



# Large-scale production of high-quality reduced graphene oxide



Shichoon Lee<sup>a,\*</sup>, Sung Hun Eom<sup>b,c</sup>, Jin Suk Chung<sup>c</sup>, Seung Hyun Hur<sup>c,\*</sup>

<sup>a</sup> Department of Materials Science and Engineering, Jungwon University, Goesan 367-805, Republic of Korea

<sup>b</sup> JDT International Co. 421 Daun-dong, Jung-gu, Ulsan 681-802, Republic of Korea

<sup>c</sup> School of Chemical Engineering, University of Ulsan, 93 Daehak-ro, Namgu 680-749, Republic of Korea

## HIGHLIGHTS

- A process for large-scale (2 kg/day) GO production was designed.
- The process parameters were systematically studied for safe operation.
- The expanded graphite was used as a raw material to enhance the exfoliation.
- The graphene exhibits excellent electrical conductivity and a large surface area.

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## ABSTRACT

Large-scale (2 kg/day) solution-based graphene was fabricated in a continuous pilot process. It was found that controlling the heat of solution,  $\Delta H_{soln}$ , rather than that of the oxidation reaction,  $\Delta H_{rxn}$ , was crucial for safe operation because the heat-release rate of the dissolution of the oxidizer to sulfuric acid was higher than that of the oxidation of graphite to graphite oxide (GO). A small amount of water can also suppress the formation of the peroxide form that can cause an explosion. Three continuous stirred tank reactors (CSTRs) in series were used to feed the graphite and oxidizer step by step with slightly diluted sulfuric acid solution. The main oxidation reaction requires more than 2 h at 50 °C for adequate oxidation when the Hummers method is used. Reduced graphene oxide (RGO) prepared using the continuous thermal reduction equipment shows electrical conductivity of 600 S/m and a BET surface area of 400–600 m<sup>2</sup>/g, which were comparable to the values for RGOs fabricated using well-controlled laboratory scale procedures.

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## 1. Introduction

Several methods for graphene synthesis have been introduced since its discovery, and the outstanding properties of two-dimensional (2D) graphene have been reported [1–3]. Mechanical exfoliation of graphite (the scotch tape method) is considered a simple way to obtain pristine graphene, but this method is not applicable for large-scale production [1]. Large, high-quality 2D graphene sheets with single or few layers on Ni or Cu substrates can be obtained in less than 2 h via chemical vapor deposition (CVD) [4–6]. The obtained graphene sheets feature outstanding physical, thermal and electrical properties and are expected to be effectively used as transparent electrodes and semiconducting materials for a wide range of electronic devices [4–7].

Chemical exfoliation, which uses expandable graphite (EG) or graphite intercalation compounds (GICs), is one of the methods that can potentially be used for the large-scale production of

graphene nanoplatelets [8–17]. The EG or GIC is treated with chemicals that cause swelling and is then exfoliated with sonication and homogenized in suitable solvents. During the chemical exfoliation through an oxidation procedure, graphite oxide (GO) prepared by the oxidation of graphite is used as an intermediate, followed by various reduction steps to produce a reduced graphene oxide (RGO) [18–23]. The resulting GO has large interlayer spacing and can readily be exfoliated with simple sonication or thermal exfoliation at high temperature. This chemical exfoliation of graphite is an affordable method for the large-scale production of GO. Although RGO has many defects and remaining oxygen functional groups which cause deterioration in electrical conductivity, the obtained RGO nanoplatelets possess high porosity and large surface area, which enable RGO to be used in various applications, including as electrode materials for supercapacitors [18,19]. Some amount of remaining functional groups in RGO after reduction can enhance both the dispersion in various organic solvents and the compatibility with polymeric matrices [24–27]. The surface functional groups also can be modified by well-known chemical reactions into other groups for further applications [28–31].

\* Corresponding authors. Tel.: +82 52 259 1028 (S.H. Hur).

