}^{-1}$, $[\text{catalyst}] = 0.2 \text{ g L}^{-1}$, $\text{pH} = 7$).

5.3.6 Practical application

5.3.6.1 Effect of common matrix species

As mentioned in **Section 3.3.3**, to reflect a more realistic condition, the influence of the aqueous matrix species such as NO_3^- , humic acid and Cl^- (the selection of their contents was based on the secondary effluent from a wastewater treatment plant (Oh et al. 2015)) on the decomposition of SAM via CNU800 as a PMS activator was investigated in this study. As displayed in **Figure 5.17**, NO_3^- imposed an insignificant impact (6% decrease in k_{app}) on the PMS-activating activity of CNU800 for SAM decomposition. Humic acid induced a moderate suppression toward the SAM degradation (26% reduction in k_{app}). This inhibition can be

ascribed to the competitive consumption of $^1\text{O}_2$ by humic acid containing highly reactive functional groups (e.g., carboxylate, carbonyl and phenolic groups (Bai et al. 2008)). Cl^- (100 mg L^{-1}) exhibited a negligible influence on the SAM degradation (2% decrease in k_{app}), which indicates that $^1\text{O}_2$ -based system demonstrated resistance toward the quenching effect which Cl^- usually imposed on the $\text{SO}_4^{\bullet-}$ -based AOP ($k_{\text{SO}_4^{\bullet-} + \text{Cl}^-} = 2.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Redpath and Willson 1975)). Moreover, the SAM degradation was enhanced (23% improvement in k_{app}) as the concentration of Cl^- increased from 100, 200 to 500 mg L^{-1} , which can be attributed to the generation of HClO at a high concentration of Cl^- (Chen et al. 2016), as shown in Eq 5.3.6.1.1 (Chan and Chu 2009, Yuan et al. 2011). HClO has a high reactivity toward the aromatic nucleus due to its high instability caused by the pronounced ionic nature (Narender et al. 2002), contributing to the SAM degradation.

It has been documented that a significant inhibition can be caused by humic acid (64% decrease in k_{app}) and Cl^- (33% decrease in k_{app}) in the $\text{SO}_4^{\bullet-}$ -based AOP system (Chen et al. 2019). Thus, a higher PMS dosage was required in the WWTP effluent to maintain a comparable performance which can be achieved in the bench-scale synthetic wastewater in terms of sulfonamides degradation via PMS activation (Oh et al. 2017b). By contrast, the $^1\text{O}_2$ -based CNU800/PMS system in this study demonstrated resistance toward the quenching effect induced by the common aqueous matrix species, which implies the practical feasibility for its application in the real water treatment (e.g., WWTP effluent and drinking water).

Figure 5.17. The effect of common matrix species on the SAM degradation by CNU800/PMS (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, [Cl⁻] = 100, 200 and 500 mg L⁻¹, [NO₃⁻] = 10 mg L⁻¹, [humic acid] = 5 mg L⁻¹, pH = 7).

5.3.6.2 Durability of surface-active sites

The stability of catalytic performance of CNU800 is displayed in **Figure 5.18**. Compared with the 1st run catalytic performance of the fresh CNU800 (100% SAM degradation, 15 min, 0.321 min⁻¹), the catalytic performance of CNU800 deteriorated in the 2nd run (100% SAM degradation, 60 min, 0.102 min⁻¹) and 3rd run (94% SAM degradation, 60 min, 0.045 min⁻¹). XPS analysis was conducted to obtain the chemical composition of the used CNU800 (3rd run) (**Table 5.3** and **Figure A9, Appendix**). In comparison to the fresh CNU800, the used CNU800 (3rd run) showed a 60% increase in the O/C value, which is ascribed to the oxidation reaction caused by PMS and ROS (e.g., ¹O₂) taking place on the surface of CNU800, inducing an increase in the surface oxygen concentration of carbon materials (Tavakoli et al. 2017). Meanwhile, the used CNU800 (3rd run) exhibited a 26% decrease in the N/C value. Besides, a 29% reduction in the graphitic N, a negligible change in the pyridinic N (5%), and a 18% increase in the pyrrolic N were detected in the used CNU800 (3rd run). The changes in N bonding configuration content indicate the conversion between N bonding configuration (graphitic N → pyrrolic N (Chen et al. 2018a)) in the process of PMS activation and the role of graphitic N as one of the main reactive functionality to activate PMS. The decomposition of

