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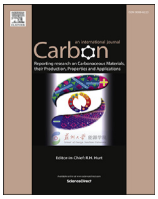

# High-rate production of few-layer graphene by high-power probe sonication

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## ABSTRACT

Graphene can be obtained via sonication-assisted liquid-phase exfoliation, but the production rate of few-layer graphene (FLG) is still low. A high-power probe sonicator was used in this study to improve the production rate of FLG, and its performance was optimized by controlling processing parameters such as the initial graphite concentration, surfactant concentration and liquid volume. By optimizing processing parameters, production rate of FLG dispersions in N-methyl-2-pyrrolidone (NMP) were greater than 1 g/h, which is the best value achieved in the sonication-assisted exfoliation process. In the case of liquid exfoliation in water/surfactant solution, production rate of FLG was achieved approximately 0.28 g/h. Our work here demonstrates that graphene concentration in a probe-sonication process does not depend on the shape of vessel, and it is predictable by power law models.

## 1. Introduction

Graphene has attracted wide interest owing to its extraordinary mechanical, electrical and thermal properties. Graphene is expected to find application as a low-cost electrode material in applications such as displays, electric devices, and energy generation devices [1,2]. In addition, graphene can be applied as an efficient reinforcement in composite materials [3–7]. In both cases, the production of large quantities of graphene will be required.

Initially, oxidative-exfoliation of graphite was proposed to produce large quantities of graphene oxide (GO) nanosheets [8–11]. GO can be converted to graphene by thermal or chemical reduction; however, structural defects introduced by the oxidation process cannot be fully removed. This structural defects degrade the mechanical and electrical properties of graphene. In order to address this issue, a technique to exfoliate powder graphite to few-layer graphene (FLG) without oxidation process was developed [12–28]. Sonication of graphite in an appropriate liquid solvent can yield defect-free FLG. The key technology to obtain FLG in liquid is to minimize the attractive force between interlamina and prevent re-aggregate of graphene. In organic solvents, graphene can be stabilized in liquid when the surface energy of the solvent is close to that of graphene (~68 mJ/m$^2$) [14]. N-methyl-2-pyrrolidone (NMP) is an excellent solvent for the exfoliation of graphite to produce graphene. However, water-based exfoliation is preferable due to its low cost and ease of handling. Because the surface energy of water is very different from that of graphene, FLG easily re-aggregates after exfoliation [16]. To prevent restacking, a surfactant or a polymer is used to stabilize FLG in water by providing a repulsive force or steric repulsion between graphene surfaces [18–20].

The production of FLG in liquid via sonication has been established, but the volume of production is extremely low. Paton et al. analyzed a number of studies and reported that 80% of the papers surveyed had production rates below 0.04 g/h [29]. Recently, they developed a scalable production method using shear mixing. The high shear rate provided by mechanical mixing can successfully exfoliate graphite to FLG [29–31]. Large-scale trials with volumes up to 300 L led to production rates as high as 5.3 g/h, which is the highest rate achieved to date.

In general, the production rate of sonication-assisted exfoliation is low because most of the research relied on low-power sonication such as bath sonication. The effective power output of bath sonication is generally less than 100 W. In addition, the cavitation generator for bath sonication is located at the bottom of bath, not inside the vessel that holds the graphite and solvent. Thus, the cavitation behavior in the vessel depends on the shape of the vessel [32], and the cavitation density of bath sonication is generally lower than that generated by high-power probe sonication, which generates cavitation in the vessel directly. It is expected that the

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production rate of FLG can be further improved with high-power probe sonication. The potential production rates of FLG via high-power probe sonication has not yet been investigated.

The purpose of this study is to maximize the FLG production rate with high-power probe sonication. The production rate of FLG depends on the initial concentration of graphite, the liquid volume, the vessel type, the solvent and the concentration of surfactant. By optimizing these parameters, we obtained production rates of FLG as high as 1 g/h, which is the best value reported for sonication-assisted exfoliation.

## 2. Experimental

### 2.1. *Materials and graphene dispersion processing*

A set of FLG dispersions was prepared by adding powder graphite (Wako Pure Chemical Industries, purity of carbon is 98%) to NMP (Mitsubishi Chemical Co.) and distill water. TritonX-100 (Aldrich) was used to stabilize the FLG in water. This non-ionic surfactant was chosen because it cannot only stabilize the FLG in water but also prevent re-aggregation during the production of polymer nanocomposites [33]. Ultrasonication was carried out by a high-power probe sonicator (SMT, UH-600S). While the nominal power output of this machine was 600 W, the actual power output was in the range of 120–180 W. Diameter of the probe was 36 mm, and it was composed of a titanium alloy. The frequency was controlled at 20 kHz. The probe tip was located 1 cm below the liquid surface. We used cylindrical vessels made of stainless-steel with dimensions of 70 mm (diameter) × 95 mm (height) with a maximum volume of 300 mL and $\Phi$ 120 mm × 133 mm with a maximum volume of 1000 mL. In order to suppress the temperature increase during sonication, the vessels were cooled in an ice bath. After sonication, the dispersions were centrifuged (Kubota, model 2420) at 1500 rpm for 45 min to sediment thick flakes. After centrifugation, the top two thirds of the dispersion were picked up carefully by pipet and retained for use.

