Supporting Information

Fast Production of High-Quality Graphene Via Sequential Liquid Exfoliation

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Material and Method:

Graphite suspensions were prepared by adding natural graphite flakes (Asbury Graphite Mills, typical size $\sim 20 \mu m$) into N-Methyl-2-Pyrrolidone (NMP, biotechnology grade, Aldrich) at a concentration of 6mg/ml at the volume of 20mL.





SI-Figure 1: Schematic of chaotic flow apparatus for pretreating the graphite suspension. The sample holder rotation (ω_2) is about ¹/₄ of the main rotation (ω_1). Centrifugation with sample rotation induces a gravity-driven mixing flow, which can be turbulent. Four cylindrical ceramic pebbles in the suspension obstruct the flow of the circulating suspension.

Suspensions were subjected to chaotic flow (ChF) in a dual-asymmetric mixing system (FlackTek, DAC150), which is a centrifuge but has, as its main feature, a tilted and rotating sample holder as shown in SI-Fig 1. In this study the main rotation was set at 2000rpm. Chaotic mixing is achieved by adding four cylindrical ceramic pebbles into the suspension. The pebbles obstruct the gravity-induced flow of the circulating suspension and cause intensive stream dividing and recombining. The fluid gets compressed in the approach of a pebble and then divided by the pebble. When flowing around the pebble, the graphite suspension gets sheared near the pebble surface and suspended graphite particles collide with the solid wall and with each other. Behind the pebble,

the fluid streams recombine and get stretched. This process of compression-dividing-shearingrecombining-stretching repeats many times but at different locations of the circulating suspension. After chaotic flow treatment (ChF), the suspensions were centrifuged (~1,400g, 30min, (Beckman JA20, 4000rpm)) to remove the top 80% supernatant. The remaining sediment was re-dispersed to the original volume and sonicated using a bath sonicator (Branson 1510R-DTH bath sonication) for various sonication times. After centrifugation (same as above), the top-80% supernatant colloid were collected to obtain the final product.

Classical process of direct sonication exfoliation: Another set of suspensions were sonicated directly (no flow treatment) in the same sonicator as above. Sonication time periods ranged from 0.5h to 8h. The sediment and the top-80% supernatant were separated by centrifuging at 1,400g for 30min. Both fractions were analyzed.

Characterization

UV-vis-IR spectura characterization

A Shimadazu-3600 UV-vis-NIR spectrometer with 10mm*10mm cuvettes was used to determine the concentration of the graphene/NMP colloid. Colloids were first diluted by 10 times in volume to qualify for Lambert-Beer behavior ($A/l = \alpha C_G$). The well-known value of the absorption coefficient, $\alpha(660\text{nm})=3620\text{mL} \text{ mg}^{-1}\text{m}^{-1}$ was taken from the literature.¹⁻²

Atomic Force Microscopy (AFM)

A silicon substrate was prepared by first treating it with a piranha solution (H_2SO_4 : H_2O_2 =3:1 in volume) at 60°C for 30min, then rinsing it with water followed by drying in nitrogen. Onto the treated silicon substrate, a drop of highly-diluted graphene/NMP colloid was spin-coated and then dried in Nitrogen. AFM was carried out in a Nanoscope DI-3100 with silicon cantilevers operating in tapping mode.

Field Emission Scanning Electron Microscopy (FESEM)

Morphological changes in graphite crystals were imaged in a FEI Magellan-400 FESEM.

Graphite sediment was drop-cast on silicon and then dried in a vacuum oven at 200°C for 24h. 2kV acceleration voltage and 13mA current were chosen to observe the crystals without any gold-sputtering. Immersion lens were needed for high magnification observation.

Transmission Electron Microscopy (TEM)

Highly-diluted graphene/NMP colloidal suspension was drop-cast on cupper grid with ultra-thin carbon film for bright field TEM observation. A FEI Tecani T12 and a JEOL JEM-2200FX Transmission Electron Microscopes were used to observe the exfoliated GS flakes with acceleration voltage at 120kV and 200kV, respectively. Electron Diffraction (ED) patterns were collected in JEM-2200 with a camera distance of 100cm. Lacey carbon grids were used for HRTEM and ED experiments.

X-ray diffraction (XRD)

Panalytical X-Pert X-Ray Powder Diffractometer was used for XRD measurements with 1.54nm wavelength X-ray, scanning angle from 5°-40°. 1 mL of untreated and ChF-treated graphite/NMP suspensions were cast on glass slides for suspension X-ray tests. 1 mL of Graphite/NMP suspension and ChF-sonication (4h) produced graphene/NMP colloid were cast on glass then vacuum dried at 140°C for 24 hour to remove solvent.