N bonding configuration in the highly-oxidative environment can be attributed to 1) the irreversible oxidative reaction between PMS and the active sites in the CNU800 for ROS (e.g., $^1\text{O}_2$) generation; and 2) the cannibalistic reaction between the active sites in the CNU800 and the produced ROS. In comparison to post-heating treatment adopted by other researchers to restore the graphitic N at the expense of energy consumption at a high thermal annealing temperature of 800-1000°C (Hou et al. 2019), it has been reported that reducing PMS dosage can effectively suppress the N species conversion and surface oxidation albeit compromising the catalytic performance to some extent (Oh et al. 2018). Thus, future efforts can be put into a delicate optimization of the reaction conditions (e.g., PMS dosage and pH) to enhance both catalytic performance and durability of the surface-active sites on carbocatalysts.

Figure 5.18. Reusability of CNU800 (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7).

Table 5.3. Chemical composition of the fresh CNU800 and used CNU800

	C	O	N	O/C	N/C	pyridinic N	pyrrolic N	graphitic N
	at.%	at.%	at.%	%	%	N_{pyridinic}-N/N_{total} (%)	N_{pyrrolic}-N/N_{total} (%)	N_{graphitic}-N/N_{total} (%)
CNU800	76.9	4.4	18.7	5.7	24.3	43.5	36.9	19.6
CNU800 3rd run	75.6	10.8	13.6	14.3	18.0	41.1	45.0	13.9

Atomic percentages of C, O and N were analyzed by XPS.

5.4 Conclusion

To sum up, this study adopted a facile, green and scalable pyrolysis approach to convert chitosan into a redox-active carbon nanosheet with NaHCO_3 as porogen and urea as nitrogen source together with a structure-directing agent. The N dopant concentration and contents of reactive functionalities (e.g., graphitic N and C=O group), graphitization degree and porous structure of CNU can be effectively tailored by T_p . CNU800 exhibited the most outstanding catalytic performance, which was associated with its high level of reactive functional groups (e.g., C=O and graphitic N), excellent graphitization degree, and its large SSA_{BET} and hierarchically porous structure comprised of mesopores and in-plane micropores.

NaHCO_3 alone can effectively convert chitosan into microporous carbon nanosheet with high adsorption efficiency but mediocre catalytic activity for PMS activation. Urea alone mainly induced mesoporous carbon nanosheets and ineffectively contributed to the catalytic activity as PMS activator in a pyrolytic process of chitosan. However, the introduction of urea with the presence of NaHCO_3 during chitosan pyrolysis can serve as a feasible approach for fabricating graphene-like carbocatalyst with hierarchically porous structure and an enhanced PMS-activating activity. Non-radical oxidation with $^1\text{O}_2$ as the main ROS was the dominant catalytic mechanism in the CNU800/PMS/SAM system, which showed a fair resistance toward the inhibition caused by NO_3^- , Cl^- and humic acid. The generation of highly reactive HClO at a high concentration of Cl^- contributed to the SAM degradation. The conversion between N bonding configurations due to cannibalistic reaction accounted for the partial deactivation of CNU800. Further efforts can be put into optimizing PMS dosage to realize the mitigation of the surface oxidation and N bonding reconstruction of carbocatalyst. This study provides insights into the PMS-activating activity of chitosan-based carbocatalyst for degradation of the recalcitrant pollutants and makes chitosan-based carbocatalyst a promising candidate for environmental restoration.

CHAPTER 6: Conclusions and recommendations

6.1 Conclusions

In the first part of this study (**Chapter 3**), the contents of N species and C=O group together with the catalytic performance of NG were delicately tailored by adjusting thermal annealing temperature. NG600 had an improved catalytic activity for SAM detoxification via PMS activation compared to NGs prepared from other synthesis methods. The efficiency of SAM degradation followed the order of NG600 > NG-NH₄NO₃-air > NG-urea-HT > NG-melamine-N₂. Non-radical pathway with surface activated PMS as the key ROS contributed more to SAM degradation than radical pathway in the NG600/PMS/SAM system.

