



## Metal-free catalytic ozonation on surface-engineered graphene: Microwave reduction and heteroatom doping



Yuxian Wang<sup>a,b</sup>, Hongbin Cao<sup>b</sup>, Chunmao Chen<sup>a</sup>, Yongbing Xie<sup>b,\*</sup>, Hongqi Sun<sup>c</sup>,  
Xiaoguang Duan<sup>d,e,\*</sup>, Shaobin Wang<sup>d,e</sup>

<sup>a</sup> State Key Laboratory of Heavy Oil Processing, Department of Chemical Engineering, China University of Petroleum, Beijing, 18 Fuxue Road, Beijing 102249, China

<sup>b</sup> Division of Environment Technology and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

<sup>c</sup> School of Engineering, Edith Cowan University, 270 Joondalup Drive, Joondalup, Western Australia 6027, Australia

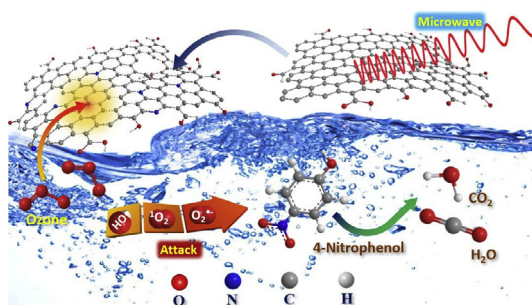
<sup>d</sup> School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

<sup>e</sup> Department of Chemical Engineering, Curtin University, Perth, WA 6845, Australia

### HIGHLIGHTS

- Reduced graphene oxide and N-doped graphene were prepared by microwave irradiation.
- Surface engineered graphene exhibited high catalytic ozonation activity.
- Microwave reduction created more edging sites and graphitic nitrogen species.
- Diverse reactive species,  $O_2^{\cdot-}$ ,  $\cdot OH$  and  $^1O_2$ , were possible for 4-nitrophenol degradation.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Keywords:

Metal-free oxidation  
N-doping  
Microwave  
Defects  
Catalytic ozonation  
ROS

### ABSTRACT

N-doped graphene has demonstrated exceptional activities in versatile metal-free catalytic processes. In this study, reduced graphene oxide (rGO) and N-doped rGO were synthesized by a facile approach via microwave reduction with a low energy input and short reaction time. The activities of the derived carbocatalysts were evaluated by catalytic ozonation of 4-nitrophenol (4-NP). Compared with thermally annealed rGOs in argon atmosphere, microwave treated rGO demonstrated a better performance in catalytic oxidation, and N-doping would further improve the catalytic activity. It is discovered that microwave irradiation not only gave rise to more edging sites and dangling bonds in rGO, making higher catalytic potentials for ozone decomposition than that from thermal annealing, but also resulted in a higher concentration of N dopants. XPS studies revealed that more graphitic N species were incorporated into the carbon basal plane during the microwave reduction processes. The reactive oxygen species (ROS) in 4-NP oxidation were evaluated and identified by liquid-phase electron spin resonance (ESR) and radical scavenging tests, which indicated the generation of  $O_2^{\cdot-}$ ,  $\cdot OH$  and  $^1O_2$  for 4-NP degradation. This study provides a facile protocol for fabricating advanced nanocarbon materials for green oxidation and enables new insights in catalytic ozonation with state-of-the-art carbocatalysis.

\* Corresponding authors at: School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia (X. Duan).

E-mail addresses: [ybxie@ipe.ac](mailto:ybxie@ipe.ac) (Y. Xie), [xiaoguang.duan@curtin.edu.au](mailto:xiaoguang.duan@curtin.edu.au) (X. Duan).

<https://doi.org/10.1016/j.cej.2018.08.134>

Received 22 May 2018; Received in revised form 8 August 2018; Accepted 20 August 2018

Available online 22 August 2018

1385-8947/ © 2018 Elsevier B.V. All rights reserved.

