CARBON 78 (2014) 622–626

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/carbon

Letter to the Editor

Kitchen blender for producing high-quality few-layer graphene

Min Yi [a,b,*], Zhigang Shen [a,*]

[a] Beijing Key Laboratory for Powder Technology Research and Development, Beijing University of Aeronautics and Astronautics, Beijing 100191, China

[b] Institute of Materials Science, Technische Universität Darmstadt, Darmstadt 64287, Germany

ARTICLE INFO

Article history:
Received 9 May 2014
Accepted 11 July 2014
Available online 18 July 2014

ABSTRACT

The application of a kitchen blender for producing high-quality few-layer graphene (FLG) is demonstrated. The obtained FLG flakes, with an average thickness of ~1.5 nm (~20% ⩽ 1 nm), are high-quality and free of oxidation and basal-plane defects. With a rotating impeller, the kitchen blender can induce multiple fluid dynamics events which are featured by shear, turbulence, and collisions. These fluid dynamics events and their cooperative effects are responsible for the exfoliation mechanism, resulting in a gentle lateral-force-dominated way for graphite self-exfoliation through its lateral self-lubricating ability.

Due to its outstanding properties, graphene has intriguing fascination for world-wide researchers in both fundamental studies and commercial applications [1]. How to prepare graphene is always one of the centers of graphene research. Recently, liquid-phase exfoliation of graphite crystals to achieve graphene makes scalable production possible [2]. Generally, graphite crystals are sonicated in suitable solvents to obtain graphene dispersions. In the widely used sonication, it is the liquid cavitation induced micro jets and compressive shock waves that mainly result in the exfoliation of graphite [3]. Such sonication-assisted methods are simple and inexpensive and so could be easily scaled. Nevertheless, sonication is a relatively harsh process which can produce high local temperature (~ several thousand K), extreme pressure (~ several thousand atm), and rapid heating/cooling rates (~ several billion K/s) [4]. These harsh conditions could result in damage to the graphene. Indeed, Polyakova et al. [5] have experimentally evidenced that graphene produced by sonication truly has more oxides and defects than expected. So developing a relatively mild method for making large quantities of high-quality graphene available and meanwhile avoiding these defects is still of significant importance. Before the recent publication by Coleman's group who used shear machine exfoliation [6] and driven by our background on fluid dynamics for preparing layered nanomaterials, we had been working independently for a long time on the scalable production of high-quality graphene through fluid dynamics. The unique contribution of the work here is developing an idea for producing high-quality graphene through fluid dynamics events. Actually, apart from the stirring induced shear as reported recently by Coleman's group [6], the collision, turbulence, and pressure release involved in the fluid

* *Corresponding authors.*
E-mail addresses: yi@mfm.tu-darmstadt.de (M. Yi), shenzhg@buaa.edu.cn (Z. Shen).
http://dx.doi.org/10.1016/j.carbon.2014.07.035
0008-6223/

dynamics events are also favorable for producing high-quality graphene. For example, beneficial from the involved fluid dynamics events, liquid spray of graphite particles or random shake of airtight containers which are full of graphite dispersions can also produce high-quality graphene (Fig. S1), though the resulted graphene concentration is low. Herein, for the high quality and simultaneously the relatively high concentration, we concentrate on the facile application of a kitchen blender for exfoliating graphite to achieve few-layer graphene (FLG).

The FLG dispersions here are produced by exfoliating graphite in solvents through a kitchen blender, as schematized in Fig. 1. Graphite crystals (Alfa Aesar, ⩽325 meshes) were firstly dispersed in N,N-dimethylformamide (DMF) with an initial concentration of 3 mg/mL to form 400 mL graphite dispersions. It should be noted that the solvent is not only limited to DMF. Solvents with suitable surface tension [2] or Hansen solubility parameters [7] and water/surfactant solutions can also be used. The graphite dispersions were treated in a kitchen blender equipped with a five-blade impeller (~5000 rpm) for 8 h. At a number of times (0.5, 1, 2, 3, 5, 8 h) during this period, we collected six aliquots of 6 mL dispersions each, followed by centrifugation for 45 min at 500 rpm to obtain FLG dispersions. When we collected graphene dispersions out of the tank, the kitchen blender will be stopped for 30 min.

