EFFECT OF MULTI-ELEMENTAL DOPING ON THE CATALYTIC ACTIVITY OF CARBOCATALYSTS FOR ANTIBIOTICS DEGRADATION VIA PEROXYMONOSULFATE ACTIVATION

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UNIVERSITI SAINS MALAYSIA

2024

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by

MOHAMED FAISAL MALIK GASIM

Thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

April 2024

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious, the Most Merciful.

All praise and gratitude to Allah who is glorious and exalted for providing me with the opportunity to undergo a PhD program, for teaching me what I did not know, and for His blessings for the completion of this thesis. And peace and blessings be upon our beloved prophet Mohammad who has taught us everything we need in our lives.

I would like to express my deepest gratitude to my main supervisor Dr. Oh Wen Da, for his continuous guidance, support, patience, and encouragement throughout my studies. His compassionate guidance along with his academic experience was of great help in easing my research journey. I would also like to thank my co-supervisor Assoc. Prof. Dr. Low Siew Chun for enhancing our academic manuscripts through her valuable comments and fast responds whenever her help is needed. My acknowledgement is also extended to Assoc. Prof. Dr. Mohd Hazwan Hussin and Dr. Tuan Sherwyn Hamidon for providing access to their electrochemical station and assistance in operating the instrument. I would also like to acknowledge my lab colleague Choong Zheng Yi especially for his great help and assistant whenever I needed it. I am also thankful to my other lab colleagues and friends for their assistance and advice throughout my program. I would also like to thank Dr. Andrei Veksha and Assoc. Prof. Dr. Grzegorz Lisak from Nanyang Technological University (NTU, Singapore) for providing us with the carbon nanotubes that was used in this research. I would like to extend my appreciation to the technical and administrative staff from the School of Chemical Sciences, Universiti Sains Malaysia (USM) for facilitating my PhD program journey, not forgetting the technical staff of the School of Archaeology and Science and Engineering Research Centre (SERC). Also, the financial support given by Ministry of Higher Education Malaysia through the Fundamental Research Grant Scheme (FRGS/1/2020/STG04/USM/02/2) was indispensable for the completion of this research.

Last but not least, my profound appreciation goes to my parents Mr. Faisal Malik and Mdm. Nimat Akoud for their patience, wise guidance, absolute love, unconditional support, and their pursuit of my happiness and welfare. I would also like to thank my siblings Mr. Esmat, Mr. Samer, and Dr. Esraa, for their endless love, emotional and financial support during my PhD journey.

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LIST OF SYMBOLS, ABBREVIATIONS AND NOMENCLATURES

AOPs	Advanced oxidation processes
ATR	Attenuated total reflection
BC	Biochar
BPA	Bisphenol A
CIP	Ciprofloxacin
CNTs	Carbon nanotubes
DEP	Diethyl phthalate
DFT	Density functional theory
EDA	Electron donor-acceptor
EDX	Energy dispersive X-ray
EIS	Electrochemical impedance spectroscopy
EtOH	Ethanol
FE-SEM	Field emission scanning electron microscopy
FLT	Fluoranthene
FTIR	Fourier transform infrared
GAT	Gatifloxacin
g-C ₃ N ₄	Graphitic carbon nitride
GO	Graphene oxide
HA	Humic acid
HAADF	High-angle annular dark-field
<i>h</i> -BN	Hexagonal boron nitride
НОМО	Highest occupied molecular orbital
HR-TEM	High-Resolution Transmission Electron
HTC	Hydrothermal carbonization
ICP-MS	Inductively Coupled Plasma Mass Spectrometer

LCMS	High performance liquid chromatography-Mass spectroscopy
LUMO	Lowest unoccupied molecular orbital
М	Metal
MB	Methylene blue
MET	Metolachlor
MP	Methyl paraben
NPX	Naproxen
OFGs	Oxygen-containing functional groups
OTC	Oxytetracycline
PAHs	Polyaromatic hydrocarbons
PDS	Peroxydisulfate
PFRs	Persistent free radicals
PMS	Peroxymonosulfate
PMS*	Activated PMS complexes
PS	Persulfate
PZC	Point of zero charge
rGO	Reduced graphene oxide
ROS	Reactive oxygen species
SAM	Sulfacetamide
SE	Secondary effluent
SMT	Sulfamethazine
SMX	Sulfamethoxazole
SSA	Specific surface area
STEM	Scanning transmission Electron
STZ	Sulfathiazole
T.E.S.T	Toxicity Estimation Software Tool
TBA	Tert-butyl alcohol

TC	Tetracycline
ТСР	Trichlorophenol
TGA	Thermal gravimetric analysis
XPS	X-ray photoelectron spectrometer
Z	Relative atomic number
χ	Electronegativity

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Appendix MM	(a) XPS survey scans, (b) C1s, (c) O1s, (d) N1s, and V2p narrow scan spectra of the V4-CN catalyst before and after catalytic cycle.
Appendix NN	LC-MS results of CIP degradation (a) before oxidation and (b) after 120 min of oxidation in V4-CN/PMS system.

KESAN PENDOPAN BERBILANG UNSUR TERHADAP AKTIVITI PEMANGKINAN KARBOMANGKIN UNTUK DEGRADASI ANTIBIOTIK MELALUI PENGAKTIFAN PEROKSIMONOSULFAT