## 1. Introduction

Excessive exploitation and utilization of natural resources by the rapid industrialization and urbanization have posed emerging challenges to environmental remediation technology, especially in decontamination of water resources. The intensive discharge and accumulation of dissolved persistent organic pollutants (POPs) such as phenolic compounds in the wastewater and nature water systems have raised great concerns, since the POPs are recalcitrant to natural degradation and present high toxicity even at a low concentration. Among these POPs, nitroaromatic compounds discharged from pesticide and pharmaceutical industries manifest severely toxic, carcinogenic and mutagenic effects on both human beings and natural lives [1,2]. Owing to the strong electron-withdrawing nitro group with the aromatic ring, the elimination of nitroaromatic compounds by conventional chemical or biological treatments are unsatisfactory [3].

In the past few decades, development of diverse advanced oxidation processes (AOPs) has provided powerful strategies for complete destruction of aqueous organic pollutants by chemical oxidation [4–6]. Unlike physical separation of organic pollutants by adsorption processes, the generated highly reactive species such as hydroxyl radicals ( $\cdot\text{OH}$ , 2.7 V NHE) in AOPs can not only oxidize the pollutants effectively, but also possess the capability for complete mineralization of the organics into harmless compounds [7]. Among various peroxides used in AOPs, ozone molecules exhibit a higher oxidation potential (2.0 V NHE). Nevertheless, they are quite selective in oxidative destruction of pollutants because ozone is more favorable to attack the unsaturated bonds rather than the saturated bonds [8]. In addition, the chemical inertness of ozone molecules under acidic solution further hinders their self-decomposition to produce reactive oxygen species (ROS) for a deeper oxidation of the organics and intermediates. The involvement of catalysts in ozonation can significantly boost the ROS generation and enable catalytic ozonation for non-selective decomposition of contaminants. Moreover, the presence of a catalyst would adjust the pH-dependent behavior in ozone activation and promote the effective ROS generation over a wider pH range [9].

Metal-based catalysts, especially the transition metals/oxides, have been proved to be catalytically active for ozone decomposition [10–13]. However, the potential secondary contamination from metal leaching can hardly be avoided due to the strong oxidative capacity of ozone. Toward a sustainable future, developing metal-free catalysts with superb performance for wastewater remediation is in urgent demand. Constructed by  $\text{sp}^2$ -hybridized carbons in six-membered rings, two-dimensional (2D) graphene and graphene-based materials have stimulated intensive research interests owing to their exceptional physicochemical features [5,14]. In environmental remediation, several studies have revealed that thermally annealed reduced graphene oxide (rGO) demonstrated as a promising alternative as metal-based catalysts for activation of persulfates in AOPs [15–17]. By integrating theoretical and experimental studies, our recent work suggested that the defective structures in graphene lattice were the dominant active sites for catalytic ozonation, meanwhile the oxygen functionalities attached on graphene basal plane promoted the ozone decomposition [17,18]. However, in previous studies, synthesis of rGO either required harsh conditions (thermal annealing at high temperature) or employed strong reducing agents (hydrazine or borohydride) with a long processing procedure (12–24 h).

In recent years, microwave irradiation has aroused extensive interest in nanomaterial fabrication, which can provide a rapid and uniform heating ambience [19–21]. Microwave irradiation can instantaneously produce intensive heat because of the reorientation of polar molecules in an alternating electric field [19]. Using this method, Wang et al. successfully synthesized monodispersed and shape-controlled nanocrystals in five-minute microwave irradiation [21]. It was found that the fast heating from microwave irradiation predominantly accelerated the reduction of metal precursors and nucleation of the

metal clusters, resulting in rapid formation of the monodispersed structures. Additionally, Voiry et al. synthesized high-quality rGO by reduction of graphene oxide (GO) using one- to two-second of microwave pulse [22]. The instantaneously high temperature led to a rapid removal of most oxygen functionalities on graphene lattice and resulted in the simultaneous exfoliation of stacked graphene layers [23].

