Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Evaluation of the O_3/graphene-based materials catalytic process: pH effect and iopromide removal

Y. Yoon [a], H. Oh [b], Y.-T. Ahn [b], M. Kwon [b], Y. Jung [b], W.K. Park [a,c], T.-M. Hwang [d], W.S. Yang [a,*], J.-W. Kang [b,*]

[a] Electronic Materials and Device Research Center, Korea Electronics Technology Institute, 25 Saenari-ro, Bundang-gu, Seongnam-si, Gyeonggi-do 463-816, South Korea
[b] Department of Environmental Engineering, Yonsei University, Yonseidae-gil 1, Wonju-si, Gangwon-do 220-710, South Korea
[c] School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 440-746, South Korea
[d] Water Resources and Environmental Research Division, Korea Institute of Construction Technology, 2311, Deawha-dong, Ilsan-gu, Goyang-si, Gyeonggi-do 411-712, South Korea

ARTICLE INFO

Article history:
Received 15 December 2015
Received in revised form 24 February 2016
Accepted 15 March 2016
Available online xxx

Keywords:
Catalytic ozonation
Graphene oxide
Reduced-graphene oxide
Non-oxidative graphene
Hydroxyl radicals
Iopromide removal

ABSTRACT

Graphene-based materials, including graphene oxide (GO), reduced-graphene oxide (rGO), and non-oxidative graphene (nOG) were evaluated for catalytic ozonation in water solutions. Among the graphene-based materials evaluated for catalytic ozonation, it was confirmed that rGO was unsuitable to apply to the ozone (O_3)/graphene-based materials catalytic process because the high electron mobility of rGO prevented the transformation of O_3 into hydroxyl radicals (•OH). On the other hand, GO, which had sufficient oxygenated functional groups on the surface, decomposed and generated the most amount of O_3 and •OH, respectively. Although O_3/nOG process produced a lower amount of •OH than O_3/GO process, nOG was more effective than GO for the transformation yields of O_3 into •OH. Furthermore, nOG could generate •OH not only in the bulk phase, but also on the surface of nOG during catalytic ozonation. However, iopromide (IPM) was effectively removed during O_3/GO process due to the more •OH generated in the bulk phase than O_3/nOG process.

1. Introduction

Graphene is rapidly becoming a popular material for use in materials science and could potentially have a significant impact on related, real-world applications [1,2]. Since this strictly two-dimensional monolayer of sp^2 carbon atoms exhibits remarkable mechanical, thermal, optical and electrical properties [3–6], graphene has emerged as a promising material for applications in various fields [7–11]. However, graphene is difficult to produce in large quantities to obtain such theoretical uses. Thus, graphene-based flake materials, such as graphene oxide (GO), reduced-graphene oxide (rGO), and non-oxidative graphene (nOG), have been widely applied because GO, which constitutes an oxygenating functional group, is easy to functionalize [12], rGO can recover sp^2 structures and physical properties [13], and nOG can be easily mass produced.

Graphene-based materials have also been used in environmental applications for water purification, such as adsorption of contaminants [14–16], membrane technology [17,18], and catalytic processes [19–21]. In particular, nano-carbon materials can be applied to chemical catalytic oxidation processes, such as catalytic ozonation. Ozone (O_3) is a strong oxidant capable of reacting with a wide range of organic and inorganic solutes in water. However, the direct reaction of O_3 is quite selective in organic oxidation because O_3 has a very low reactivity toward single-bond compounds and aromatic substitutes in the electron-withdrawing group [22]. Advanced oxidation processes (AOPs) involving the generation of hydroxyl radicals (•OH), which are the most powerful oxidants that non-selectively react with many organic species, have received much attention for overcoming the limitations of ozonation [23]. With regard to the AOPs, O_3 has been applied to catalytic ozonation using nano-particles or carbon materials, because it can accelerate the initiation of the chain reaction that transforms O_3 into •OH as a catalyst [24–26].

There have been several investigations of heterogeneous catalyses in ozonation using carbon-based materials, such as granular activated carbon (GAC) [27–30] and carbon nanotubes (CNTs)

* Corresponding authors.
E-mail address: jwk@yonsei.ac.kr (J.-W. Kang).

http://dx.doi.org/10.1016/j.cattod.2016.03.014
0920-5861/

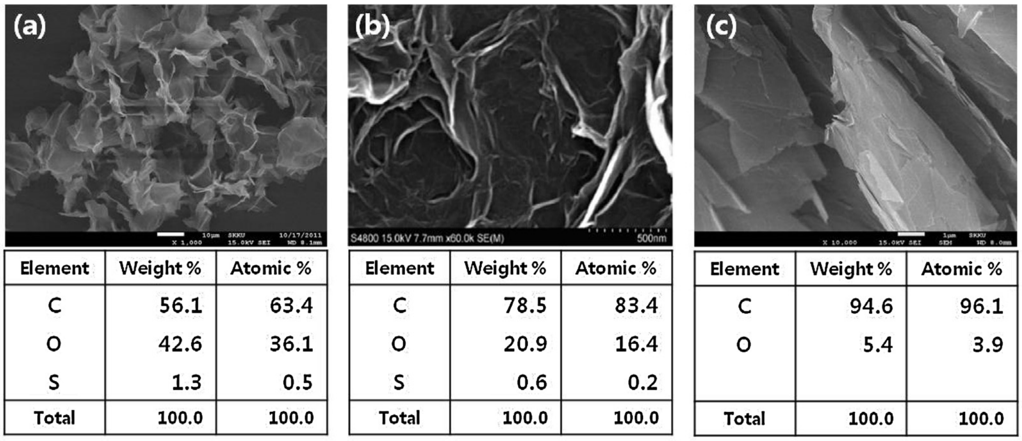

Fig. 1. SEM images and EDS data for (a) GO, (b) rGO, and (c) nOG.