ABSTRAK

Baru-baru ini, penggunaan karbomangkin terdop heteroatom dan/atau logam untuk pengaktifan peroksimonosida (PMS) bagi penyingkiran bahan pencemar organik telah mendapat perhatian penyelidik. Walau bagaimanapun, terdapat keperluan untuk penerokaan yang mendalam dalam: (i) memahami pengaruh sifat karbon pada pendopan N dan S, (ii) menilai keberkesanan bioarang terdop tiga unsur dan mengenalpasti intra-tindakan antara berbilang unsur, dan (iii) mengenalpasti logam peralihan baharu yang sesuai untuk pendopan bersama dengan N bagi meningkatkan aktiviti karbomangkin. Dengan jurang penyelidikan ini, objektif utama kajian ini adalah untuk menyediakan karbomangkin terdop berbilang unsur untuk pengaktifan PMS dan mengkaji peranan unsur terdop dalam menigkatkan aktiviti pemangkin. Pertama, lima karbomangkin terdop N dan S telah disediakan daripada prekursor karbon yang berbeza, iaitu habuk papan (SD), bioarang (BC), karbonnanotiub (CNTs), grafit (GP), dan grafena oksida (GO) dan dibandingkan. Secara amnya, apabila tahap grafitisasi meningkat, tahap pendopan N dan S berkurangan, konfigurasi N grafit lebih diutamakan, dan konfigurasi S tidak diubah. Didapati NS-CNTs dapat mengaktifkan PMS dan menunjukkan penyingkiran ciprofloxacin (CIP) tertinggi (0.037 min⁻¹) disebabkan oleh kekonduksian yang luar biasa (3.38 S m⁻¹) dan tapak defeksi yang tinggi ($I_D/I_G = 1.28$). Laluan pengaktifan PMS didominasi oleh penjanaan oksigen singlet dan rejim pemindahan elektron. Kedua, bioarang terdop N, S dan B telah disediakan melalui teknik pengkalsinan satu periuk. Kesan keadaan sintesis terhodap sifat permukaan dan prestasi pemangkin bioarang telah disiasat untuk menjelaskan tindakan intra heteroatom. Didapati peningkatan suhu pengkalsinan daripada 500 kepada 800 °C meningkatkan kandungan BC₂O (2.0 kepada 13.67 at.%), mengurangkan kandungan S sebanyak >95%, dan meningkatkan penyingkiran tetrasiklin (TC) daripada 20.09% kepada 85.71%. Peningkatan nisbah asid borik:tiourea mempunyai kesan positif ke atas kandungan BC₂O, menggalakkan pembentukan N pirolik/piridin, dan meningkatkan prestasi pemangkin daripada 56 kepada 97%. Sumbangan utama penyingkiran TC adalah melalui laluan pengaktifan bukan radikal dengan tingkah laku kompetitif antara PMS dan TC ke atas penjerapan. Pengaktifan pada permukaan pemangkin juga dapat diperhatikan, dengan BC₂O memainkan peranan penting dalam pengaktifan PMS. Ketiga, karbomangkin terdop V dan N telah disediakan melalui kaedah pengkalsinan. Didapati atom N dan C berkoordinasi untuk membentuk karbon nitrida grafit (g-C₃N₄, CN) dan atom V berkoordinasi dengan -N dan -O dalam unit triazina CN. Kehadiran V (0.10 at.%) meningkatkan aktiviti pemangkin CN (daripada 0.025 kepada 0.051 min⁻¹), dan sistem V-CN/PMS/CIP mengaktifkan PMS melalui laluan pemindahan elektron bukan radikal (50.0%), laluan oksigen singlet (30.8%), penjanaan SO₄ · (11.5%) dan spesies reaktif lain (7.7%). Proses pengaktifan datang daripada kitaran redoks $V^{5+}/V^{4+}/V^{3+}$. Dalam semua kes, pemangkin optimum mempunyai toleransi yang tinggi terhadap matriks air dan spesies penganggu. Juga, perantaraan degradasi bahan pencemar telah dikenal pasti, laluan degradasi dicadangkan, dan ketoksikan bahan perantaraan telah diramalkan. Secara keseluruhannya, kajian ini (i) mendedahkan kepentingan memilih alotrop karbon yang sesuai bagi pendopan N dan S, (ii) memaparkan potensi pendopan N, S and B dan kemungkinan intra-tindakan antara unsur berlainan, dan (iii) menunjukkan kapasiti bahan berasaskan V dalam pengaktifan PMS pemangkin.

EFFECT OF MULTI-ELEMENTAL DOPING ON THE CATALYTIC ACTIVITY OF CARBOCATALYSTS FOR ANTIBIOTICS DEGRADATION VIA PEROXYMONOSULFATE ACTIVATION

ABSTRACT

Presently, the utilization of heteroatoms- and/or metal-doped carbocatalysts for the degradation of organic pollutants via catalytic peroxymonosulfate (PMS) activation has drawn significant attention. Yet, there exists a necessity for an in-depth exploration in: (i) understanding the influence of carbonaceous properties on N, S-codoping, (ii) assessing the effectiveness of heteroatoms tri-doping and apprehending the intra-actions among multiple heteroatoms, and (iii) identifying new transition metals that are suitable for co-doping with N to improve the catalytic activity of carbocatalysts. In view of these research gaps, the main objective of this study is to prepare multi-doped carbocatalysts for PMS activation and unveil the roles of the doped elements in the catalytic activity. Firstly, five N, S-co-doped carbocatalysts were prepared from different carbonaceous precursors, namely sawdust (SD), biochar (BC), carbon-nanotubes (CNTs), graphite (GP), and graphene oxide (GO) and compared. Generally, as the graphitization degree increased, the extent of N and S doping decreased, graphitic N configuration is preferred, and S configuration is unaltered. NS-CNTs illustrated the highest catalytic removal of ciprofloxacin (CIP) under PMS activation (0.037 min⁻¹) due to its remarkable conductivity (3.38 S m⁻¹) and defective sites ($I_D/I_G = 1.28$). The PMS activation pathway was dominated by singlet oxygen generation and electron-transfer regime. Secondly, N, S, B-tri-doped biochar was fabricated via a one-pot calcination technique. The effects of synthesis conditions, the surface properties and catalytic performance of the biochar were investigated to elucidate the heteroatoms intra-actions. Increasing the calcination temperature from 500 to 800 °C significantly increased the BC₂O content (2.0 to 13.67 at.%), reduced S-content by >95%, and increased the catalytic removal of tetracycline (TC) from 20.09% to 85.71%. Increasing the boric acid: thiourea ratio had a generally positive effect on BC₂O content promoted pyrrolic/pyridinic N formation and increased the catalytic performance from 55.96 to 97.03%. Major contribution of nonradical activation pathway with a competitive behavior between PMS and TC over adsorption and activation on the catalyst surface was observed, with BC₂O playing a decisive role in PMS activation. Thirdly, V, N-co-doped carbocatalyst were prepared via a facile calcination method. The N and C atoms were found to coordinate for the formation of graphitic carbon nitride $(g-C_3N_4, CN)$ and the V atoms were found to coordinate with the -N and -O in the triazine units of g-C₃N₄. It was found that the presence of V (0.10 at.%) noticeably enhanced the catalytic activity of CN (from 0.025 to 0.051 min⁻¹), and the V-CN/PMS/CIP system encompassed of a nonradical electrontransfer pathway (50.0%), singlet oxygen pathway (30.8%), SO₄⁻ generation (11.5%), and other reactive species (7.7%). The activation process was due to the $V^{5+}/V^{4+}/V^{3+}$ redox cycles. In all cases, the optimum catalysts were found to have high tolerance against water matrixes and interfering species. Also, the pollutant's degradation intermediates were identified, a degradation pathway is proposed, and the toxicity of the intermediates was predicted. Overall, this study (i) reveals the importance of the carbonaceous allotrope selection before N, S-co-doping, (ii) displays the potential of N, S, B-tri-doping and the possible heteroatoms intra-actions, and (iii) demonstrates the capacity of V-based materials in catalytic PMS activation.