In order to further improve the catalytic activity of NG, 2sNBG was synthesized through two-step thermal annealing (**Chapter 4**). The concentration of pyridinic N and BC3 as well as catalytic activity of 2sNBGs were delicately maneuvered through tuning the thermal annealing temperatures. The catalytic performances of the doped graphene in this study followed the order of 2sNBG800 > 2sNBG900 > 2sNBG700 > 2sNBG600 > NG600 > 1sNBGs > BG800. 2sNBG800 exhibited the best catalytic activity for PMS activation to degrade SAM. The introduction of B into NG can facilitate the shift of reaction pathway from a non-radical oxidation dominating in the NG/PMS system to the coexistence of non-radical and radical oxidations in the 2sNBG/PMS system. The synergistic coupling effect from bonding configuration of B-C-C-pyridinic N was the main reason for the enhanced catalytic activity of 2sNBG800.

Chapter 5 presents CNU which was synthesized as a renewable, cheap and easily accessible alternative to graphene-based carbocatalyst. The contents of graphitic N and C=O groups, graphitization degree and porous structure of CNU can be effectively tailored by T_p . CNU800 exhibited the best PMS-activating activity for SAM removal. The introduction of urea with the presence of NaHCO₃ during chitosan pyrolysis can serve as a feasible approach for fabricating graphene-like carbocatalyst with hierarchically porous structure and an enhanced PMS-activating activity. Non-radical oxidation with ¹O₂ (the main detected ROS) was the dominant

catalytic mechanism in the CNU800/PMS/SAM system.

In summary, the application of carbocatalysts with outstanding corrosion resistance and biocompatibility properties as a metal-free alternative for PMS activation can overcome the metal leaching problem of transition metal for PMS activation or circumvent the constant external supply needed for the energy activator for PMS activation. The surface chemistry, textural and structural properties of both graphene- and chitosan-based nanocarbon materials can be effectively tuned by adjusting synthesis conditions (e.g., temperature, precursors, and inert/ambient atmosphere) in this study. All the as-prepared carbocatalysts can efficaciously activate PMS to degrade sulfonamides in water (Table 6.1). The carbon nanomaterials as carbocatalysts can be potentially used as alternatives to metal-based catalysts in the water decontamination. 2sNBG outperforms NG as PMS activator for SAM degradation. The incorporation of B atoms into NG facilitates the shift of non-radical oxidation to radical oxidation in the 2sNBG800/PMS/SAM system. Compared with graphene-based nanocarbon materials, chitosan-based nanocarbon materials with cheap, sustainable and easily accessible chitosan as carbon precursor exhibit the relatively higher degradation efficiency with $^1\text{O}_2$ as the main ROS in the CNU/PMS/SAM system, and the higher resistance toward scavengers in real water matrix. However, the reusability of the nanocarbon materials needs further improvement (Table 6.1).

Table 6.1. Comparison between NG600, 2sNBG800 and CNU800

	SAM degradation performance ^a	Catalytic mechanisms	Inhibition by NO_3^- , Cl^- , and humic acid ^c	Reusability
NG600	4% (ads ^b), 100% (50 min), 0.090 min ⁻¹	Non-radical (surface activated PMS)	NO_3^- : negligible, Cl^- : 25%, humic acid: 43%	92% decrease in k_{app} , pyridinic N / graphitic N → pyrrolic N
2sNBG800	9% (ads), 100% (20 min), 0.182 min ⁻¹	Non-radical + radical	NO_3^- : negligible, Cl^- : 33%, humic acid: 64%	66% decrease in k_{app} , the adsorbed intermediates
CNU800	4% (ads), 100% (15 min), 0.321 min ⁻¹	Non-radical ($^1\text{O}_2$)	NO_3^- : negligible, Cl^- : negligible, humic acid: 26%	86% decrease in k_{app} , 26% decrease in N/C, graphitic N → pyrrolic N

^a Condition: [PMS] = 0.5 mM, [SAM]=10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7.

^b Adsorption condition: [SAM] =10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7.