Atomic force microscopy (AFM) analyses show that lots of FLG flakes are 0.6–1.2 nm thick, as exhibited in Fig. 2a–d. Fig. 2e and f show the AFM-based statistical results for flakes' dimensions (Fig. S2). The number fraction of ⩽1 nm-thick flakes keeps ~14.6–20% (Fig. S3). Fig. 2g gives the average thickness per flake, $\langle t \rangle$, and the average area per flake, $\langle A \rangle$. $\langle t \rangle$ remains at ~1.5 nm. In contrast, $\langle A \rangle$ decreases with preparation time, falling from ~2.4 μm^2 at 0.5 h to ~0.1 μm^2 at 8 h. FLG flakes with different shape are captured by AFM and transmission electron microscopy (TEM), as shown in Fig. S4–S6. The graphene nature of these flakes is evidenced by collecting the Raman spectra of the same flake captured by AFM (Fig. S5).

The oxides and defect content of the FLG flakes were also explored. The absorption peaks at ~270 nm (Fig. 3a) and the featureless Fourier transform infrared (FTIR) spectrum (Fig. 3b) show no oxidation. The X-ray photoelectron spectroscopy (XPS) (Fig. 3c and d) shows the same bonds and similar composition in the pristine graphite and FLG-based film, indicating that the low level of oxides in the FLG are caused not by residual solvent or oxidation but by water, CO_2 or oxygen from the atmosphere. These prove that the kitchen blender does not chemically functionalize the FLG flakes.

As shown the Raman spectra in Fig. 4c, when compared to the bulk graphite, a significant change appears in the shape of the 2D band in individual FLG flakes. These spectra from the Raman mapping in Fig. 4a manifest the well exfoliated FLG flakes. The defect content can be characterized by the intensity of the D band relative to the G band, I_D/I_G [2]. Such defects can be divided into two main types: basal-plane defects and edge defects. Basal plane defects can generally result in G bands' obvious broadening as found in the chemically reduced graphene. The introduction of edge defects is unavoidable because of the fragmentation effect. Seeing that the narrow G band is not broadened, the weak and narrow D band in the filtered film is dominated by the edge contributions instead of the basal-plane defects. Also, I_D/I_G for the filtered film is less than ~0.12, much lower than that of graphene oxide and chemically reduced graphene. These Raman spectra results indicate that no basal-plane defects are introduced during the kitchen blender-assisted exfoliation. Further evidence for the high-quality FLG is the high conductivity. We vacuum filtered FLG dispersions to form a ~20 μm thick film whose sheet resistance was measured to be ~2.3 Ω/□, corresponding to a high DC conductivity of ~2.2×10^4 S/m.

The FLG concentration C_G can reach ~0.22 mg/mL within 8 h treatment (Fig. S8). These results on concentration are

Fig. 1 – The schematic of a kitchen blender for preparing FLG flakes. (A color version of this figure can be viewed online.)