CHAPTER 1

INTRODUCTION

1.1 Background study

In recent years, the increment in human population and industrialization caused adverse effects to the environment through unregulated release of significant amounts of organic pollutants. In particular, organic pollutants such as antibiotics have been increasingly found in water bodies [1]. Depending on their chemical structure, antibiotics can be classified into various types with fluoroquinolones, sulfonamides, macrolides, tetracyclines, and β -lactams being very common [2]. The undesirable presence of antibiotics in our water bodies presents an omnipresent threat that can cause the emergence of antibiotic-resistant bacteria strains, negatively affecting our water quality and human health. As a result, a diversity of innovative methods to treat antibiotics-contaminated water including adsorption, biological treatment, and advanced oxidation processes (AOPs) have been utilized. Among these methods, AOPs are preferred as they can destroy the organic pollutants and experience less selectivity towards the changes in the pollutants characteristics [3]. Compared with conventional AOPs (i.e. photocatalysis, sonocatalysis, Fenton-like reactions), heterogenous catalytic persulfate (PS) activation is highly desirable as they possess environmental and economic merits. Particularly, the use of external energy sources (i.e. heat, ultrasound, light irradiation) is not needed for the activation process. Also, unlike common oxidants that are used in gaseous (i.e. ozone) or liquid (i.e. hydrogen peroxide, peracetic acid) forms, PS are commercially available in solid salts which is relatively more easily transportable and handled.

PS can be obtained as peroxymonosulfate ($E_0 = 1.82 V_{NHE}$, PMS) and peroxydisulfate ($E_0 = 2.01 V_{NHE}$, PDS). PMS is an asymmetrical compound with a structure derived from H₂O₂ upon the substitution of an H atom with an SO₃⁻ group, whereas PDS structure is symmetrical due to the substitution of both H atoms in H₂O₂ with two SO₃⁻ groups (**Figure 1.1**). Both PMS and PDS are thermodynamically considered as relatively strong oxidant that can be used directly for oxidation or be activated to produce more reactive species [4,5].



Figure 1.1 Comparison between the chemical structures of H₂O₂, PMS, and PDS.

Catalytic activation is considered the most cost-effective technique to activate PMS as no external energy sources (e.g. heat, light irradiation, ultrasound) are required [6]. The catalytic activation of PS is able to produce reactive oxygen species (ROS) such as sulfate radicals (SO₄^{-,}), hydroxyl radicals ('OH), singlet oxygen ($^{1}O_{2}$), and other surface-confined reactive species. These products of the catalytic activation of PS can effectively and efficiently attack and degrade antibiotics for its mineralization. Overall, PS activation is drawing significant attention year-by-year as reflected by the amount of research focused on this topic (**Figure 1.2**). Furthermore, between PMS and PDS, research is directed more towards PMS activation as illustrated in **Figure 1.2**.

This can be ascribed to (i) PMS being more easily activated than PDS due to its asymmetricity of structure [7], and (ii) PMS (Oxone, 26.4/kg) costing almost-half of PDS (Na₂S₂O₈, 50.8/kg) (Sigma Aldrich). As catalytic PMS activation is more promising that catalytic PDS activation, current research should be more focused on PMS activation.



Figure 1.2 Comparison on the number of publications in Scopus on "PMS catalytic activation" and "PDS catalytic activation" between 2015 and 2022.

Between homogenous and heterogenous catalytic activation, the latter is preferred due to low susceptibility to environmental influences and the ease of separation and recovery of the solid catalyst from the treated solution [8]. Among the heterogeneous catalysts, transition metal oxides with multiple oxidation states such as Co₃O₄ Fe₃O₄ and Mn₃O₄ are widely reported as efficient PMS activators [9–12]. However, these transition metal catalysts may excessively leach during the application, leading to their poor stability and the need for secondary treatment to remove the leached metals [13]. To overcome this problem, nonmetal-based materials are utilized to replace the transition metal oxides, completely avoiding metal leaching issue. Catalytic activity of nonmetal-based catalysts such as biochar (BC), hydrochar, graphene oxide (GO), reduced graphene oxide (rGO), and carbon nanotubes (CNTs), has been proven in PMS activation [14–16].

Despite carbonaceous catalysts providing a more biocompatible alternative to metal-based catalysts, their catalytic activity remains inferior. This is attributed to pristine carbonaceous materials being composed mainly of carbon, oxygen, and hydrogen only. This significantly limits the number and variety of surface catalytic active sites which generates functional groups that have inferior catalytic activity compared with that of metallic materials. As a result, modification of carbocatalysts for the purpose of catalytic PMS activation is a must. The modification of carbocatalysts for PMS activation is made by exogenous doping, either using (i) heteroatoms (i.e. N, S, B, P) (ii) or metallic species (e.g. Co, Fe, Cu, Mn).

Heteroatom doping is often used to enhance the catalytic activity of carbonaceous materials with nitrogen, sulfur, and boron as the natural choices as dopants. Nitrogen, having a comparable atomic radius with carbon (N= 0.75 Å, C= 0.77 Å) yet a lower electronegativity allows desirable changes in the electronic behavior of the carbon lattice. The doped nitrogen can form graphitic N, pyrrolic N, and pyridinic N configurations, in which graphitic N promotes n-type doping whereas pyrrolic N and pyridinic N introduce p-type doping [17]. Boron which can bind at the graphitic sites (BC₃/B₄C) and in oxide-forms (BCO₂/BC₂O), can introduce defects, enhance charge transfer between surrounding C atoms, and provide PMS adsorption and activation sites [18–20]. Lastly, sulfur as an electron-rich atom, serves as a radical pathway inducer and is able to modify spin charges in the neighboring carbon

environment [3]. Metallic doping allows the introduction of strong redox species that will serve as catalytic active sites for PMS activation. The redox cycles of these transition metals allow the activation of PMS for the in-situ generation of ROS.