E-mail addresses: [tonygren@jwu.ac.kr](mailto:tonygren@jwu.ac.kr) (S. Lee), [shhur@ulsan.ac.kr](mailto:shhur@ulsan.ac.kr) (S.H. Hur).

Graphene oxide is also a promising precursor for high-quality graphene films and coating applications. It can be easily deposited as a single layer onto various substrates for microelectronic applications by spray coating [18,32]. The defects can be remedied by ethylene treatment at high temperature, and the  $sp^2$  networks can be restored by the reduction of GO to RGO in a solution by chemical or thermal treatment, which recovers the electrical conductivity of the final products [33].

Several methods for the oxidation of graphite to GO using strong acids and oxidants in the laboratory have been used for a long time, such as the methods proposed by Brodie [34], Staudenmaier [35], and Hummers and Offeman [36]. Both the Brodie and Staudenmaier methods use hydrochloric acid, where a highly toxic chlorine dioxide gas is liberated during the reaction. On the other hand, relatively less gas may evolve at the reaction temperature used in the Hummers method, and the reaction completes within a short time as 2 h. Both the Brodie and Staudenmaier methods require more than 24 h reaction time. Taking into consideration safety and productivity, the Hummers method is considered to be the best for establishing a process for GO production. So far, the production of GO on a laboratory scale using the Hummers methods has been extensively performed, but only limited attempts have been made for large-scale production. The peroxide formed in sulfuric acid during the oxidation of graphite not only causes a sudden explosive reaction above a solution temperature of 55 °C, but also has deterred the development of large-scale production facilities [37,38]. In this paper, we report for the first time a large-scale continuous stirred tank reactor (CSTR) process in which about 2 kg of GO is fabricated per day. The optimized reaction conditions that can be used to avoid an explosion during the oxidation of graphite to GO on a large scale were studied using calorimetry experiments. The modified Hummers method with minimal additives was used during the pilot GO production. The RGO fabricated in this study exhibits a large surface area and high electrical conductivity.

## 2. Experimental section

Natural graphite flakes with a size of 50  $\mu\text{m}$  (QKG 296 grade) and expanded graphite with a mean size of 100  $\mu\text{m}$  (ES grade) were purchased from Qingdao Carbon Co. in China and Samjung C&G in Korea, respectively. A reaction calorimeter (RC-1, Mettler Toledo, SI-1) was used to measure the heat generated during the dissolution of the oxidizer and the oxidation reaction during the modified Hummers process. The ratio of graphite to  $\text{KMnO}_4$  oxidizer was varied from 1:3 to 1:5 with 860 g of 97% sulfuric acid. The calorimetry experiments were carried out at 10 °C, 35 °C, and 100 rpm. The amount of heat released was first measured in the dissolution of the oxidizer in the absence of graphite in order to determine the heat of solution of the oxidizer to the sulfuric acid,  $\Delta H_{\text{soln}}$ . The heat of reaction,  $\Delta H_{\text{rxn}}$ , and the heat released during the oxidation reaction of the graphite in the solution were then measured in the presence of graphite.

The formation of peroxide was monitored with the color change in  $\text{H}_2\text{SO}_4$  solutions and UV–vis spectroscopy (UV–vis, Cary 5000, Varian) when the oxidizer  $\text{KMnO}_4$  was dissolved in aqueous  $\text{H}_2\text{SO}_4$  solutions of various concentrations without adding graphite. The absorbance was measured after calibration of each concentration of  $\text{H}_2\text{SO}_4$  in the absence of the oxidizer.

