Expanding characteristics of graphite in microwave-assisted exfoliation

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Abstract—The exfoliating nature of graphite is critically important to a variety of engineering applications. Much, however, still remains uncertain and controversial about the mechanophysical parameters and processes involved in graphite exfoliation. This leads to the need for quantitative characterization of the expansion of graphite in the microwave-assisted exfoliation where KMnO₄ and HNO₃ are used as oxidant and intercalation agent, respectively. Here, the expanding characteristics of graphite in microwave-assisted exfoliation are examined as a function of: (i) mixing ratio (by weight) of graphite, KMnO₄, and HNO₃; (ii) mixing time; (iii) graphite form (natural vs. synthetic), type (lump vs. flake), and size (10 to 40 μm in diameter). Based on experimental measurement, we construct a fluid-dynamics-based model that describes the dependence of expansion ratio on graphite form, type, and size. Also investigated is the effect of reduction process on C:O ratio for raw graphite, expanded graphite with reduction process, and expanded graphite without reduction process. The findings of this study should lead to better understanding of the expanding characteristics of graphite.

Keywords—graphite; microwave-assisted exfoliation; expansion ratio; mechanophysical parameter; fluid-dynamics based model

I. INTRODUCTION

The exfoliation of graphite (with layered nature) is a volumetric expansion of graphite by up to hundreds of times resulting from the crystallographic delamination along its c axis. A sudden, rapid expansion of intercalation agent exerts a force on the adjacent layers of graphite during exfoliation, thus creating a worm-shaped, accordion-like material with low density, high temperature resistance, high lubricity, and high flexibility. Due to the inherent features, exfoliated or expanded graphite (EG) have been widely and successfully used in diverse applications such as packings [1], fire extinguish agents [2], thermal insulators [3], adsorption substrate [4], etc. Recently, EG is being recognized as a promising material for the industrial-scale production of defect-free graphene that can be used for multiple industries from flexible, wearable, and transparent electronics to high performance computing and spintronics [5]. Among large-scale, cost-effective production methods for graphene (e.g., micromechanical cleavage, liquid-phase exfoliation, chemical vapor deposition, molecular beam epitaxy, etc.) [6], the exfoliation of graphite by microwave irradiation (i.e., microwave-assisted exfoliation) is considered rapid and efficient because it can be carried out at room temperature in a few minutes with a simple laboratory facility, that is, a microwave oven.

Despite intensive progresses in understanding the mechanism and structure of EG prepared by microwave irradiation, the dependence of graphite expansion ratio, ER, on mechanophysical parameters including mixing ratio, mixing time, and graphite properties (e.g., form, type, and size) has not been paid attention and it still remains challenging and illusive. Most reported researches in this field are methodological [7-9], focusing on the effect of diverse oxidants and intercalation agents on the ER of EG by microwave irradiation. Considering the engineering significance of producing graphene in industrial quantities, the quantitative characterization of the expanding nature of graphite as a function of the mechanophysical parameters is therefore essential for achieving a breakthrough in graphene commercialization and furthermore understanding the chemothermal processes involved in microwave-assisted exfoliation.

In this paper, the microwave-assisted exfoliation method proposed by Wei et al. [8] where potassium permanganate (KMnO₄) and nitric acid (HNO₃) are respectively used as oxidant and intercalation agent is applied to prepare EG by reason of a simple and cheap preparation process achieved in minutes. Based on the measurements of ER obtained by the method, we investigate the expanding characteristics of graphite in microwave-assisted exfoliation as a function of mixing time, mixing ratio (by weight), and the form, type, and size of graphite. Furthermore, this leads to building a comprehensive, fluid-dynamics-based model that can be used to quantitatively predict the ER of graphite prepared with microwave irradiation when the form, type, and size of the graphite are given. The quantitative analyses of C/O ratio (or content) in original graphite, EC without reduction process using benzyl alcohol [10], and EG with reduction process with Raman spectrometer and x-ray photoelectron spectrometer (XPS), thus examining the effect of the reduction process on C/O ratio. The unique features of our approach considered, the findings of this study lead to better understanding of the chemothermal processes involved in microwave-assisted exfoliation and propel us towards an ever-expanding horizon of the industrial-scale production of defect-free graphene.
II. EXPERIMENTAL