1.2 Knowledge gap and motivation/Problem statement

As a result of industrialization and human population growth, antibiotics such as ciprofloxacin (CIP) and tetracycline (TC) are detected in water bodies. CIP as a second-generation fluoroquinolone antibiotic is the most widely found fluoroquinolone antibiotic in raw drinking water (0.032 µg/L) and wastewater treatment plants (11–99 μ g/L) and can cause the emergence of antibiotic-resistant bacteria strains, adversely affecting water quality and human health [21]. Similarly, TC is a widely prescribed antibiotic known for its high stability and persistence, raising environmental concerns [22]. To treat such antibiotics, PMS activation by heterogenous activation is highly fruitful. Compared with metal-based catalysts (e.g. metal oxides), carbocatalysts are favoured due to their environmental merits (no metal leaching drawbacks) and cost-effectiveness. Nonetheless, the catalytic performance of pristine carbocatalyst must be enhanced to achieve satisfactory degradation of antibiotics. Overall, enhancing the catalytic performance of carbocatalysts is best made by doping foreign elements [3]. The doped elements can be heteroatoms (i.e. N, S, B) or metallic elements. Currently, research on enhancing the catalytic activity of carbocatalysts requires detailed investigation in three aspects, namely (i) carbonaceous properties effect on co-doping, (ii) effectiveness of tri-doping and intra-actions of multi-heteroatoms, and (iii) finding novel metallic species to be co-doped with N for enhancing the catalytic activity of carbocatalysts.

Co-doping of multiple heteroatoms into carbocatalysts has been shown to be more effective than single heteroatom doping due to the synergistic interactions between the heteroatoms [4]. Among the possible co-dopant selections, N and S are emerging as natural choices of heteroatoms for enhancing the PMS activation performance of carbocatalysts due to the rising synergistic effects occurring when N and S are joined in one carbonaceous platform. These synergistic effects occur due to the changes to the chemical and physical properties of the carbocatalyst such as shifting the Fermi level to the conduction band and facilitating electron transfer within the carbon framework and promoting the adsorption affinity of the co-doped carbocatalyst increasing the total charge of carbon active sites [3]. The enhanced PMS activation performance due to N and S co-doping has been reported for several carbocatalysts such as BC [23,24], CNTs [25], and rGO [26]. To this point, research has focused on enhancing the catalytic PMS activation performance of heteroatom doped carbocatalysts by (i) controlling the heteroatoms content (e.g. maximizing N content [27] or avoiding excessive S content [24]), (ii) modulating the bonding configurations of the heteroatoms (e.g. increasing graphitic N content [28]), (iii) and tailoring the carbonaceous properties of a single carbocatalyst (e.g. controlling graphitization or defective degree in BC [29,30]). Comparison between the catalytic potential of different N, S-co-doped carbocatalysts remains unexplored. Such comparison provides a better understanding on the selection of possible carbon structure for producing a high-performance PMS activator. The carbon structure has a pivotal rule in modulating the extent of N and S doping which in turn, controls the catalytic performance. Enhancement in graphitization degree of carbocatalysts facilitates electron-transfer and strengthen conductivity for promoted PMS activation [31]. Nonetheless, as the graphitization degree increases, it becomes strenuous for the heteroatoms to penetrate into the carbon structure [32]. As the positive pragmatic effects of N, S-co-doping on carbocatalysts are already proven, a gap emerges in finding the supreme carbocatalysts to be co-doped for PMS activation. In the trade-off between the carbonaceous properties (i.e., graphitization degree) and heteroatoms content, finding the feature to be worth of being modified to achieve the superlative catalytic performance remains ambiguous. To the best of our knowledge, identification of a suitable carbon structure along with the fundamental investigation of the N and S bonding configuration in different carbon structures is limited.

Secondly, despite the co-doping of heteroatoms such as N, S [23,24,33], N, B [34–37], and N, P [38,39] showing great potential in PMS activation, the co-doping process can have multiplex intra-actions between the different heteroatoms, resulting in complex reaction dynamics. For example, Chen et al. [37] found that sequential B doping into N-doped graphene changed the N bonding configurations. Also, the heteroatoms can form secondary phases such as graphitic carbon nitride $(g-C_3N_4)$, Sdoped g-C₃N₄, or *h*-BN, particularly in one-pot synthesis, which could hinder PMS activation. Tri-doping is rationally expected to bestow the carbonaceous catalyst with additional diverse active sites. These active sites can serve separately as electrontransfer facilitators (i.e. graphitic N), radical pathway initiators (i.e. thiophenic sulfur), organics and PMS adsorption sites (i.e. B sites) [3,40]. This is beneficial in obstructing the undesirable competition between adsorption and catalytic PMS activation on the carbonaceous catalyst active sites. However, detailed investigation on the mechanism involving the heteroatoms intra-action affecting each other's content and bonding configuration status to effectively construct a tri-doped environment that is efficient in PMS activation is required. Hitherto, non-metallic tri-doped catalyst for PMS

activation is only reported for N, S, P-tri-doped hollow carbon shells. Nonetheless, the doping process was done as post-treatment [41].

Thirdly, catalytic application of sole metal-based catalysts (e.g., metal oxides) is limited by metal aggregation, severe metal leaching, and poor stability. Doping metals (Me) onto carbon-based materials as support can significantly aid in retarding metal leaching and preventing agglomeration of metal nanoparticles [42]. The codoping of N and Me can promote synergistic effects. The electronegativity of N allows it to better coordinate with Me compared with C atoms. The metallic sites in N, Me co-doped carbonaceous materials allows maximum dispersion of metallic species over the carbon structure and formation of highly active catalytic sites [43]. Recently, several N, Me co-doped carbonaceous materials (Me = Co, Fe, Mn, Cu) illustrated great activity towards PMS activation [44,45]. These materials are referred to as "metal-nitrogen-carbon (Me-N-C) catalysts" [43]. During catalytic PMS activation by metal sites, the activation process is occurring because of the redox reactions between the metal's various oxidation states. Unlike transition metals such as Co, Fe, and Ni that illustrate dual-oxidation states (i.e. Co³⁺/Co²⁺, Fe³⁺/Fe²⁺, Ni³⁺/Ni²⁺) change during PMS activation [46,47], vanadium exhibits quadrable-oxidation states (V^{5+} , V^{4+} , V^{3+} , V^{2+}) during PMS activation [48–50]. This allows a productive utilization of metallic active sites and a greater chance of inducing several PMS activation pathways (i.e. radical and nonradical) for water decontamination. Catalytic activity of V-species towards PMS activation has been proven in heterogenous systems. Materials such as vanadium trioxide (V₂O₃) [49], vanadium sulfide (VS₄) [51], and fluorinated V₂AlC (F-V₂AlC) [50] have shown effective PMS activation performance for organics decontamination. Despite the great potential that V-species hold in catalysis, V-doped

carbocatalysts, particularly V-N-C catalysts, for PMS activation remains limitedly explored.

