

# Fast Production of High-Quality Graphene via Sequential Liquid Exfoliation

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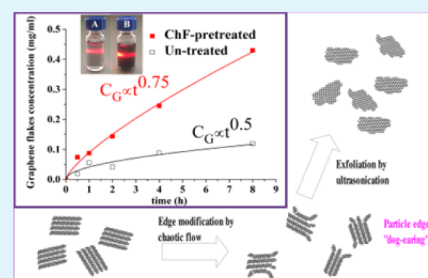
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## S Supporting Information

**ABSTRACT:** A novel and practical approach of exfoliating graphite into graphene uses a sequence of flow and sonication on graphite suspensions. Graphite sediment after intense mixing is found to be altered, graphite having curled-up edges, which increases its sensitivity to ultrasound. Quadrupled graphene yield is achieved through introducing flow pretreatment.

**KEYWORDS:** graphene, liquid exfoliation, chaotic flow, sonication, graphite edge modification



Graphene sheets (GS),  $sp^2$ -hybridized, two-dimensional (2D) carbon monolayers, are attracting intense interest because of their inherent exciting physical and electronic properties.<sup>1</sup> Graphene sheets can be produced through the exfoliation of graphite, a widespread mineral in nature, by mechanical cleavage, ball-milling, or direct exfoliation in liquids.<sup>2</sup> Liquid-exfoliation of graphite through the sonication of graphite suspensions in specific liquid environment, such as Dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP) has been attracting widespread interest since it was first reported by Coleman et al. in 2008, for its simplicity and cost-effectiveness.<sup>3–5</sup>

However, it is found that the affinity of such solvent molecules to graphene is too weak to overcome the strong van der Waals force between the  $\pi$ - $\pi$  stacked layers of graphite.<sup>6</sup> As a result, the liquid exfoliation process is superficial and slow. Graphite surface roughening and exfoliation were achieved only after hours of sonication.<sup>7</sup> Other exciting advances suggest that shear should be used for liquid exfoliation of graphite into graphene.<sup>8,9</sup> Nevertheless, these methods still encounter one major challenge: their relatively low efficiency. Typically,  $\sim 0.1$  mg/mL of graphene could be produced after having applied hundreds of hours of bath-sonication or hours of shear (if applying relatively rigorous centrifugation ( $>1000g$ ) to remove the unexfoliated large flakes).<sup>2,3,9–12</sup> Exfoliating graphite in water/surfactant, polymer solution, and ionic liquids were also reported as promising approaches, but washing-off the residual molecules from graphene flakes was necessary after the exfoliation step to alleviate negative impact on the electrical and mechanical performances of GS-based devices by such molecules.<sup>11–13</sup>

In this study, we report a novel and efficient approach for liquid exfoliation of graphite into GS. NMP was chosen as the solvent due to its widely reported effectiveness in graphite exfoliation by sonication. The graphite/NMP suspensions were first placed in a chaotic flow (ChF) with rapid liquid stream dividing around and recombining between cylindrical pebbles, which causes fierce interparticle and particle-pebble collisions. As a result, the graphite particles become “dog-eared”, i.e. the edges of the crystals were curled-up. Moreover, these edge irregularities (“dog-ears”) in the graphite particles seem to act as weak points, which help solvent molecules to “wedge” in between layers during the subsequent sonication process, thus leading to significantly improved exfoliation efficiency as shown in Figure 1 and discussed below.

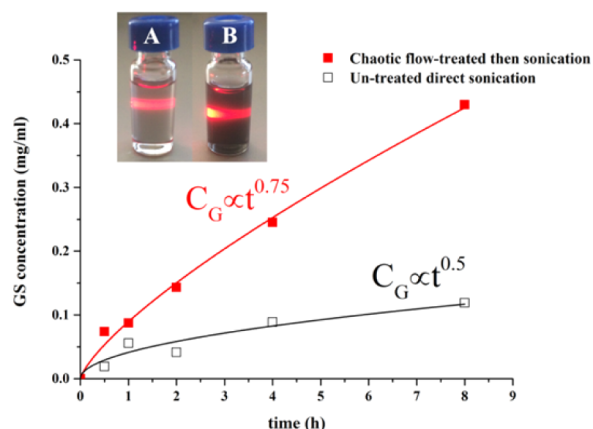
In our initial study of this novel flow/sonication process, dispersions of graphite in NMP in a concentration of 6 mg/mL was first subjected to a chaotic flow (ChF) for 2 min, which was induced by a dual-asymmetric mixing system (illustrated in Figure S1, detailed description of the apparatus and experimental conditions are provided in the Supporting Information). Then the suspension was centrifuged at 4000 rpm for 30 min ( $RCF \approx 1400g$ , all centrifugation was carried out under these conditions hereafter). The top-80% supernatant (ChF-SP), which already contained some amount of graphene ( $\approx 0.034$  mg/mL as described later), was removed by a pipet and the sediment (ChF-SD) was collected for further processing by sonication.