A. Microwave-assisted Exfoliation

Starting materials were 12 groups of graphite samples: 3 natural lump graphite samples having average particle diameters of 10, 20, and 40 μm, respectively (NG10, NG20, NG40, Kansai Coke and Chemicals Co., Ltd.); 3 natural flake graphite samples having average particle diameters of 10, 20, and 40 μm, respectively (FK44, TG5799, FK150, Graftech Co., Ltd.); 3 synthetic lump graphite samples having average particle diameters of 10, 20, and 40 μm, respectively (KS44, KS75, KS150, TIMCAL Graphite and Carbon); 3 synthetic flake graphite samples having average particle diameters of 10, 20, and 40 μm, respectively (T44, T75, T150, TIMCAL Graphite and Carbon). The graphite sample, KMnO₄ (399124, Sigma-Aldrich Co., LLC.), and HNO₃ (1.00456.1000, Merck KGaA) were mixed by a glass rod in a Pyrex glass jar with different mixing-weight-ratios (graphite: KMnO₄:HNO₃=1:0 to 2.5:0 to 2.5) at room temperature for different times of 0.5 to 360 minutes. The mixture was put into a microwave oven (RE-C21VB, Samsung Electronics Co., Ltd.) and irradiated at a power of 700 W and an operating frequency of 2.45 GHz for different times of 10 to 120 seconds. Here, the ER of each sample was determined by measuring the post irradiation expansion volume resulted from 100 mg of the sample. In short, ER was the quotient of graphite’s expanded volume and original graphite’s mass, therefore having a unit of volume/mass (e.g., ml/g). All ER data were collected from at least 10 independent experiments per each group and presented as means and standard error of the mean.

B. Reduction Process

In an effort to characterize the effect of reduction process on the extent of oxygen in the EG samples, a mixture of 100 mg of EG in 12.5 ml of benzyl alcohol (BnOH, 24122, Sigma-Aldrich Co., LLC.) was stirred for 24 hours at 100°C. The resulting solution was then poured into ethanol (459844, Sigma-Aldrich Co., LLC.) to form precipitation, followed by filtration and drying under vacuum [10].

C. Raman Spectroscopy Measurement

Raman spectra were recorded from 1200 cm⁻¹ to 2800 cm⁻¹ on a Renishaw confocal Raman spectrometer at room temperature. All Raman measurements were performed by using 532 nm laser radiations. The samples were measured with a 50X lens. Spectra were obtained in a backscattering geometry using a standard 50x objective with numerical aperture value 0.52 and the spot area of 1.274 μm². The energy at the sample was 0.213 mW.

D. X-ray Photoelectron Spectrometer Measurement

The presence of chemical species and their ratio were quantified using an XPS (Thermo Fisher) equipped with Al K-alpha source. The electron analysis was made with a passing energy of 200 eV and an analyzing spot area diameter of 400 μm. During measurements, the base pressure in the chamber was below 911 0⁻⁶ mbar. The chemical fractions of C-C and C-O present in each sample were estimated by calculating the area under the individual peaks (corresponding to C-C and C-O bonds, respectively) and the atomic sensitivity factor, thus investigating the extent of oxygen in the EG samples.

III. RESULTS AND DISCUSSION

A. Graphite Exfoliation

The course of conversion of graphite to EG starts with the mixing together of graphite, KMnO₄, and HNO₃ before microwave irradiation, and the two key processes of intercalation and exfoliation are made in a microwave oven in a short time, in contrast with other microwave-assisted exfoliation methods [7, 9]. Intercalation agent molecules (HNO₃) migrate and deposit between the graphene layers of graphite in the intercalation process, and then the intercalation agent molecules are vaporized under microwave irradiation,
generating enough force to overcome the van der Waals force between adjacent layers of graphite [11] and expanding the graphite along the c-axis, in the exfoliation process (Fig. 1a). After the exfoliation of which the completeness was verified by the disappearance of fuming and lightening, EGs with hundreds of times larger volume than original graphite were successfully obtained (Figs. 1b, c). The worm-shaped, accordion-like morphology of EG is a conspicuous mark of the full and regular expansion of graphite.