1.3 Objectives

The objectives of this study are:

- To synthesize N, S co-doped, N, S, B tri-doped, and V, N-co-doped carbocatalyst using pyrolysis techniques.
- ii) To systematically characterize the physicochemical properties and carbonaceous characteristics, and formation mechanisms of the asprepared carbocatalysts.
- iii) To evaluate the catalytic performance of the as-prepared carbocatalysts for antibiotics degradation *via* PMS activation.
- iv) To investigate the catalytic activity of the as-prepared carbocatalysts under different reaction conditions, in the presence of interfering species, in different water matrixes, and for several consecutive cycles.
- v) To propose the activation mechanism of PMS *via* the as-prepared carbocatalysts and the degradation pathway of the pollutants.

1.4 Scope of study

This study focuses on the degradation of antibiotics by catalytic PMS activation. The antibiotics that are used as model pollutants are CIP and TC. This study is separated into three parts. As N, S co-doping is proven to be effective in enhancing the PMS activation performance of carbocatalysts, the first part focuses on comparing different carbonaceous allotropes (i.e. BC, CNTs, rGO, graphite) to find the optimal carbocatalyst and to understand the effects of the carbonaceous properties on the N, S-

co-doping behavior and PMS activation performance. The second part of the study investigates the effects of synthesis conditions (temperature and precursors ratio) on the carbocatalyst properties in a N, S, B-tri-doped BC to understand the heteroatoms intra-actions during synthesis and their influence on the PMS activation performance. The third part focuses on improving the catalytic activity of carbocatalysts by formation of a V-N-C catalyst with trace levels of vanadium to understand the metallic redox cycles involvement in the catalytic activation of PMS.

1.5 Organization of thesis

Chapter 1 presents an overview of the background of this research and provides a discussion on the current research gaps and motivations. Also, the research objectives and organization of thesis are stated in this chapter.

Chapter 2 outlines the literature review on the major aspects related to enhancing the catalytic activity of carbocatalysts for PMS activation. Firstly, the chapter discusses the basic chemistry of peroxides followed by a discussion on the principles of PMS catalytic activation by heterogenous catalysts. Thereafter, an overview of common nonmetallic materials and their properties is given. Then, the performance of modified nonmetal-based catalysts with heteroatoms and metallic species for PMS activation is discussed.

Chapter 3 describes detailed experimental procedures on the materials used, synthesis techniques, catalytic reactions, characterization methods, and instrumental details.

Chapter 4 describes the preparation of five different N, S co-doped carbocatalysts and discusses the significance of the carbonaceous structure on the N, S co-doping behavior. The chapter also gives insights on the important carbonaceous properties that promote superior PMS catalytic activation for CIP removal.

Chapter 5 gives detailed discussion on the preparation and formation of N, S, B-tri-doped BC, and the effect of pyrolysis temperature and precursors ratios on the properties and catalytic activity of the as-prepared materials. The chapter also detailly discusses the catalytic activation mechanism of PMS by the N, S, B-tri-doped BC during TC degradation.

Chapter 6 describes the preparation of V, N-co-doped carbocatalyst (V-N-C) for the removal of CIP *via* PMS activation. The catalytic performance is investigated, and the catalytic activity and the activation mechanism is outlined. Specifically, the involvement of the V-redox cycles in the activation of PMS is discussed.

Chapter 7 provides a general discussion and a comparison between the catalysts prepared and studied in Chapter 4, 5, and 6.

Chapter 8 summarizes the findings from **Chapter 4**, **5**, and **6**. Furthermore, this chapter provides useful recommendations and future prospects for the development of carbocatalysts for PMS activation *via* doping of heteroatoms and atomically dispersed metals.

CHAPTER 2

LITERATURE REVIEW

2.1 Chemistry of persulfates

2.1.1 Comparison between peroxides

Ozone (O₃) was widely used for wastewater disinfection due to its high redox potential ($E^{\circ} = 2.08 V_{NHE}$) that enables it to initiate hydroxyl radical ('OH) based reactions with more efficiency compared to other conventional oxidants when used alone [52,53]. O₃ may also directly oxidize organic pollutants with targeting of C=C or N=N bonds [52]. However, the generation of O₃ from oxygen requires the use of an electrical discharge over pure oxygen or air. This process consumes significant amounts of energy and capital cost and therefore considered economically undesirable [52]. The fact that O₃ exists in nature in gaseous form requires additional capital cost to be compressed into transportable liquid. Furthermore, O₃ is known to be unstable and suffers from low-mass transfer yield [4].

On the other hand, hydrogen peroxide (H_2O_2) is a well-known chemical oxidizer. Due to its decomposition products being only oxygen and hydrogen, it is considered as an environmental option for water treatment [54]. Oxidative characteristics of H_2O_2 alone are not strong [52]. Despite that H_2O_2 activation with certain systems (e.g. homogenous and heterogeneous catalyst, UV, O_3 , Fenton-based) has shown enhanced oxidative properties [52,55–57], yet, H_2O_2 is thermodynamically unstable. Also, due to its natural liquid form, it is not facile to store and transfer.