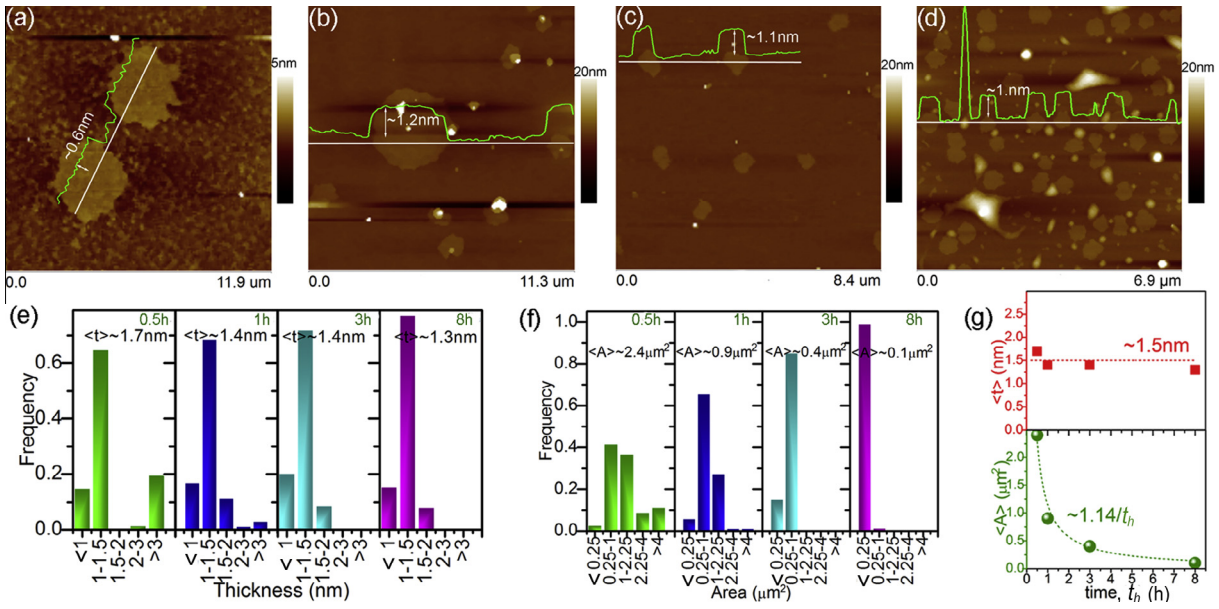

Fig. 2 – AFM images and the height profiles of FLG flakes prepared under treating time of 0.5 h (a), 1 h (b), 3 h (c), and 8 h (d). Statistical histogram derived from plenty graphene flakes (Fig. S2) showing the thickness (e) and area (f) distribution. Calculated (g) average thickness, ⟨t⟩, and (h) average area, ⟨A⟩, as a function of treating time. (A color version of this figure can be viewed online.)

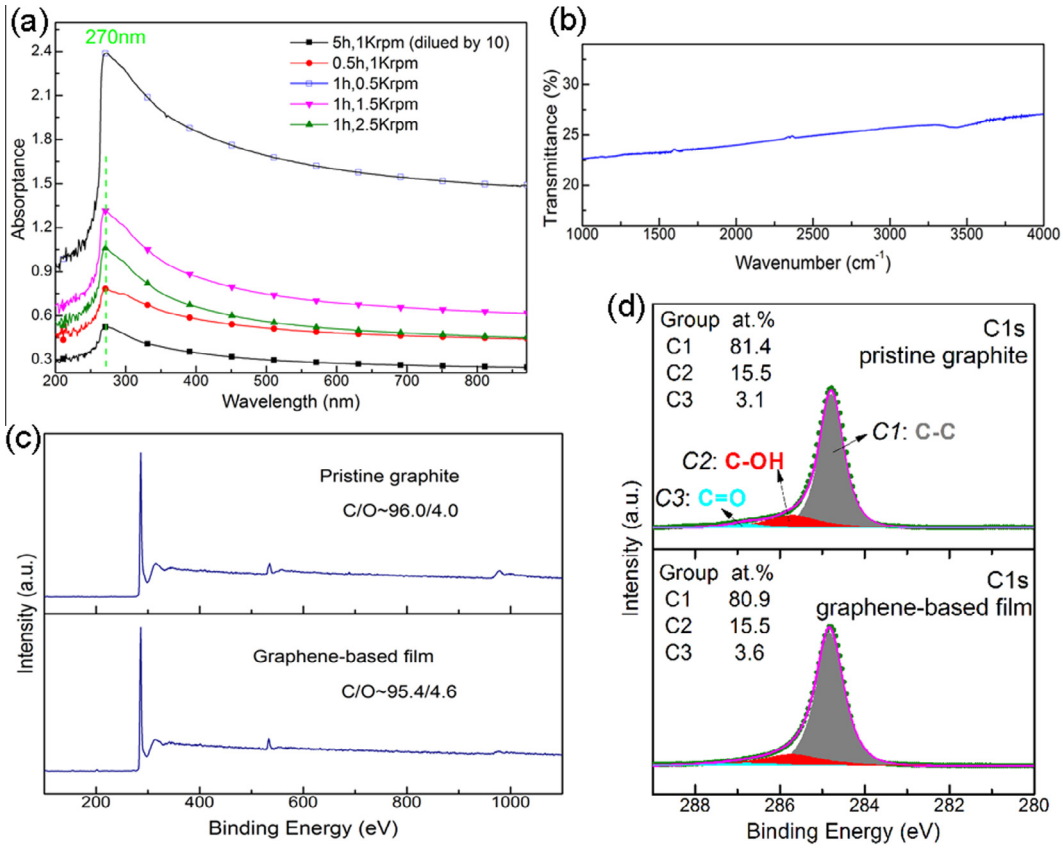

Fig. 3 – (a) UV–vis spectra of the FLG dispersions. (b) FTIR spectrum of the FLG flakes. XPS survey spectra (c) and carbon 1s core-level XPS spectra (d) of the pristine graphite and the FLG-based film vacuum filtered from the dispersions. (A color version of this figure can be viewed online.)