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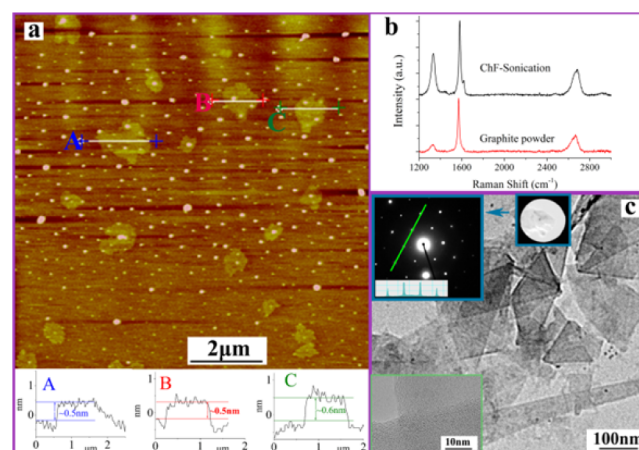
**Figure 1.** Correlation between graphene concentration ( $C_G$ ) and sonication time ( $t$ ). Filled red: novel process with chaotic flow pretreated graphite followed by sonication; open black: direct sonication of pristine graphite. The concentration of the supernatant,  $C_G$ , was determined by UV–vis spectra following the Lambert–Beer law ( $A = \alpha \cdot C_G \cdot l$ , using the well-established absorption coefficient  $\alpha = 3620 \text{ mL mg}^{-1} \text{ m}^{-1}$ ).<sup>4,5,14</sup> The image above demonstrates the Tyndall effect generated by graphene colloids produced via (A) direct 0.5 h sonication and (B) novel ChF-pretreatment followed by 0.5 h sonication. Rigorous centrifugation ( $\text{RCF} \approx 1400 \text{ g}$ ) was used to separate the unexfoliated flakes.

To continue with the second part of the exfoliation process, the chaotic flow sediment (ChF-SD) was redispersed in NMP (volume equal to original graphite NMP suspension volume) to form a graphite suspension. Sonication times of 0.5–8 h were applied to the redispersed suspensions to achieve further exfoliation. Using the centrifuge to remove the unexfoliated particles, the top 80% supernatant was collected for further characterization by UV–vis spectra, which appeared flat and featureless through the 400–1000 nm wavelength range as shown in Figure S2. The concentration of GS was determined by the Lambert–Beer law ( $A/I = \alpha C_G$ , using the well-established absorption coefficient  $\alpha = 3620 \text{ mL}/(\text{mg mL})$  at  $660 \text{ nm}$ <sup>4,5,14</sup>). The calculated concentration is shown in Figure 1 (filled symbols/red line). The ChF-treated sample exhibits high time-efficiency for exfoliation with a GS concentration–time correlation of  $C_G \propto t^{0.75}$ . After 8 h of sonication, the GS concentration reached  $0.430 \text{ mg/mL}$ , which is comparable to graphene oxide (GO) exfoliation in organic solvents.<sup>15</sup>

For comparison, the pristine graphite suspensions with the same graphite concentration were sonicated for various times without any pretreatment. After centrifugation, the supernatant and residual sediment were collected. The colloidal supernatants were characterized as above and the calculated concentration is shown in Figure 1 (open symbols/black line). The direct sonication induced exfoliation of graphite exhibits a  $C_G \propto t^{0.5}$  correlation, suggesting a flake-size-controlled concentration evolution, which is in good agreement with previously reported results.<sup>3,10,14</sup>

Figure 1 demonstrates that the flow pretreatment greatly enhances the graphene yield. For instance, after 0.5 h of sonication, the concentration of graphene increased from  $0.019 \text{ mg/mL}$  in the case of untreated graphite suspension to  $0.074 \text{ mg/mL}$  in the ChF-treated graphite suspension. The untreated graphite suspension yielded only  $0.119 \text{ mg/mL}$  GS colloid after sonication for the same period of time (8 h), whereas the ChF-treated graphite had reached  $0.430 \text{ mg/mL}$ .