PS that are produced and sold in solid form (salts) overcome the stability, storing, and transportability drawbacks encountered with O_3 and H_2O_2 . PMS is commercially available in a triple-salt form (2KHSO₅.KHSO₄.K₂SO₄) under the trade name of Oxone[®]. On the other hand, PDS is available in sodium and potassium-based salts (Na₂S₂O₈ and K₂S₂O₈). Between PMS and PDS, the former is more reactive than PDS due to their different molecular structures (PMS is asymmetric and PDS is symmetric). The structure of PMS allows it to be more prone to nucleophilic attack by organic pollutants compared to PDS [5]. Also, PMS has a higher peroxide bond dissociation energy (377 kJ mo1⁻¹) compared to PDS (92 kJ mo1⁻¹). This makes catalytic PMS activation by carbon- or noble metal-based catalysts more efficient in oxidizing organics, whilst PDS is more effectively activated by energy transfer regime (i.e., thermolysis, photolysis) to homolytically break the peroxide bond [58].

PMS is a strong oxidant (1.82 V_{NHE}) which can be used directly for the oxidation of organic contaminants without the formation of any radicals [4]. In such cases, the direct oxidation will take place through one or more of the following processes; one-electron oxidation, two-electron oxidation, or ${}^{1}O_{2}$ oxidation [5]. Despite that PMS is applicable for direct oxidation of certain organic contaminant, low reactivity will be achieved with PMS against organic contaminants with electron-deficient species (e.g., nitro and carboxyl groups) [5]. PMS reactivity against majority of compounds is considered too slow compared to radical-based systems [59]. PMS reacts with the electron-rich moieties rather than the bulk of the organic compound (heterocyclic rings), which will consequently generate incompletely degraded by-products. As a result of the aforementioned drawbacks of PMS-based direct oxidation, activation is therefore required.

2.1.2 Principles of catalytic PMS activation

Generally, PMS activation by heterogenous catalysts can occur *via* radical and nonradical pathways [10]. The active sites on the catalyst can have the ability to facilitate both radical and nonradical pathways. The radical pathway involves free radicals (SO4[•] and •OH) formation [60] while the nonradical pathway involves surface-confined reaction and ${}^{1}O_{2}$ generation [5]. The reactive species generated from the nonradical pathway are relatively milder than the radical pathway, resulting in a lower degradation rate and mineralization extent [61]. **Table 2.1** summarizes the main differences between the radical and nonradical pathways.

pathways.							
Pathway	Active species	Selectivity	Half- life	Redox potential	Deactivator species	pH range of effectiveness	
Radical pathway	SO4	Organics with electron rich groups, unsaturated bonds and aromatic π - electrons [10,62]	30– 40 μs [63]	2.5V _{NHE} – 3.1V _{NHE} [64]	Scavenged by natural organic matters and inorganic ions [4]	2.0–8.0 [10,62,65]	
	.ОН	Highly non- selective [66]	≤1 μs [63]	1.8V _{NHE} – 2.7V _{NHE} [4]		Moderate to basic conditions are preferred	
Nonradical pathway	$^{1}O_{2}$	Electron- rich substances [61]	2 μs [60]	2.2V _{NHE} [67]	Exhibits more tolerance towards conventional scavengers compared with free radicals [4]	Adapts with pH changes in water matrixes	
	Surface- activated PMS		-	Milder redox powers compared with free radicals			
	Surface- bounded radicals						
	Direct						

Table 2.1Comparison between the major properties of radical and nonradical
pathways.

electrontransfer

2.1.2(a) Radical pathway

During the radical pathway, an electron-transfer mechanism involving catalyst and PMS will promote the dissociation of the peroxide bond (O-O) leading to the insitu formation of free radicals (mainly as SO₄⁻ and 'OH) that will subsequently attack organic pollutants. OH is a powerful non-selective oxidant (2.8 V_{NHE} , pH = 0 [68]) with a short life-time $(t_{1/2} \le 1 \mu s [63])$ that reacts with majority of organics at a diffusion-controlled rate. 'OH attack organic pollutants through four mechanisms, namely i) radical combination, ii) radical addition, iii) hydrogen abstraction, and iv) electron-transfer [68–70]. Meanwhile, SO₄⁻ has a longer life-time ($t_{1/2} = 30-40 \,\mu s$ [63]) and a higher redox potential (2.5–3.1 V_{NHE} [64]) compared to 'OH. SO₄⁻ is selective towards one-electron oxidation of organics containing electron-rich groups, unsaturated bonds, and aromatic π -electrons through hydrogen and electron abstraction/addition reaction [71]. SO4⁻⁻ also illustrates superior flexibility towards pH change (within pH 2–8) [10,62,65]. PMS activation via radical pathway is also capable of generating superoxide radicals ($^{\circ}O_2^{-}$) through a side reaction with H₂O₂ [72,73]. Compared to SO₄⁻ and 'OH, reports on the reliance of organic pollutants degradation on O_2^- in PMS-based systems are less. This is ascribed to (i) the relatively short halflive of O_2^{-} [74], (ii) the prerequisite of formation of H₂O₂ via self-decomposition of PMS (a relatively slow reaction) [72], and (iii) the fact that O_2^- often undergoes hydrolysis for the generation of ${}^{1}O_{2}$ [75].

2.1.2(b) Nonradical pathway

Nonradical pathways induced from PMS activation has been drawing great interest recently. Despite its relatively milder oxidative potential compared to radical pathways, nonradical pathway has advantages of its own, such as having high tolerance towards inorganic ions in aqueous solutions, pH changes, common scavengers, and different water matrixes [60,76]. This pathway also reduces the formation of toxic halogen by-products that can be formed during a radical pathway reaction. Moreover, nonradical activation of PMS lowers excessive radicals' generation that react aggressively on the catalyst surface causing the deactivation of the catalyst and allows the complete utilization of PMS [10,60]. Unlike radical pathway, the dissociation of the peroxide bond of PMS does not occur in the nonradical pathway. The nonradical pathway is considered generally selective towards the degradation of electron-rich substances with electron-donating groups attached on the aromatic structure [4,5,77]. The nonradical activation of PMS can take place by four pathways, namely surface-activated PMS complexes, surface-bounded radicals, direct electron-transfer, and ${}^{1}O_{2}$ generation.

Surface-activated PMS complexes formation: During PMS activation through nonradical pathway, metastable activated PMS complexes can be formed on the catalysts surface. Interaction of the activated PMS complexes with pollutant at a specific orientation can promote electron-transfer, which subsequently leads to the decomposition of the pollutant [78]. Ding et al, concluded that the nonradical pathway involving surface-activated PS complex is more easily realized in the PDS-based system compared to the PMS-based system. As PMS asymmetric in its structure and charge distribution, its activation *via* one-electron reduction (to produce of SO₄^{+-/*}OH) or one-electron oxidation (to produce of SO₅⁺⁻) is more easily achieved compared to PDS (symmetrical in structure and charge distribution) systems [5].