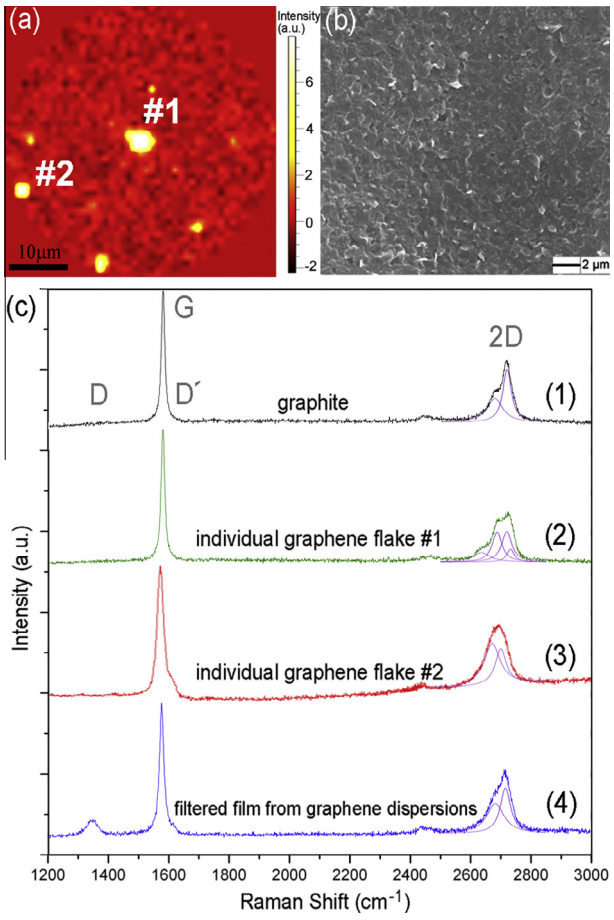

Fig. 4 – (a) A Raman mapping image. The Raman map plots the intensity integral of the spectra between 2600 and 2800 cm^{-1}. The excitation wavelength was 532 nm. (b) SEM image of the vacuum filtered film. (c) Raman spectra for bulk graphite (1), individual flake #1 (2), individual flake #2 in (3), and the vacuum filtered film (4). (A color version of this figure can be viewed online.)

very attractive. A comparison between the method and other published methods is presented in Table S1 and Fig. S7. Compared to that the sonication based works with high yield and concentration rely on sonication for very long time (~500 h) which would introduce much more defects [8], the kitchen blender with reasonably high concentration (0.22 mg/mL), yield (7.3%), and efficiency (0.92%/h) shows comprehensive advantages.

We suggest the superiority of the kitchen blender be attributed to the exfoliation mechanism. There are two kinds of force to exfoliate graphite into graphene flakes, i.e. normal force and lateral force (Fig. S9). Through graphite self-lubricating ability in the lateral direction, it is much easy for lateral force to promote the relative motion between two graphene layers. The fluid dynamics in the kitchen blender is considered for the exfoliation mechanism. The Reynolds number of the flow in the tank can be calculated as $R_e = \rho N D^2/\mu \approx 2 \times 10^6$ (Supplementary data), thus corresponding to a full turbulent flow [9]. Considering the flow characteristics within the kitchen blender (Fig. S11), we suggest four fluid dynamics events responsible for the exfoliation and fragmentation: (I) velocity gradient can induce viscous shear stress; (II) intensive velocity fluctuations in turbulence can induce Reynolds shear stress; (III) in the turbulence, Reynolds number is very large, and thus the inertial forces dominate viscous forces to enhance graphite-graphite collisions; (IV) it is possible that turbulent pressure fluctuations induced pressure difference can also exfoliate graphite in a normal-force style. In addition, these fluid dynamics events have fragmentation effects which also facilitate exfoliation; because smaller graphite flakes are easier to exfoliate due to that the collective Van der Waals force between layers is lower in smaller graphite flakes. The mechanism is illustrated in Fig. 5c. The cooperative effects of these fluid dynamics events mainly generate lateral-force for exfoliation. Beneficial from the affinity of the solvent molecules for graphene [2] and the graphite's lateral self-lubricating ability, this exfoliation process is not harsh and guarantees the FLG's high quality. For the evidence