Raman Spectrum

Raman Spectro-microscope (Thermo Scientific) with a 633nm (beam size 1 m) activation laser. The produced GS/NMP colloid was diluted 10 times, spin-coated on SiO2 (200nm SiO2 on Silicon), and then washed with isopropanol to remove any residual NMP. Samples were dried overnight in nitrogen in preparation for the Raman tests, which were performed in a DXR. Raman Spectro-microscope (Thermo Scientific) with a 633nm (beam size 1 µm) activation laser.

Supporting data



SI-Figure 2. Representative UV-vis absorbance curves of the GS/NMP colloid. Lower curve: direct sonication of the graphite/NMP suspension; upper curve: chaotic-flow pre- treatment followed by 0.5h sonication. Note that the colloids were all diluted 10 times in volume. The UV-vis absorbance spectrums are flat and featureless, consistent with previous reports.^{1, 3} The concentration of the supernatant, was determined by UV-Vis spectra following the Lambert-Beer law ($A = \alpha \cdot C_G \cdot I$, using the well-established absorption coefficient α =3620 mL/(mg m).



SI Figure 3. Additional AFM results and the representative line scans on the ChF Sonication produced graphene flakes deposited on Si substrate, ~30 flakes were observed.

The tapping mode AFM was used to determine the layer thickness and lateral size. Graphene colloid was highly diluted (~50 times by volume), and then deposited on Si-wafer. More than 30 flakes were observed (line-scans crossing 16 flakes were shown in SI-Fig 3) by AFM, which often exhibit thicknesses ranging from $0.5 \sim 1.8$ nm. Herein, given that the apparent thickness of a single layer graphene was reported as ranging from 0.4nm~1nm and is dependent of the types and condition of cantilever, substrate and scanning parameter etc.⁴⁻⁷, the apparent height profile indicates that flakes produced from ChF-Sonication sequence are often ≤ 3 layers, with lateral size of hundreds of nanometers.

As can be seen in SI-Figures 4 and Figure 2C (main text), the lateral size of ChF-sonication produced flakes ranged from a few hundred nanometers to $\sim 1 \mu m$, in consistent with the lateral size observed in AFM height profile analysis shown in SI-Fig3.



As can be seen in Si-Fig4 and Figure 2c (main text), the lateral size of ChF-Sonication produced

SI Figure 4. Additional TEM (a,b) and HRTEM (c,d) images of ChF-sonication graphene. Combined with the TEM provided in main text, ~30 flakes were observed in bright field image.



SI-Figure 5.Graphene flakes generated by direct sonication of pristine graphite. In the middle are three zoomed-in images of three individual flakes (scale bar represents $1 \square \mu m$) Below each of the images is the corresponding height profile taken along the red line.

Graphene flakes produced by direction sonication of graphite/NMP suspension exhibit lateral size $\sim 1 \mu m$ and thickness of $\sim 5 nm$, as can be seen in SI-Fig 5. TEM&SED characterization (SI-Fig 6) also shows few-layered graphene flakes with lateral size $\sim 1 \mu m$, in consistent with AFM tests and other researcher's results.1,8-9



SI-Figure 6.TEM images of a graphene flake generated by direct sonication of pristine graphite. Inset: SAED pattern of the black circle area in the image



SI-Figure 7. a: XRD spectra of ChF-treated (up) and untreated (down) graphite/NMP suspension; b: powder XRD of dried graphite powder (black) and ChF-Sonication graphene (red)

As can be seen in SI-Fig 7a, the (002) diffraction peak of graphite evolved to a broad diffraction with greatly declined diffraction intensity after being treated by chaotic flow, suggesting the starting of breaking-down of the stacks (delamination) and probably confined NMP molecules in between graphite layers. The powder diffraction XRD experiment (SI-Fig 7b) indicates the

occurrence of exfoliation as the 26.5° diffraction peak significantly declined. The residual (002) diffraction detected in ChF-sonication produced graphene powder could be ascribed to re-aggregation and re-stacking of graphene flakes during solvent evaporation.¹⁰⁻¹¹



SI Figure 8. Graphene flakes generated by chaotic flow. In the middle are three zoomed- in images of three individual flakes (scale bar represents 100nm).Below each of the images is the corresponding height profile taken along the red line.

As can be seen in SI-Fig 8, the chaotic flow also exfoliates graphite producing detectable graphene flakes. The reason could be the severe shearing and stretching of the suspension when flowing around the pebbles, as shear in liquid environment was recently reported as another feasible approach to achieve exfoliation of graphite.¹² It also could be due to collision-induced "dog-ears", which came off from graphite particles and dispersed in NMP as exfoliated flakes.



SI-Figure 9. Graphene concentration after centrifugation as a function of chaotic flow time.

As shown in SI-Fig 9, the concentration of GS in the supernatant increases when prolonging the chaotic flow time. 2 min of chaotic flow produces relatively low yield concentration of GS flakes (0.034mg/mL).

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