B. Mixing Ratio

The amounts of graphite, KMnO₄, and HNO₃ (i.e., mixing ratio (by weight)) are one of the most important mechanophysical parameters that affect the intercalation and exfoliation processes and eventually determine the expansion performance of graphite. We therefore investigated the effect of the mixing ratio of raw graphite, KMnO₄, and HNO₃ on the ER by independently adjusting the weights of KMnO₄ and HNO₃ within a range of 0 to 250 mg where the weight of graphite was set as 100 mg (Fig. 2). The maximum ER of 212.33 ml/g was obtained from the mixing ratio of 1:1:2 (raw graphite: KMnO₄:HNO₃), which was close but slightly higher than that of previous study based on microwave-assisted exfoliation [12]. Considering the working mechanism of the microwave-assisted exfoliation, the outermost sides of graphite need to be oxidized and opened before intercalation process. The ER therefore increased noticeably as the weight ratio of KMnO₄ played as an oxidant increased until 1. However, when the amount of KMnO₄ was excessive (i.e., weight ratio more than 1), the ER decreased because the intensive oxidation due to excessive oxidant tore down the layered structure of graphite. The amount of HNO₃ used as intercalation agent and acidity source in the reaction was in the same with KMnO₄. The ER increased until the weight ratio of HNO₃ increased until 2 but started to decrease when that of HNO₃ was larger than 2. This is because superfluous HNO₃ also provides critical damages on the structure of graphite. The results shows that, as might be expected, there is a tradeoff among the mixing ratio of raw graphite, KMnO₄, and HNO₃.

C. Mixing Time and Microwave Irradiation Time

The second, and equally important, parameters that affect the expanding behavior of graphite are mixing time (of the mixture of 3 ingredients) and microwave irradiation time. To examine the dependence of the ER of graphite on mixing time and microwave irradiation time, we measured the ER by controlling the mixing time from 0.5 to 360 minutes and the irradiation time from 5 to 180 seconds, respectively. As to the mixing time, 5 minutes of agitation produced the maximum ER of graphite by microwave irradiation (Fig. 3). The results indicate that too much mixing of the mixture deteriorates the expanding natures of graphite, in contrast to common knowledge that the extent of mixing is proportional to mixing time. This is blamed on an overlong agitation that breaks down the layered nature of graphite both chemically (i.e., long exposure to KMnO₄, and HNO₃) and mechanically (i.e., smashing by a glass rod). Regarding the microwave irradiation time, the signs of exfoliation such as fuming and lightening were begun after 5 seconds of microwave irradiation and then finished after 50 to 60 seconds of microwave irradiation under our conditions (i.e., a power of 700 W and an operating frequency of 2.45 GHz). This means that a microwave irradiation time of about 60 seconds is enough to fully expand the graphite in the microwave-assisted exfoliation.

Fig. 2. A filled contour plot of the ER as a function of the mixing ratio (by weight) of raw graphite (especially, FK150 natural flake graphite having an average particle diameter of 40 μm), KMnO₄, and HNO₃ where the weights of KMnO₄ and HNO₃ are normalized by that of raw graphite (100 mg) with a mixing time of 5 minutes and a microwave irradiation time of 60 seconds. The maximum ER (212.33 ml/g) is achieved when the mixing ratio is 1:1:2 (raw graphite: KMnO₄:HNO₃).