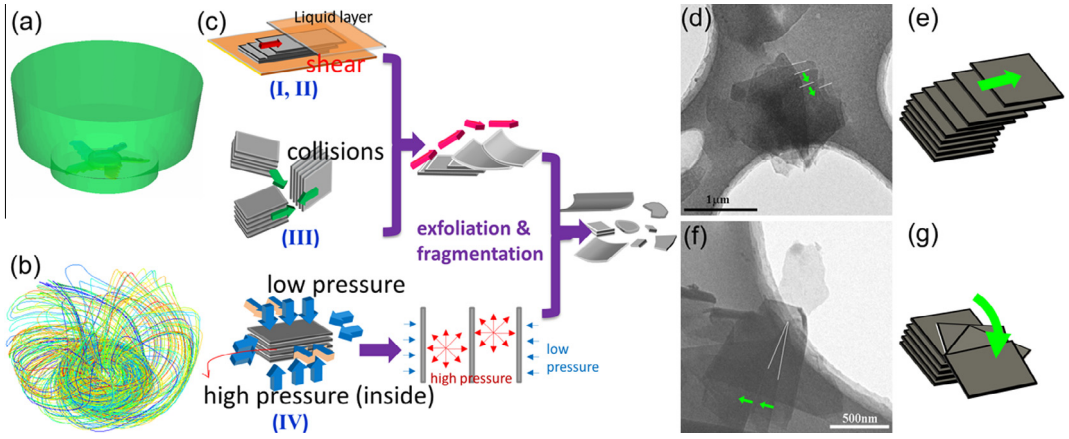

Fig. 5 – (a) Schematic of the simplified model used for computational fluid dynamics analyses. (b) Pathlines released form the impeller surface colored by particle ID. (c) Illustration for the exfoliation mechanism. Deliberately captured partially exfoliated FLG flakes with translational (d, e) and rotational (f, g) lateral exfoliation. (A color version of this figure can be viewed online.)

of lateral exfoliation, by using TEM we deliberately captured several partially exfoliated flakes, as shown in Fig. 5d and f. Apparently, these stacked flakes present a slipped configuration with lateral relative displacement of translation (Fig. 5e) or rotation (Fig. 5g), indicating that lateral exfoliation really happens and there coexist two ways (translation and rotation).

In conclusion, we have demonstrated the application of a kitchen blender for producing high-quality FLG. The produced FLG flakes are ~1.5 nm thick in average, highly conductive, and free of basal-plane defects and oxidation. Shear, turbulence, and collisions in the liquid result in a gentle lateral-force-dominated way for graphite self-exfoliation through its lateral self-lubricating ability. This method could be widely accessible and easily scalable.

Acknowledgements

This works was funded by Beijing Natural Science Foundation (Grant No. 2132025) and the Innovation Foundation of BUAA (YWF-14-YJSY-052).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2014.07.035.

REFERENCES

[1] Geim AK. Graphene: status and prospects. Science 2009;324:1530–4.
[2] Hernandez Y, Nicolosi V, Lotya M, Blighe FM, Sun Z, De S, et al. High-yield production of graphene by liquid-phase exfoliation of graphite. Nat Nanotechnol 2008;3:563–8.
[3] Cravotto G, Cintas P. Sonication-assisted fabrication and post-synthetic modifications of graphene-like materials. Chem -Eur J 2010;16:5246–59.
[4] Flint EB, Suslick KS. The temperature of cavitation. Science 1991;253:1397–9.
[5] Polyakova EY, Rim KT, Eom D, Douglass K, Opila RL, Heinz TF, et al. Scanning tunneling microscopy and X-ray photoelectron spectroscopy studies of graphene films prepared by sonication-assisted dispersion. ACS Nano 2011;5:6102–8.
[6] Paton KR, Varrla E, Backes C, Smith RJ, Khan U, O'Neill A, et al. Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids. Nat Mater 2014;13:624–30.
[7] Yi M, Shen Z, Zhang X, Ma S. Achieving concentrated graphene dispersions in water/acetone mixtures by the strategy of tailoring Hansen solubility parameters. J Phys D Appl Phys 2013;46:025301.
[8] Khan U, O'Neill A, Lotya M, De S, Coleman JN. High-concentration solvent exfoliation of graphene. Small 2010;6:864–71.
[9] Bakker A, Gates LE. Properly choose mechanical agitators for viscous liquids. Chem Eng Prog 1995;91:25–34.