^c [Cl^-] = 100 mg L⁻¹, [NO_3^-] = 10 mg L⁻¹, [humic acid] = 5 mg L⁻¹.

6.2 Recommendations for future works

6.2.1 Quantification of radical and non-radical reactive oxygen species

Currently, it is difficult to precisely quantify the contribution of radical and non-radical pathway. The mechanism of non-radical pathway is also not fully understood. It is essential to select the suitable radical scavengers, chemical probes and spin trapping agents, which 1) have high reactivities toward the target ROS albeit without remarkable reaction with other co-existent oxidants or ROS (e.g., PDS, PMS, $\text{O}_2^{\cdot-}$ / $^1\text{O}_2$), 2) form stable and quantifiable byproduct, and 3) will not affect the carbocatalysts (e.g. deposition/adsorption onto carbocatalyst surface passivating the active sites or reaction with target organic substrates, etc.). Moreover, due to the intrinsic distinction between PDS and PMS, further investigation is necessary to elucidate the mechanisms in the carbocatalysts/ PDS and carbocatalysts/PMS systems, respectively.

In general, the insightful understanding collectively requires 1) exploring persulfates decomposition (for the determination of electron shuttle mechanism or the formation of surface-confined complex) and substrate specificity/intermediate distribution; 2) employing the state-of-art characterization and analysis technologies; and 3) exercising the theoretical calculation improved by the adoption of relative solutions to the corresponding DFT limitations.

6.2.2 Practical application

For the practical application of carbocatalysts, three critical issues, namely poor catalyst durability, environmental concerns, and complexity of waste, must be addressed.

Carbocatalyst stability

The catalyst stability is compromised due to the occurrence of cannibalistic reaction whereby the generated ROS attack both organic substrates and carbocatalysts. The cannibalistic reaction can lead to the undesirable decomposition of carbocatalysts. The comparison between NG600, 2sNBG800 and CNU800 was presented in **Table 6.1**. The reconstruction of the N bonding configuration mainly

accounted for the deactivation of NG600 and CNU800. Apart from thermal annealing, other post-treatment methods such as UV-C irradiation and hydrogenation at a mild condition can be performed to remove the adsorbed organic substrates and intermediates as well as recover the reductive degree of carbocatalysts from oxidation. It has been reported that ultrasonication performs better to recover the PMS-activating capability of NG than washing and thermal annealing (Sun et al. 2013a).

Moreover, to improve the catalyst stability, future research can be focused on the following two aspects: 1) rationally designing (with the assistance of computational method) and synthesizing (selection of suitable synthesis methods) simplified and robust nanocarbon-based materials consisting of oxidation resistance surface functional groups conducive to redox reaction or special structure to improve the oxidative resistance. Further efforts can be put into the investigation on the change in other types of oxygen-containing functional groups (e.g., ester, carboxyl, phenolic, lactone, etc.) or fluorine-related functional groups at different temperatures and the resultant effect on the PMS activation by carbocatalysts. It has been reported nitrogen and fluorine co-doped graphene exhibited a higher cycling stability and electron conductivity than fluorine-doped graphene and NG for electrochemical application due to the intrinsic stability provided by F atoms (Huang et al. 2015), the formation of the strong covalent C–F bond (Jeon et al. 2015, Nakajima 2007), and the sp^2 hybridization of semi-ionic C–F bond (Lee et al. 2013a). Besides, the core-shell structure with graphene nanosheets as shell and functional material as core is a promising method to improve the stability of carbocatalyst. The out-sphere graphene nanosheets with high surface area, remarkable mechanical stiffness, excellent conductivity, and chemical and electrochemical stabilities (Geim and Novoselov 2007) can restricts the corrosion of the functional carbon core under the harsh operating conditions (Wu et al. 2015a). Conversely, this existence of core can inhibit the restacking of graphene nanosheets caused by van der Waals interactions (Li et al. 2008).