### 2.2. *Characterization*

The concentration after centrifugation was determined by optical absorbance of liquid. The FLG concentration can be calculated based on the Lambert–Beer law ($A = \alpha Cl$). The absorbance per unit length $A/l$ at 660 nm was measured with an IUV-1240 spectrophotometer (Shimadzu Co.) using optical grade glass cuvettes. We confirmed that the absorption above 450 nm was dominated by the concentration of graphene and that the effect of surfactant on the absorption properties was negligible at a wavelength of 660 nm. In order to determine the extinction coefficient $\alpha$, the concentration of FLG was measured by evaporating the water or NMP after measuring $A/l$. Graphene dispersions with a volume of 100 mL after centrifugation were poured into PFA dishes, and the solvent was evaporated at 180 °C for NMP and at 80 °C for water-based dispersions. After evaporation, the residue was vacuum dried at the same temperature. The residue were weighed, and the concentrations of FLG were determined. In the case of water-based dispersions, we assumed that the surfactant was uniformly dispersed in water, and the weight of surfactant was subtracted. We conducted this procedure five times, and the average $\alpha$ was 1300 $Lg^{-1}$ $m^{-1}$ for both NMP and water-based dispersions. This value corresponds well to previously reported values [17,20,22].

Raman spectra were recorded on a LabRAM HR Evolution (HORIBA Scientific). The samples were prepared by evaporation on PTFE film. A 532 nm excitation laser and a 1800/mm grating were used. Spectra were recorded with a 50× lens. Ten spectra were recorded and averaged for each trial. At least three trials for each sample were conducted.

TEM images were taken using a JEM2100F (JEOL Ltd.). The TEM samples were prepared by pipetting a few drops of the dispersions onto holey carbon grids. To observe isolated FLG without overlapping or stacking, diluted dispersions less than 0.1 g/L were used.

## 3. Results and discussion

### 3.1. *Characteristics of FLG*

It was important to confirm initially whether probe sonication produced FLG or not. Raman spectroscopy is an effective tool to analyze the defects and thickness of graphite sheets. Typical spectra for graphite powder, NMP dispersion and water dispersion are shown in Fig. 1. All spectra are normalized by the intensity of the G band. Spectra of graphitic materials are characterized by a D band (1350 $cm^{-1}$), a G band (1582 $cm^{-1}$) and a 2D band (2700 $cm^{-1}$). The nature of defects in graphite is identified by the ratio of the intensities of the D band and G bands. A D band intensity that is smaller than the G band intensity indicates that the graphite and the graphite film after sonication possess a high structural quality. The ratio of $I_D/I_G$ of the starting materials was 0.06, and it increased to approximately 0.2–0.4 after sonication. This range is similar to the range for FLG produced by bath sonication ($I_D/I_G = 0.2–0.6$) [13,16,22] but slightly higher than that of shear exfoliated FLG ($I_D/I_G = 0.17–0.37$) [29]. It is well known that the ratio of $I_D/I_G$ is associated with the FLG flake size. A higher $I_D/I_G$ indicates a smaller flake size because the ratio of edge defects is higher for smaller flakes. Thus, sonication generates smaller FLG flakes than shear exfoliation. This is because the exfoliation mechanisms in sonication and shear mixing are completely different. It should be noted that the FLG flake size also depends on the centrifugation speed [34].

It is known that the thickness of a graphite sheet is reflected in the shape of its 2D band [35]. In multi-layer graphene (more than 10 layers), the 2D peak consists of two components, as shown in the magnified 2D spectrum for graphite powder. The shape of the 2D band becomes more symmetric and shifts to the lower side for FLG. A symmetric, intense peak is obtained with monolayer graphene. It was expected that the thin films after sonication consisted of FLG. Although reaggregation undoubtedly occurred during film formation, the degree of aggregation is limited for both FLG made in NMP- and water-based dispersions. The sonication time did not affect the shape of 2D band and $I_D/I_G$, indicating the quality of FLG is almost independent of sonication time (Fig. S1).

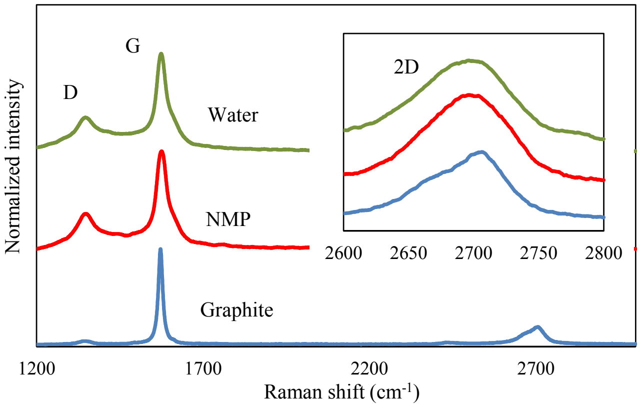

**Fig. 1.** Raman spectra of graphite powder and of thin film prepared after 1 h sonication for NMP and water based dispersion. Inset: Detailed 2D Raman bands. (A colour version of this figure can be viewed online.)