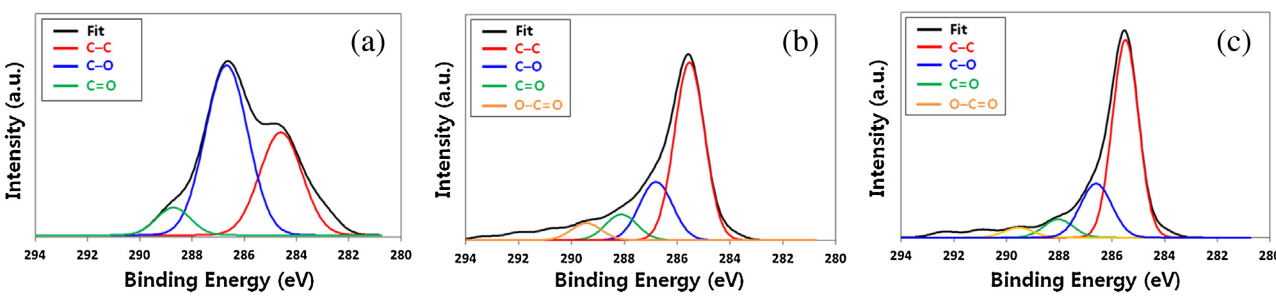

Fig. 2. XPS C1s spectra of (a) GO, (b) rGO, and (c) nOG.

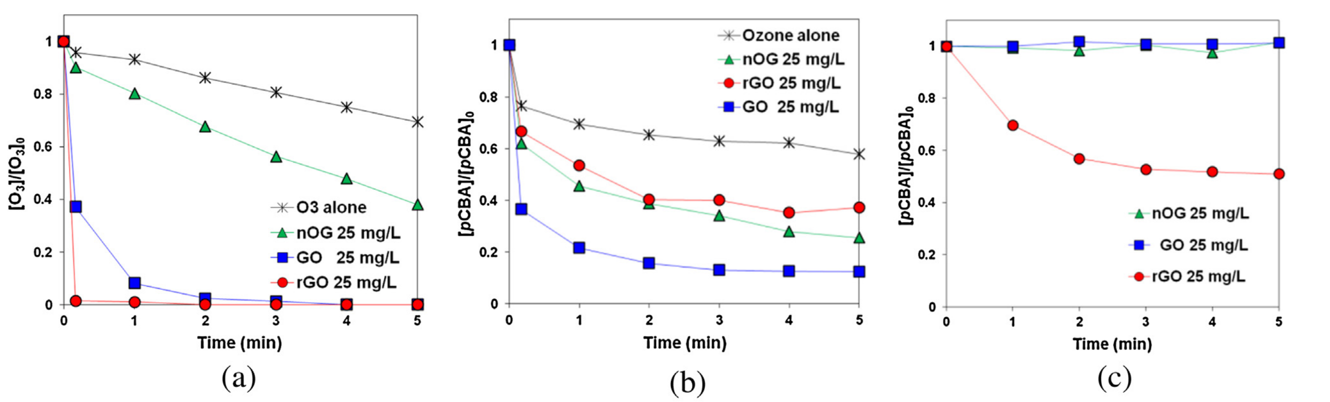

Fig. 3. Decomposition of (a) O_3 and (b) *p*CBA by O_3 alone and by the O_3/graphene-based materials catalytic process using different materials, including GO, rGO, and nOG ($[O_3]_0$ = 1 mg/L, $[pCBA]_0$ = 0.5 μM, materials concentration = 25 mg/L, pH 5). (c) The adsorption of *p*CBA by GO, rGO, and nOG ($[pCBA]_0$ = 0.5 μM, materials concentration = 25 mg/L, pH 5).

Table 1
R_{ct} values and •OH yields of the O_3/graphene-based materials processes ($[O_3]_0$ = 1 mg/L, $[pCBA]_0$ = 0.5 μM, nOG and GO concentration = 0, 25, 50, 100 mg/L, pH 5).

Parameters	O_3 alone		25 mg/L		50 mg/L		100 mg/L	
	R_{ct}	•OH yield	R_{ct}	•OH yield	R_{ct}	•OH yield	R_{ct}	•OH yield
nOG	9.7×10^{-9}	6.7×10^{-8}	4.8×10^{-8}	8.3×10^{-8}	8.3×10^{-8}	6.6×10^{-8}	5.4×10^{-7}	5.5×10^{-8}
GO	1.1×10^{-8}	7.1×10^{-8}	1.2×10^{-6}	6.7×10^{-8}	2.1×10^{-6}	6.7×10^{-8}	8.4×10^{-6}	6.8×10^{-8}

[31–33]. Although graphene-based materials have been used as catalysts in catalytic ozonation, Li et al. [34] and Wang et al. [35] reported the removal of bisphenol A and 4-nitrophenol respectively using rGO modified with metal oxide (MnO_2), which is generally well known as a catalyst [36,37], and Rocha et al. [38] used metal-free and nitrogen-doped graphene-based materials. Currently, there have been no comparative evaluations completed of catalytic ozonation using different virgin graphene-based materials. To understand the catalytic effect of the graphene-based materials accurately, it is needed to investigate the pure materials without further doping or modification. Additionally, the