After ChF-sonication treatment and purified by centrifuging, the diluted supernatant was spin-coated on a silicon substrate and dried carefully. We characterized the flakes' size and thickness using atomic force microscopy (AFM). Figure 2a is a

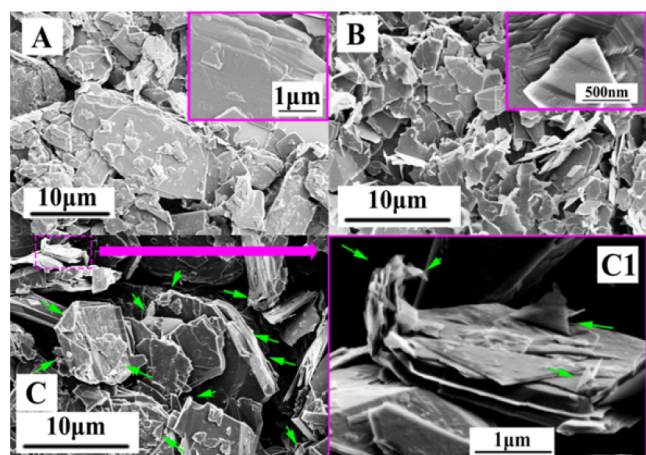


**Figure 2.** Characterization of the graphene flakes produced via ChF-Sonication (8h); (a) AFM height image of such graphene deposited on silicon and corresponding height profile (A–C); (b) Raman spectra of the starting graphite powder and produced graphene flakes; c: TEM image of the exfoliated graphene; in-sets: selected area electron diffraction (SAED) pattern (top) from the flake shown in the left and high-resolution TEM image on the edges of the GS).

$10 \mu\text{m} \times 10 \mu\text{m}$  AFM height image depicting a large number of flakes with submicrometer lateral size, similar to those flakes observed by transmission electron microscopy (TEM) (Figure 2c). Along with tens of nanometers sized graphene “nanodots”,<sup>16</sup> the produced flakes exhibited apparent thickness ranging from  $0.5$ – $1.8 \text{ nm}$  as measured by AFM (additional AFM image and corresponding height analysis provided in Figure S3), which we suggest should be considered as  $\leq 3$  layers graphene, as several literature reports show that the apparent height of GS monolayers measured by tapping-mode AFM ranged from  $0.4$  to  $1 \text{ nm}$ .<sup>7,13,17</sup> Raman spectroscopy of such GS's thin film also suggests these flakes to be less than 5 layers thick<sup>3,18</sup> (Figure 2b). The D-band ( $\sim 1350 \text{ cm}^{-1}$ ) with increased intensity as compared to pristine graphite was observed, which we suggest could be ascribed to profound edge effects given the size of the laser beam ( $1 \mu\text{m}$ ) and the lateral size of graphene (hundreds of nanometers). High-resolution TEM (HR-TEM) bright field image on the flake edges displayed the edges of a single-layer graphene. Hexagonal electron diffraction (ED) pattern was collected when focusing the e-beam to an individual flake, which exhibits characteristics of single-layer graphene that features a typical plot of a line section through  $(1-210)$ – $(0-110)$ – $(-1010)$ – $(2110)$  diffraction dots, as shown in insets of Figure 2c. The lateral size of the graphene flakes were estimated to be  $\sim 1 \mu\text{m}$  based on AFM and TEM imaging, on average (additional TEM images and statistical estimation are shown in Figure S4). For comparison, the GS flakes exfoliated by direct sonication of graphite suspensions were also characterized by AFM, TEM, and SAED (Figures S5 and S6), following the same sample preparation protocol. The GS produced by direct sonication of graphite suspension exhibits thicknesses of several nanometers and an average lateral size of approximately  $1 \mu\text{m}$ , consistent with numerous earlier publications.<sup>7,14,19</sup> Thus, the GS produced

from pretreated graphite suspensions are a few layers thick with lateral size of hundreds of nanometers, relatively thinner, and similar in lateral size compared to our control group (direct sonication).

In search for the underlying cause for the significantly heightened sensitivity of the ChF-treated graphite to ultrasound, we took graphite sediment from both direct sonication (no flow) and just ChF-treatment (no sonication) and searched for structural differences. The reference state is the pristine graphite used in this study. Because of the strong interlayer  $\pi$ - $\pi$  interaction in the pristine graphite (Figure 3A), the