The pilot process for graphite oxidation consists of three steps: solid feeding of an oxidizer and graphite with mixing in a series of CSTRs, oxidation reaction in the main reactor, and dilution and collection of the final product. In the solid feeding step, three CSTRs (1.5 L) are operated in series in order to avoid an abrupt temperature increase. The powdery graphite and  $\text{KMnO}_4$  were fed into the

solution using a solid feeder. The 90% cold  $\text{H}_2\text{SO}_4$  solution was prepared at 7 °C in an aqueous  $\text{H}_2\text{SO}_4$  tank and fed to the reactor at a volumetric rate of about 300 mL/min (550 g/min mass flow rate). The graphite was fed to the first reactor at 4 g/min and mixed with sulfuric acid solution with vigorous stirring. The oxidizer was fed into the second reactor at a rate of three times of the graphite feeding. The third reactor was designed to provide a longer residence time, further mixing, and effective removal of the generated heat during the oxidation of the graphite. All three reactors were equipped with cooling jackets to control the temperature. In the CSTRs, the accumulated heat can be dissipated by dispensing the solution to the next tank as well as by vigorous stirring inside the reactor [39]. During normal operation, the solution temperature of the reactor was maintained around 15 °C during oxidizer feeding and dissolution into the sulfuric acid, which indicates the stabilized steady state of the CSTR.

The mean space time (reactor volume/flow rate) is estimated to be about 5 min at each reactor (15 min for all three CSTRs) [39]. Acid-proofed plastic tubes and volumetric diaphragm pumps were used to deliver the solutions to the next CSTRs. The total length of plastic tube was about 50 m, which corresponded to 30 min of space time. The length of the tube can be modulated to control the space time for better dispersion and mixing before the slurry enters the reactors. Empirically, the residence time in the reactor should be at least 30 min at around 15 °C for better dispersion and mixing during the oxidation reaction [36].

The safely-mixed solution was pumped into the main reactor with a reactor volume of 40 L. By using a series of three CSTRs charged with a slightly diluted  $\text{H}_2\text{SO}_4$  solution, the heat generated during the dissolution of  $\text{KMnO}_4$  in sulfuric acid can be effectively managed so that an abrupt temperature increase does not occur. After complete dissolution of the oxidizer, the oxidation reaction of graphite is not drastically exothermic and would no longer cause an abrupt temperature rise or an explosive reaction in the main reactor. The main reactor was designed to provide a mean space time of about 130 min and a reaction temperature up to 80 °C at atmospheric pressure to provide an adequate oxidation reaction.

Reduction and expansion of GO was carried out with a continuous thermal expansion machine at around 1100 °C with 30–60 s residence time. The feeding rate of GO was around 100 g/h with 10 L/min  $\text{N}_2$  flow. The feeding of the GO powder, thermal expansion, and collection are carried out in a continuous process. The as-dried GO powder is fed with a solid feeder and delivered into a heating chamber while an inert carrier gas is blown in. The thermal processing should be carried out under an inert gas environment to avoid burning the GO in the presence of oxygen. As the GO powder is passed through the heating chamber, the oxygen functional groups are readily decomposed into  $\text{CO}_2$  and water vapor [40,41], and the evolved gas causes the layers to be lifted and exfoliated. Regulation of the flow rate of the carrier gas is important to properly control the space time of the powder in the heating chamber.

The resulting GO and RGO were analyzed with a scanning electron microscope (SEM, Supra40, Carl Zeiss) after deposition on a Si wafer. The compositions of C, H, O, N, and S in the prepared GO and RGO were measured with an elemental analyzer (EA, Flash 2000, ThermoScientific). Atomic force microscopy (AFM, MultimodeV, Veeco) was used in the experiment to measure the dimensions and sheet thicknesses of the GO and the RGO. The samples were dispersed in 0.5 mg/mL and sonicated for 10 min in *n*-methyl pyrrolidone (NMP). AFM was carried out on the Si wafer after spin-coating of the GO solution, followed by blow-drying with a nitrogen gun. Raman spectroscopy (Raman) was performed using helium neon with a laser wavelength of 532 nm (alpha 300R, WITec). X-ray diffraction (XRD) results were obtained with  $\text{Cu K}\alpha$  0.1545 nm radiation (D/max 2500, Rigaku). The surface area

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