Fig. 3. Measured ER of graphite as a function of the mixing (or agitation) time of the mixture of raw graphite (especially, FK150 natural flake graphite having an average particle diameter of 40 μm), KMnO₄, and HNO₃ with a mixing ratio of 1:1:2 (raw graphite: KMnO₄:HNO₃) and a microwave irradiation time of 60 seconds, showing that 5 minutes of agitation produce the maximum ER of graphite by microwave irradiation.
D. Graphite Form, Type, and Size

Next, we characterized the dependence of ER on the form (natural vs. synthetic), type (lump vs. flake), and size (10 to 40 μm in diameter) of graphite. As shown in Figs 4a-d, the expansion capacity of graphite in the microwave-assisted exfoliation was specific to certain forms and types of graphite and differences in particle size: natural graphite achieved about 4.3 times larger ER than synthetic one; flake-type graphite showed about 2.4 times larger expansion capacity than lump-type one; large graphite had higher ER than small one. The first phenomenon related to graphite form can be explained by the physical fact that natural graphite exhibits a much higher crystalline structure than synthetic one; the second is because flake-type graphite has more open areas (or spaces) for intercalation and exfoliation than lump-type one with the highest degree of cohesive integrity. The last but not least phenomenon can be understood by constructing a fluid-dynamics-based model. The main assumption of this model is that the expansion of graphite by microwave irradiation is due to the pressure exerted by an accumulating gas from the expansion of intercalation agent. Thus, we model the exfoliation of graphite as a steady, laminar flow occurred in the space between two fixed parallel and circular plates separated by a gap of 2b (Fig. 4e). Rapid gas escape inhibits full development of the gas pressure required to move the adjacent graphite layers apart, resulting in low ER. It is therefore a reasonable assumption to make that the ER of graphite must be proportional to $R_f$ where $R_f$ is a flow resistance of the gas [13].

$$ER = R_f = \frac{3\mu \ln(r_1/r_2)}{4\pi b^2 \rho} = C_1 \ln r_2 + C_2,$$

where $2b$ is an interlayer spacing of graphite (in general, $2b = 0.34$ nm), $r_1$ is the minimum size of the related chemical reaction site, set as a constant value of 0.1 μm, and $r_2$ is the radius of graphite. Unlike the previous approach in which the ER is directly proportional to $d_g$, it would be more desirable that the ER of graphite in microwave is in direct proportional to...
In $d_\text{p}$. These findings offer strategies to maximize the ER of graphite in the microwave-assisted exfoliation. First of all, natural, flake-type graphite having large particle size (the larger, the better) is preferred to achieve the industrial-scale production of defect-free graphene through ER maximization. Secondly, there is a flooring value for graphite size (less than 4.7 to 9.4 μm depending on the form and type of graphite) that can be exfoliated by microwave irradiation (Figs 4a-d).

E. Reduction Process Using Benzyl Alcohol

Together with Raman spectrometer and XPS, the changes in the extent of oxygen through reduction process with benzyl alcohol were measured for raw graphite, EG with reduction process, and EG without reduction process, thus examining the effect of the reduction process on C:O ratio. For 2 kinds of samples (i.e., EG with reduction process and EG without reduction process), their Raman spectra were recorded, as shown in Fig. 5a. The Raman spectra of EG with reduction process and EG without reduction process showed G band at 1584 cm$^{-1}$, 2D band at 2673 cm$^{-1}$, and almost no line at 1370 cm$^{-1}$, which were well matched with the reported fundamental content of the EG decreases slightly but not significantly with the reduction process. This conforms that the microwave-assisted exfoliation method employed in this study produces EG having a relatively low oxygen content of 13.5% and the oxygen content of the EG decreases slightly but not significantly (8.7%) with the reduction process.

IV. CONCLUSIONS

The expanding nature of graphite in the microwave-assisted exfoliation has been understood to build the backbone for the industrial-scale production of defect-free graphene and oil adsorption material. In detail, the dependence of the ER of graphite on mechanophysical parameters (e.g., mixing ratio, mixing time, microwave irradiation time, and graphite properties) can be summarized as follows: among the combination of graphite, KMnO$_4$ and HNO$_3$ amounts, a mixing ratio of 1:1:2 is desirable to achieve the maximum ER; 5 minutes of agitation produce the maximum ER of graphite; a microwave irradiation time of 60 or larger seconds is enough to fully expand graphite; natural, flake-type graphite having large particle size is preferred. Noticeably, the last phenomenon can be predicted from our fluid-dynamics-based model. Extrapolation of this study to other exfoliation method might help us to investigate the critical expanding nature of graphite, therefore mass-producing high-quality graphene.

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