2) Controlling/optimizing the reaction conditions (e.g., PMS/PDS dosage, pH, etc.). The solution pH can simultaneously affect the adsorption and catalytic performance of carbocatalyst in the carbocatalyst/PMS/SAM system. As for the

catalytic performance, it has been reported that the effect of solution pH on the pollutant degradation is relative to the main ROS existing in the carbocatalyst/PMS/SAM system. Radical oxidation can be more affected by the change in the solution pH than nonradical oxidation (Guan et al. 2018). Thus, further investigation is needed for the effect of solution pH in the carbocatalyst/PMS/SAM system. Besides, as shown in **Table 6.1**, compared with NG600 and 2sNBG800, the CNU800/PMS/SAM system with $^1\text{O}_2$ as the main ROS showed a fair resistance toward the inhibition caused by NO_3^- , Cl^- and humic acid. Investigation using real wastewater should also be emphasized to reflect the realistic treatment condition.

Environmental concerns

Critical environmental concerns related to the carbocatalysts/persulfates system are 1) inadvertent release of carbocatalysts deployed in suspensions after treatment process into the environment; and 2) potential formation of toxic and carcinogenic oxyanions (ClO_3^- and BrO_3^-). To address the first concern, the alternative application platforms (or reactor) are necessary to limit the risk of nanocarbon material release. For instance, the catalytic oxidation and membrane separation process can be integrated into a hybrid system to improve carbocatalyst retention and reduce undesirable nanocarbon material release into the environment. As for the second concern, typically, the ROS generation in AOPs can potentially lead to cannibalistic reaction and formation of toxic and potentially carcinogenic ClO_3^- and BrO_3^- (Oh et al. 2016). The oxyanions (ClO_3^- and BrO_3^-) are formed when the generated ROS such as $\text{SO}_4^{\bullet-}$ react with halides (X^-), particularly Cl^- ($k_{\text{Cl}^- + \text{SO}_4^{\bullet-}} = 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and Br^- ($k_{\text{Br}^- + \text{SO}_4^{\bullet-}} = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Redpath and Willson 1975), via one-electron oxidation (Von Gunten 2003), as shown in Eqs 6.2.2.1 - 6.2.2.2 (Anipsitakis et al. 2006, Anipsitakis et al. 2008, Fang and Shang 2012, Yu et al. 2004).

To overcome the abovementioned second concern, the carbocatalyst offers a significant advantage over the metal-based catalyst because of its ability to induce the occurrence of nonradical pathway which has the following properties: higher substrate specificity and milder redox potential. The extent of radical and nonradical pathways are influenced by the many factors including heteroatom doping, surface

functional groups, and graphitization degree. Notably, the non-radical reaction is surface-based, and hence, to improve the contribution of nonradical pathway in the degradation of organic substrates, it is of great importance to design and synthesize a carbocatalyst with the capability of synergistic adsorption and carbocatalysis, which is not possible with metal oxides and other inorganic catalysts.

Suitable synthesis methods should be selected for surface functionalization to endow carbocatalysts with desirable surface affinity (e.g., incorporating oxygen-containing functional groups into the graphitic carbon network), complexing activity and electrostatic charge. This will promote better contact between persulfates/organic substrates and carbocatalyst surface, facilitating electron transfer within the charge-transfer complex for non-radical reaction.

Complexity of Waste

Although the adoption of the low-value wastes (e.g., waste plastic, waste vegetable, animal oil and industrial wastes) as precursors facilitates the green production of carbocatalyst, different waste precursors have different characteristics. Thus, it is important to optimize the synthesis technique to endow various waste precursors with the desired redox active functional groups. The relationship between the intrinsic nature of active sites, reaction mechanism (radical and non-radical pathways), and catalytic performance of carbocatalyst derived from waste remains equivocal and should be further explored.

