



# Influence of (photo)bromination on the transformation, aggregation and sedimentation of graphene oxide

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## HIGHLIGHTS

- Functionalities of GO was reduced, and morphology fragments during bromination.
- Bromination enhances the reduction of GO during sunlight irradiation.
- $\cdot\text{OH}$ ,  $\text{Br}\cdot$ ,  $\text{BrO}\cdot$  and  $\text{Br}_2\cdot^-$  are effective on the GO photobrominated transformation.
- $\zeta$  potential, functionality and particle size all affect the environmental fate of GO.

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## ABSTRACT

The rapidly increasing use of graphene oxide (GO) necessitates the immediate investigation of the environmental fate and effects of this unique material. To date, little is known about the transformation of GO in environmental media, especially in water and wastewater treatment systems. This study explored the changes in the physicochemical properties of GO that result from (photo)bromination by simulating the reactions experienced by GO during water and wastewater treatment. The surface oxygen functionalities of GO considerably changed upon treatment. Specifically, the C–OH and COOH groups of GO were lost under bromination, and the reduction of GO was enhanced under photobromination. GO sheets wrinkled and fragmented under bromination, and GO decomposition was enhanced by photobromination. The decreases in O/C ratio and GO decomposition in the presence of bromine were mainly attributed to the relatively high oxidation potential of bromine, which can oxidize carbon nanosheets. The oxidation of carbon nanosheets, in turn, resulted in the decomposition and formation of brominated disinfection by-products. Irradiation, hypobromous acid/hypobromite ( $\text{HOBr}/\text{OBr}^-$ ), and reactive radicals, such as  $\cdot\text{OH}$ ,  $\text{Br}\cdot$ ,  $\text{BrO}\cdot$  and  $\text{Br}_2\cdot^-$ , may all affect the physicochemical transformation of GO in the presence of bromine and simulated solar light. Bromination and photobromination drastically changed the aggregation and sedimentation behavior of GO. The findings of this study advance knowledge on the transformations of GO in water treatment systems and provide insight on the environmental fate of the transformation products of GO.

## 1. Introduction

Graphene oxide (GO) is a structural analog of graphene and contains numerous O-containing functional groups [1]. GO can be applied in the energy [2], environment [3], biomedicine [4], and electronics [5] fields because of its various tunable properties. The global production capacity of GO is increasing given the extensive application prospects of this material. The annual production of GO in 2019 is estimated to be 10

times that in 2015 [5]. The continuously increasing production and application of GO and its isomers will release GO into the environment, where GO will be inevitably transformed. Although studies that focus on GO transformation are not numerous, they indicate that naturally existing compounds, such as sulfide [6,7] or ferrous compounds [8], or natural processes, such as solar irradiation [9], can drastically change the physicochemical characteristics of GO. Thus, the toxicity of GO to human beings, as well as its environmental fate, will be changed upon

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its release [7,8].

Released GO may possibly enter water bodies and wastewater treatment systems [10–12]. Given its small size, GO is difficult to remove through coagulation and sedimentation in traditional water treatment processes. Thus, GO is likely to contact and react with disinfectants during disinfection. To date, some important studies which are related to the water and wastewater treatment are working on the effects of carbon or metal based nanomaterials on the organic compound [13–17]. However, the change of physicochemical characteristics of GO are rare, only a few studies reported the GO transformation during reactions with disinfectants (e.g., chlorine or chloramine) [18,19]. However, other ions, such as  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{CO}_3^{2-}$ , will be involved in the reaction of GO and disinfectants and may drastically affect the transformation and behavior of GO in natural water bodies.

Among all naturally occurring ions,  $\text{Br}^-$  is the most ubiquitous and naturally exists in surface waters.  $\text{Br}^-$  levels in the US natural waters ranged from non-detectable to 2200  $\mu\text{g/L}$  with an average of 100  $\mu\text{g/L}$  [20] or 70  $\mu\text{g/L}$  [21], while the typical concentrations of  $\text{Br}^-$  in seawater is orders of magnitude higher than that in freshwater [22,23]. During the disinfection of drinking water,  $\text{Br}^-$  can be oxidized by chlorine to hypobromous acid/hypobromite ( $\text{HOBr/OBr}^-$ ) and other oxidative bromine-containing species [24,25].  $\text{HOBr}$ , an oxidant, reacts rapidly with some inorganic compounds, i.e., ammonia, iodide, and sulfite. Moreover, its reactions with natural organic matter (NOM) yield bromine-containing organic compounds, such as brominated disinfection by-products (Br-DBPs) [23]. Different from NOM, GO may have more aromatic structure, with functional groups mostly at their edges [26]. Although the structures of GO and NOM are very different, the basic composition of them are similar [27],  $\text{HOBr}$  may also react with GO to change its O-containing functional groups and morphology. Given that some of the brominated organic compounds, like brominated disinfection by-products or brominated naphthalenes, are considerably more toxic to human beings than their chlorinated homologues [28–30], understanding the bromine-related transformation and environmental behavior of GO is necessary.

This study aimed to understand the mechanisms that control the physicochemical transformation of GO under the  $\text{Br}^-$  concentration of 2 mg/L (as bromine), which is similar to that in surface water. The physicochemical transformation of GO under high  $\text{Br}^-$  concentration (10 mg/L as bromine) was also investigated. To avoid the interference of  $\text{Cl}_2$  or  $\text{Cl}^-$ , ozone was used to oxidize  $\text{Br}^-$  to  $\text{HOBr/OBr}^-$ . The mechanism underlying the bromine-induced transformation of GO was explored and discussed. Aggregation and sedimentation experiments were performed to illustrate the implications of GO transformation under (photo)bromination in the environmental fate of this material.