- ii. Surface-bound radicals formation: Surface-bounded radicals such as SO4⁻⁻ and/or 'OH are radicals that are bounded to the catalyst surface and are resistant to scavenging [4]. The surface-bounded radicals are less reactive compared to the free radicals existing in the aqueous solution due to the surface confinement effect [60,79]. Also, in the case of free radicals, the organic pollutant molecules have more chance to meet and react with these radicals as they exist in the bulk of the solution, however, for the organic molecules to react with surface-bounded radicals, the interaction between the oxidant and the substrate can only take place on the catalyst surface. This limits the reaction system to only the catalyst surface rather than the entire aqueous solution.
- iii. Direct electron-transfer: During this pathway, the catalyst acts as an electron-mediator to facilitate the electron-transfer from the electron donors (adsorbed organics) to the acceptors (PMS) [63]. During this pathway, the PMS molecules are expected to maintain their chemical structures intact (O–O bond length). For the nonradical activation through surface-activated complexes pathway or direct electron-transfer pathway to arise, superb electrical conductivity of the catalyst is needed [5].
- iv. ${}^{1}O_{2}$ formation: ${}^{1}O_{2}$ with a moderate oxidative potential (2.2 V_{NHE}) and a relatively short lifetime ($t_{1/2} = 2 \mu s$) represents the excited state of a molecular oxygen. Although it exists in the bulk of the aqueous solution (not surface-bounded), ${}^{1}O_{2}$ is considered as a nonradical ROS due to its selectivity towards organics with electrophilic nature, mild oxidative

potential, and resistance towards conventional scavengers [4,60,80]. $^{1}O_{2}$ can be generated by PMS self-decomposition [81] or PMS catalytic activation.

2.2 PMS activation by pristine carbocatalysts

Pristine nonmetal-based catalysts or carbocatalysts are mainly composed of carbon and oxygen. The composition distribution varies significantly between the different carbocatalysts. To perform effectively as a PMS activator, the catalyst must have a large specific surface area (SSA) and porosity to host active sites and allow greater interactions between the catalyst, PMS, and organic pollutant. The main active sites of carbocatalysts include oxygen-functional groups (OFGs), sp² hybridized carbon, defective sites, and persistent free radicals (PFRs). The OFGs including C=O, C–OH, and C–OOH can initiate both radical and nonradical pathways due to their electron-rich nature. Particularly, electron-rich ketonic (C=O) and C–OH moieties can mediate the catalytic reaction with the PMS, involving the production of ROS [82] and have been accounted as the main active site for ¹O₂ generation from PMS [83].

PFRs can act as a PMS activator by facilitating the generation of free radicals in oxidant-containing systems [84]. PFRs can exist in carbon-based materials in three statuses: oxygen-centred, carbon-centred, and carbon-centred PFRs with OFGs [85]. PFRs can promote PMS activation *via* electron-transfer from PFRs to either PMS or adsorbed O_2 to form SO_4^+ and O_2^+ , respectively [86].

Since carbon atoms are the building blocks of carbocatalysts, understanding the carbon structural characteristics is paramount important for the successful utilization of carbocatalysts in environmental applications. These characteristics encompass graphitization degree, carbon hybridization status, and defective degree. The degree of graphitization can be interpreted as the extent of similarity between the studied material and graphene. Meanwhile, the sp² hybridized carbon can provide electron-rich sites for catalysis and allows π - π electron donor-acceptor (EDA) interactions with organics [87]. Furthermore, a high graphitization degree allows better conductivity throughout the carbon framework, fostering a higher electron-transfer regime, facilitating the nonradical activation of PMS [88]. Also, the extensive conjugation of sp² hybridized carbons furnishes the catalyst with an excellent electrical conductivity and enhanced electron-transfer capability through the carbon structure [31]. As for the hybridization status, the co-existence of sp²/sp³ hybridization can have a positive effect on catalyst activity, particularly by promoting an internal electron flow from sp³-carbon (donor) to sp²-carbon (acceptor), followed by an external electron migration from the later carbon configuration to oxidants [87,89].

Meanwhile, the formation of defective sites (i.e. edge defects, vacancies, curvatures) can destroy the stability of the graphitized structure and provide superior electron-donating capacity. Typically, the graphene-like structure is composed of carbon layers, in which each carbon atom is covalently bonded to three adjacent carbon atoms by three electrons. As a result of its half-filled orbital, the final fourth valence electron forming π -bonds, is delocalized and unconfined from movement through the carbon structure. These delocalized π -electrons prefer to migrate and form dangling σ -bonds states at the edges and defects to fill in the missing carbon atom at these sites [29,87]. Dangling σ -bonds with delocalized π -electrons at the defects will foster the electron-transfer process from the edged carbon for catalytic reactions.

2.2.1 Graphene-based materials

Graphene is a 2D oriented sheet-like composite with abundant and long range conjugated sp^2 hybridized carbons configurated in a honeycomb-like (hexagonal) structure with a thickness equal to an atom diameter. As graphene is composed of pure carbon, the carbon atoms are linked *via* covalent bonding and the graphene layers are interconnected by van der Waals forces [90,91]. Graphene is the parent form of other graphitic carbon allotropes [4]. Bending the two-dimensional structure of graphene into zero-dimensional, one-dimensional, and three-dimensional brings rise to fullerene (0D), CNTs (1D), and graphite (3D), respectively [92]. Graphene is known of its thermal conductivity, biocompatibility, low cost of production, and satisfactory electrical conductivity [93]. Oxidation of graphite leads to the formation of GO, and the following reduction of GO causes the formation of reduced-GO (rGO) [94] (Figure 2.1). Between the graphene-based materials, pristine graphite and GO are least studied in PMS due to their extremely packed and well-arranged sp² graphitized structure. Generally, a intact sp^2 carbon farmwork is not efficient during catalysis due to chemical inertness and lack of active functional groups [95]. Therefore, rGO with higher abundance of OFGs and structural defects is reported more often as a catalyst for PMS activation. For instance, Duan et al. [96] found that GO was only able to oxidize 12.4% of phenol in 180 min while rGO completely oxidize phenol within 150 min with the later showing a reaction rate 27-times higher than the former. The catalytic performance variation was ascribed to the presence of defective sites and highest content of ketonic groups (C=O) in rGO.