Appendix

Appendix 1: Synthesis protocols for GO, NGs and g-C₃N₄

GO synthesis

GO was prepared via the modified Hummers' method (Hummers Jr and Offeman 1958). Typically, 23 mL H₂SO₄ in the 250-mL conical flask was put into an ice bath to be cooled to 0°C. 1 g of graphite and 0.5 g of NaNO₃ were added and the mixture was stirred for 0.5 h with the temperature kept below 5°C. 3 g of KMnO₄ was added slowly and the mixture was vigorously stirred to control the mixture temperature at below 10°C. Afterwards, the mixture was heated to 35°C and stirred at 500 rpm for 1 h. The color of the mixture turned from black into brownish grey. 46 mL of water was added slowly. Then the mixture was vigorously stirred until its temperature was raised to 98°C and the color became dark brown. Then the mixture was transferred to a 98°C water bath and stirred at 500 rpm for 15 min, followed by adding 140-mL warm water and 10 mL of H₂O₂. The mixture color turned into bright yellow. The mixture was then filtered and washed by HCl (1 L, 1 mol L⁻¹) and a large amount of Milli-Q ultrapure water. Finally, the GO cake was freeze-dried at -56°C for further use.

NG-melamine-N₂ synthesis

1 g of GO was dispersed in 100-mL water in a 250-mL beaker and sonicated for 30 min, followed by adding 1 g melamine. The mixture was stirred at 500 rpm for 30 min for melamine dissolution. Then the temperature of the mixture was increased to 50°C while stirring using a hotplate to evaporate water. Afterwards, the dried GO/melamine mixture was grinded and calcined at 450°C for 1 h with the ramping rate of 5°C min⁻¹ in the muffle furnace. Then the mixture was transferred to the tubular furnace for further calcination at 600°C in a N₂ atmosphere for 1 h with the ramping rate of 5°C min⁻¹. The final products were grinded, filtered and washed by a large amount of water and absolute ethanol in sequence and dried at 60°C in a vacuum oven overnight. The nitrogen-doped product was denoted as NG-melamine-N₂.

NG-urea-HT synthesis

0.08 g of GO was dispersed in 80-mL water in a 250-mL beaker and sonicated for 30 min, followed by adding 24 g urea. The mixture was stirred for 30 min and then sonicated for another 2 h. Then the homogeneous dispersion was transferred to a 125-mL autoclave bomb, sealed and put in the oven at 180°C for 12 h. The final product was grinded, filtered and washed by a large amount of water and absolute ethanol in sequence and dried at 60°C in the vacuum oven overnight. The nitrogen-doped product was denoted as NG-urea-HT.

NG-NH₄NO₃-air synthesis

1 g of GO was dispersed in 100-mL water in a 250-mL beaker and sonicated for 30 min, followed by adding 1 g NH₄NO₃. The mixture was stirred at 500 rpm for 30 min. Then the temperature of the mixture was increased to 50°C while stirring using a hotplate to evaporate water. Afterwards, the dried GO/NH₄NO₃ mixture was grinded and calcined at 350°C for 1 h with the ramping rate of 5°C min⁻¹ in the muffle furnace. The final product was grinded, filtered and washed by a large amount of water and absolute ethanol in sequence and dried at 60°C in a vacuum oven overnight. The nitrogen-doped product was denoted as NG-NH₄NO₃-air.

Synthesis protocol for bulk g-C₃N₄

A thermal polymerization method was employed to prepare bulk g-C₃N₄. In a typical run, exactly 2 g of urea was put in a crucible with a cover and then transferred to a Muffle furnace under ambient pressure in air. Urea was heated to 500°C for 3 h with the ramping rate of 5°C min⁻¹. Afterwards, the yellowish product was grinded, filtered and washed several times with 0.1 M nitric acid and water, and then dried in an oven at 80°C.

Table A1. Adsorption and catalytic activity of GO, rGO600 and NG400-NG800

	Adsorption removal ^a (%)	Total removal ^b (%)	k_{app} (min ⁻¹)
GO	2	40	0.0086
rGO600	34	75	0.019
NG400	1	39	0.0081
NG500	9	85	0.031
NG600	4	100 (50 min)	0.090
NG700	4	100 (60 min)	0.061
NG800	2	100 (60 min)	0.071

^a Condition: [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7.

^b Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7.