## 2. Experimental

### 2.1. Carbon nanomaterial and chemicals

GO (> 99%) was purchased from Tianjin Plannano Energy Technology Co., Ltd. (Tianjin, China). The information provided by the supplier stated that the product was prepared from graphite through a modified Hummers method [31]. The thickness of GO was 0.8–1.2 nm as inferred from atomic force microscopy (AFM) images. The oxygen/carbon (O/C) ratio of GO was 0.58 as inferred from X-ray photoelectron spectroscopy (XPS) spectra.

Bromine ( $\text{HBrO}/\text{BrO}^-$ ) stock solution (~20 mg/L as bromine) was prepared from KBr and  $\text{O}_3$  solution. The concentration of  $\text{HBrO}/\text{BrO}^-$  was measured through the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method by using a portable spectrophotometer (Hach 58700–00, USA).  $\text{O}_3$  stock solution (~20 mg/L) was prepared by bubbling  $\text{O}_3$  gas through ice-cold deionized water in a 2 L glass container.  $\text{O}_3$  gas was produced from  $\text{O}_2$  (99.99% purity) by using a 3S-A  $\text{O}_3$  generator (Tonglin Technology, China) supplied with a constant flow from a cylinder.  $\text{O}_3$  concentration was determined through a modified

indigo colorimetric method using a UV–visible spectrophotometer (UV-2401 PC, Shimadzu, Japan).

Indigo carmine (analytical reagent (AR) grade) was purchased from Sigma-Aldrich (St. Louis, USA). KBr (99.99% metal basis) was obtained from Shanghai Aladdin Biochemical Polytron Technologies Inc. in China. Disodium phosphate dodecahydrate (guarantee reagent (GR) grade) was purchased from Tianjin Guangfu Fine Chemical Reagent Research Institute (Tianjin, China), DPD powder pillows were purchased Tianjin Laoer Technology Co., Ltd. Concentrated hydrochloric acid (~37 wt%), and NaOH (AR grade) were purchased from Tianjin Chemical Reagent Co. (Tianjin, China).

### 2.2. GO suspension preparation

GO stock suspension was prepared through the ultrasonic dispersion approach. In a typical procedure, 30 mg of GO mixed with 100 mL of deionized water was added into a sealed amber vessel to obtain an inhomogeneous brown dispersion. This mixture was intensively stirred for 30 min and then ultrasonicated (SB25-12DTDN, NingBo Scientz Biotechnology Co., Ltd., China) at 40 Hz until no visible conglomerations were observed. The GO suspension was stored in the dark at 4 °C prior to the follow-up experiment and was stable over a period of 3 months.

### 2.3. GO irradiation and (photo)bromination

GO subjected to simulated solar irradiation was designated as GO (light) and was prepared by irradiating 10 mg/L of raw GO colloid dispersion in a quartz reactor (50 mL) with simulated sunlight for 24 h (Fig. S1). Irradiation was performed by using a photochemical reactor (XPA-7 (G5), Nanjing Xujiang Electromechanical Plant, China) equipped with a 420 W xenon lamp and a 290 nm cut-off filter. Two different concentrations of bromine-treated GO, which were designated as LBGO and HBGO, were obtained by mixing raw GO colloidal dispersion with 2 and 10 mg/L of bromine solution, respectively. GO samples that were simultaneously treated with bromine and simulated solar irradiation were designated as LBGO (light) and HBGO (light). LBGO (light) was prepared by spiking 2 mg/L of bromine solution into 10 mg/L of raw GO colloid dispersion with simulated sunlight irradiation for 24 h, while HBGO (light) increased bromine concentration to 10 mg/L.

### 2.4. Material characterization and chemical analysis

To examine the physicochemical changes exhibited by GO after bromination, photobromination and irradiation, the obtained samples were first ultrafiltrated through a 100 kDa filter (Millipore, USA) and then freeze dried using a vacuum freeze drier (LGJ-18, Beijing, China). The prepared powder-like samples were used for the following instrumental characterizations.

X-ray photoelectron spectroscopy (XPS) analysis was conducted using a photoelectron spectrometer (ESCALAB 250Xi, Thermo Fisher Scientific, USA). Transmission infrared spectra were recorded using a Fourier transform infrared spectroscopy (FTIR) spectrometer (Tensor 37, Bruker Co. Germany). Raman spectra were acquired by using a Raman microscope (TEO, RTS-HiR-AM, China). Surface microstructure was investigated through atomic force microscopy (AFM; MMAFM/STM, D3100M, Digital Ltd., USA) and scanning electron microscopy (SEM; FEI Nanosem 430, Netherlands).

The concentrations of  $\text{CHBr}_3$  and bromine-containing haloacetic acids (Br-HAAs) were analyzed through gas chromatography (6890N, Agilent Technologies, USA) in accordance with USEPA Methods 551.1 and 552.2, respectively, with some modifications. The gas chromatography setup in this study was equipped with an electron capture detector (GC- $\mu\text{ECD}$ ) (Agilent Technologies, USA) and an HP-5 fused silica capillary column (30 m  $\times$  0.25 mm I.D. with 0.25  $\mu\text{m}$  film thickness) (J

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