Figure 2.1 Formation of GO and rGO from graphite. Obtained with permission from Ghulam et al. [97]. (Copyright 2022 MDPI).

2.2.2 Ordered mesoporous carbon

Ordered mesoporous carbon (OMC) are a new type of non-silica mesoporous materials with extraordinarily well-ordered porous structure (2 nm < pore size < 50 nm). These materials usually illustrate high SSA, are thermo-mechanically stable, and enrichment with surface functional groups [92,98,99]. This allows OMC to have great potential in catalytic oxidation reactions. Duan et al. [69] prepared a series of carbon-based materials for PDS activation for the removal of phenolic compounds. Namely, the study compared the catalytic performance of CNTs, 3D cubic-ordered mesoporous carbon (CMK-8), rGO, nanodiamonds, $g-C_3N_4$, and fullerene (C60). The results illustrated that CMK-8 was in the top-three catalysts for PDS activation in which the defective edges, OFGs, and the three-dimensionality of CMK-8 structure were implicated as the possible catalytic driving factors. Research on the utilization of pristine OMC for PMS activation is highly limited.

2.2.3 Nanodiamonds

Nanodiamonds are a well-known nanocarbon-based material. They are comprised a diamond core and an amorphous carbon shell [100]. Therefore, the carbonaceous lattice of nanodiamonds is composed of hybrid sp^3/sp^2 structure. Also, nanodiamonds are abundant with OFGs (e.g. C=O, C-OH) and can be functionalized to produce new surface functional groups (i.e. C-N, C-S, C-O, C-Si) [100–102]. Hence, nanodiamonds have been widely used in catalytic applications [101]. The carbon system of optimal amounts of both sp^2/sp^3 hybridization can have positive effect on initiating radical based reactions. As sp^3 hybridization contains less S orbital composition (1/4 S orbital) where electrons are less restricted to nucleus allow the sp^3 carbon to have stronger electron-donating capacity than the sp^2 (1/3 S orbital). The coexistence of both hybridizations promotes an internal electron flow from the sp^3 carbon (donor) to the sp^2 -carbon (acceptor), followed by an electron migration from the sp^2 -carbon to PMS its activation [87,89]. Duan et al. [77] concluded that the synergistic effect of the sp^2/sp^3 hybridization of nanodiamonds were the driving factor for its affinity towards PMS activation *via* radical and nonradical pathways.

2.2.4 Carbon nanotubes

Carbon nanotubes (CNTs) are 1D-tubed carbonaceous materials composed of C-C covalent sp²-bonds in a hexagonal order. CNTs have high thermal conductivity, adequate mechanical strength, superior electrical conductivity and electron mobility [4,103]. Adil et al. [104] prepared oxygen-functionalized CNTs for PMS activation. During catalytic application, defective sites and OFGs played a major role in activating PMS for the generation of surface-bound and free SO4⁺⁻ and ⁺OH species. Similarly, Lee et al. [78] concluded that CNTs were able to activate PMS *via* the formation

reactive complexes on the CNTs' surface that reacted with the organic pollutants through electron abstraction, rather than the conventional radical pathway.

2.2.5 Biochar and hydrochar

Chars derived from biomass have drawn significant attention due to their fascinating properties, including high porosity and favorable surface chemistry. Also, since the chars can be synthesized from biomass (a practically free and abundant precursor), their application is eco-friendly and economically desirable compared to other catalysts. Depending on the synthesis pathway, chars are classified as hydrochar and biochar [105]. Typically, hydrochar is produced using the wet hydrothermal carbonization (HTC) method where biomass precursor is heated in an enclosed vessel at 180-250 °C to create a pressurized system [106]. Meanwhile, biochar is produced using a dry carbonization process (pyrolysis) performed under inert conditions at a relatively higher temperature (T > 400 °C) [107]. The extrinsic (surface area, porosity, morphology) and intrinsic (surface chemistry) properties of both chars differ significantly due to their different synthesis environments. The key differences between hydrochar and biochar are (i) hydrochar generally has a lower specific SSA and porosity than biochar [105,108], (ii) hydrochar has higher surface OFGs than biochar [109,110], (iii) biochar surface chemistry is mainly aromatic while hydrochar surface chemistry has more alkyl moieties [111], (iv) biochar has higher resistance towards oxidation during catalytic oxidation than hydrochar due to its higher aromaticity degree [109], and (v) the amount of PFRs found in biochar is generally higher than that in hydrochar [112]. Considering that chars are synthesized from biomass *via* thermal treatment, their properties are highly dependent on the synthesis conditions.

Biomass conversion into biochar can be achieved via torrefaction, gasification, and pyrolysis. Torrefaction is done under mild temperature (200–300 °C) with a relatively slow heating rate (10–15 °C min⁻¹) and short residence time (30 min - 4 h). However, it is not suitable to fabricate biochar for PMS activation because the milder synthesis conditions (temperature below 400 °C) will only yield a partially carbonized char (incomplete biomass conversion) with lower SSA and poor durability under oxidative environment [113]. Gasification is also inadequate for biochar fabrication because this method typically produces significantly lower product yield (<10%) with biochar containing a high amount of alkaline and alkali earth metals (e.g. Ca, Si, K), and polyaromatic hydrocarbons (PAHs) that are considered highly toxic [107,114]. Meanwhile, pyrolysis (heating the biomass in the absence of oxygen) is the most suitable biochar fabrication technique for PMS activation.

Activation of PMS by both hydrochar and biochar has been reported. For example, Liu et al. [115] found that food waste-derived hydrochar with a graphitized structure and abundant C=O groups can effectively activate PMS to degrade 2,4-dichlorophenoxy acetic acid with the cooccurrence of radical and nonradical pathways. Similarly, vacancies, edge defects, and curvatures in pine needle-derived biochar were found to be able to donate electrons to PMS to form ¹O₂, 'OH and SO₄'- for the removal of 1,4-dioxane [116].

2.2.6 Graphitic carbon nitride

Graphitic carbon nitride $(g-C_3N_4)$ is a conjugated polymeric semiconductor composed of mainly carbon and nitrogen. This material is known for its physicochemical stability, biocompatibility, and low cost of synthesis [117,118]. The fabrication of g-C₃N₄ is conducted by thermal polymerization of carbon and nitrogen-