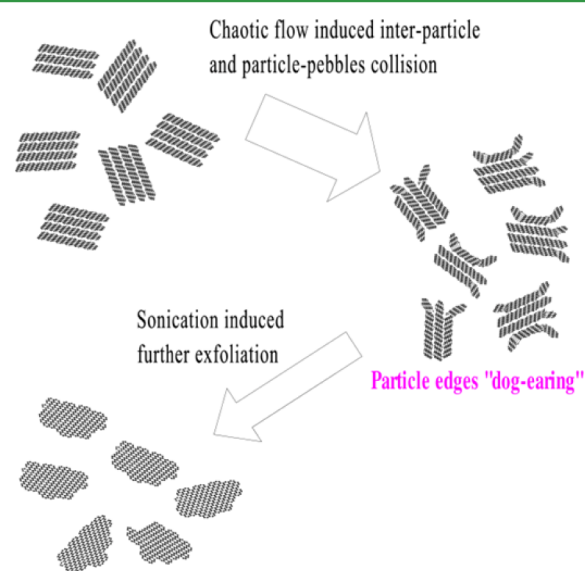
**Figure 3.** SEM images of (A) pristine graphite, (B) sediment after 4 h sonication; (C) sediment after 2 min chaotic flow; (C1) magnified image of the framed area in C.

wetting and wedging process of NMP molecules was expected to be relatively slow and inefficient. After sonication only (Figure 3B), the edges of graphite remained straight and intact, and flat terraces similar to the ones observed in the pristine graphite were also observed, which indicate that the sonication-induced exfoliation started at the (002) surface of the crystal.<sup>7</sup> As can be seen in Figure 3B, after 4 h of sonication the graphite particles were broken down from  $\sim 20 \mu\text{m}$  of pristine graphite to several microns. In comparison, after 2 min of chaotic flow treatment of the graphite suspension, the edges of graphite particles started to curl-up forming a “dog-ear” morphology (indicated by green arrows in Figure 3C). We note the graphite particle lateral size in the (002) plane direction remained over  $10 \mu\text{m}$ , which is desirable for producing large flakes, while the thickness of the crystal stacks were reduced by ChF. The chaotic flow, through causing intensive collision to the suspended graphite, delaminated graphite stacks and possibly left confined NMP molecules in between layers as indicated by a broadened and declined (002) XRD peak of the treated suspension shown in Figure S7.

We also noticed that there were few-layered GS flakes in relatively low concentration existing in ChF-SP (as shown in Figure S8). Moreover, the concentration of GS in the supernatant increases if we prolong the chaotic flow time (Figure S9). We propose two potential mechanisms that may cause these phenomena: (i) it could be due to the shearing of the suspension, probably while flowing around the pebbles, as shear in a liquid environment was recently reported as another approach to achieve exfoliation of graphite,<sup>9</sup> or (ii) it could be that collision-induced “dog-ears” came off from graphite substrate and dispersed in NMP as exfoliated flakes. The

chaotic flow was stopped after a relatively short time (2 min) in order to preserve the integrity of the main part of the graphite crystals. And, even though higher yield of GS could be achieved if we directly sonicate the post flow-treatment suspension (kept the ChF-SP without centrifuging, pipetting and redispersing), in this study, in order to investigate the influence of the graphite’s edge morphology and its influence on the sensitivity to sonication, we removed the ChF-SP and characterized it separately after separation by centrifugation.

In summary, the sonication yield of graphene flakes has been significantly increased by pretreating the graphite crystals with an intense mixing flow (chaotic flow for this study). Intensive interparticle and particle-pebble collisions induced curled-up edges (“dog-ears”). The edge-modified graphite particles exhibit higher sensitivity to sonication in the liquid state, which leads to faster exfoliation of graphite and higher yield of graphene flakes (as illustrated in Figure 4). After a short time



**Figure 4.** Schematic representation of chaotic flow-sonication induced exfoliation of graphite into graphene.

(0.5 h) of bath sonication, we observed a GS concentration of  $0.074 \text{ mg/mL}$ , which is extraordinarily time-efficient in liquid exfoliation of graphite (highest concentration for 0.5h hour bath sonication). Moreover, pretreated graphite suspensions produce GS flakes with substantially lower thickness (often down to  $\sim 1 \text{ nm}$ ), close to monolayer graphene. We emphasize that via a ChaoticFlow-Sonation fast exfoliation sequence, the produced GS flakes are more likely to be free of topological defects, as the shortened duration of sonication avoids building up of bulk disorder.<sup>20</sup> We also believe that flow pretreatment would lead to similar enhanced efficiency in other flow geometries and in other liquid environments such as water/surfactant, ionic liquid, polymer solution etc., because this flow effect is assumed to be universally achievable in liquid environment. The aim of this initial study is to demonstrate the effectiveness of the proposed exfoliation process. Optimization of the process conditions and in-depth structural analysis will require a separate study.



## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b08494.

Experimental details and supplementary results (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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