Table A2. Adsorption and catalytic performance of GO, rGO, NG, NBGs and BG

	Adsorption removal ^a (%)	Total removal ^b (%)	k_{app} (min ⁻¹)
GO	2	40 (60 min)	0.009
rGO800	35	76 (60 min)	0.020
NG600	4	100 (50 min)	0.090
NG800	2	100 (60 min)	0.071
2sNBG600	1	100 (45 min)	0.110
2sNBG700	2	100 (30 min)	0.133
2sNBG800	9	100 (20 min)	0.182
2sNBG900	9	100 (30 min)	0.161
1sNBG600	4	54 (60 min)	0.013
1sNBG700	2	57 (60 min)	0.014
1sNBG800	6	60 (60 min)	0.014
1sNBG900	2	56 (60 min)	0.013
BG800	10	42 (60 min)	0.009

^a Condition: [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7.

^b Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7.

Table A3. Adsorption and catalytic performance of CNUs, CN and CU

	Adsorption removal^a (%)	Total removal^b (%)	k_{app} (min⁻¹)
Chi600	3 (60 min)	40 (60 min)	0.009
Chi800	4 (60 min)	41 (60 min)	0.009
CNU600	-	37 (60 min)	0.007
CNU700	-	83 (60 min)	0.031
CNU800	10 (60 min)	100 (10 min)	0.482
Chi700	5 (60 min)	44 (60 min)	0.009
CN700	81 (60 min)	100 (10 min)	0.541
CU700	6 (60 min)	37 (60 min)	0.008
CN800	53 (5 min)	100 (5 min)	-

^a Condition: [SAM] = 10 mg L⁻¹, [catalyst] = 0.3 g L⁻¹, pH = 7.

^b Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.3 g L⁻¹, pH = 7.

Table A4. Adsorption and catalysis of CNU800 with different catalyst loadings

Catalyst loading (g L⁻¹)	Adsorption removal^a (%)	Total removal^b (%)	k_{app} (min⁻¹)
0.1	2 (60 min)	100 (50 min)	0.101
0.2	4 (60 min)	100 (15 min)	0.321
0.3	10 (60 min)	100 (10 min)	0.482

^a Condition: [SAM] = 10 mg L⁻¹, pH = 7.

^b Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, pH = 7.

Figure A1. (I) C1s scan and O1s scan of GO. (II) N1s scans of NG-melamine-N₂ (a), NG-urea-HT (b) and NG-NH₄NO₃-air (c). (III) O1s scans of NG400 (a), NG500 (b), NG600 (c), NG700 (d), NG800 (e), rGO600 (f), NG-melamine-N₂ (g), NG-urea-HT (h) and NG-NH₄NO₃-air (i). (IV) XPS survey spectrum of NG600.

Figure A2. The pH_{pzc} of NG600 (a), 2sNBG800 (b), Chi700 (c), CN700 (d), CU700 (e), CNU700 (f) and CNU800 (g).

Figure A3. The SAM degradation byproducts after reaction (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7).

Figure A4. (a) N1s scan and (b) B1s scan of 2sNBG600. (c) N1s scan and (d) B1s scan of 2sNBG700. (e) N1s scan and (f) B1s scan of 2sNBG800. (g) N1s scan and (h) B1s scan of 2sNBG900. (i) N1s scan of NG600. (j) B1s scan of BG800. (k) N1s scan and (l) B1s scan of 1sNBG800. (m) XPS survey spectra of NG600, BG800, 2sNBGs and 1sNBG800.

Figure A5. The SAM degradation byproducts in the 2sNBG800/PMS/SAM system (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7).

Figure A6. N1s scan of CNU600 (a), CNU700 (b), CNU800 (c) and Chi800 (d). XPS survey spectra of Chi800 and CNUs (e). C1s scan of CNU600 (f), CNU700 (g), CNU800 (h) and Chi800 (i).

Figure A7. N1s scan of Chi700 (a), CN700 (b), CU700 (c) and CNU700 (d). (e) XPS survey spectra of Chi700, CN700, CU700 and CNU700. C1s scan of CN700 (f), CU700 (g) and Chi700 (h).

Figure A8. Mass spectra of the detected SAM degradation byproducts in the CNU800/PMS/SAM system (Condition: [PMS] = 0.5 mM, [SAM] = 10 mg L⁻¹, [catalyst] = 0.2 g L⁻¹, pH = 7).

Figure A9. N1s scan of the fresh CNU800 (a) and CNU800 3rd run (b). Survey scans (c) of the fresh CNU800 and CNU800 3rd run.

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