Heteroatom doping within graphene lattice has been recognized as an effective approach to tailor the chemical states and electrical properties of graphene by modulation of the band structure and electron transfer capacity of graphene [24]. Owing to the higher electronegativity of nitrogen atom than carbon (3.04 vs. 2.55), N-doping can promote the electron transfer from the adjacent carbon atoms to nitrogen, giving rise to a manipulated re-distribution of charge density by the conjugation between nitrogen lone pair electrons and graphene  $\pi$ -system [25–27]. These properties envisage the promising catalytic potentials for the N-doped graphene [15,24,28,29]. In this study, we prepared rGO and N-doped rGO (N-rGO) by microwave irradiation utilizing ammonium nitrate and GO as the nitrogen and carbon precursors, respectively. In addition, thermally annealed rGO and N-rGO in argon atmosphere were also prepared. Activities of the as-synthesized graphene-based materials were evaluated by catalytic ozonation of 4-nitrophenol (4-NP). Moreover, oxalic acid (OA) was employed as a target pollutant for further distinguishing the catalytic activities by excluding the ozone attacking. Raman, cryo-electron spin resonance (ESR) and X-ray photoelectron spectroscopy (XPS) analyses were performed to provide in-depth understanding of the structural differences between the microwave treated and the thermally annealed rGOs. Liquid-phase ESR and radical scavenging tests were performed to obtain the mechanistic insights into the catalytic ozonation by N-doped graphene and the contribution of ROS in 4-NP degradation.

## 2. Experimental

### 2.1. Chemicals and materials

Commercial graphite (99.99%) and para-benzoquinone (p-BQ, 99.9%) were purchased from Alfa Aesar. Potassium permanganate (99.5%), sulfuric acid (98%), hydrochloric acid (37%), tert-butanol (t-BA, 99.0%), ammonium nitrate (99.5%) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%) were obtained from Beijing Chemical Plant. Oxalic acid (OA, 99.9%) and 4-nitrophenol (4-NP, 99.9%) were procured from Sinopharm Chemical Reagent Co., Ltd. Sodium azide ( $\text{NaN}_3$ , 99.0%) was obtained from Fuchen Chemical Reagent Co., Ltd. 5,5-Dimethyl-1-pyrroline (DMPO) and 2,2,6,6-tetramethyl-4-piperidone (TEMP) were purchased from Sigma-Aldrich. All the chemicals were used without further purification. The initial reaction pH was adjusted by diluted NaOH and HCl solutions without buffering.

### 2.2. Synthesis of nitrogen doped reduced graphene oxide (N-rGO)

A modified Hummers' method [30] was employed for preparation of the graphene oxide (GO) utilizing commercial graphite as the carbon precursor (detailed synthesis route was described in [Supplementary Data](#)). In a typical synthesis, 1 g GO and 1 g ammonium nitrate were firstly dispersed into a mixture solution containing absolute ethanol (50 mL) and ultrapure water (50 mL) by ultrasonication for 30 min. The mixed solution was stirred overnight at 80 °C to ensure the complete evaporation of the solvent to derive the mixed products. Nitrogen-doped rGO was synthesized by treating GO with microwave irradiation or high-temperature annealing. For synthesis of N-rGO by microwave irradiation, the as-achieved solid mixture was ground finely and transferred into a quartz beaker followed by successive irradiation in a Kelvinator commercial microwave oven under the microwave power of 1200 W for 1 min. During the reduction process, electric arc accompanied by bright light halo was observed. The obtained black powder was labeled as MWI-rGO-N. MWI-rGO-N-0.5 and MWI-rGO-N-2 were

Download English Version:

<https://daneshyari.com/en/article/8946802>

Download Persian Version:

<https://daneshyari.com/article/8946802>

[Daneshyari.com](https://daneshyari.com)