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Electronic Supplementary Information (ESI)

A green, rapid and size-controlled production of high-quality graphene sheets by hydrodynamic forces

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TC1: A comparison of our research and other published works

Tab. S1 shows experimental details and results of our work and other previous reports, aiming to make a comparison. Small graphene sheets (GNSs, less than 1 μm) can be used for printing novel flexible electrical products by inkjet technique. Besides, graphene quantum dots (GQDs, less than 100 nm in lateral size) have also received enormous attention since they possess unique electronic, magnetic and catalytic properties. However, there exist many problems in the production of small GNSs and GQDs. Firstly, band structure of graphene is prone to be disrupted when chemical methods are employed to exfoliate thin sheets and reduce the dimension, which could reduce the electrical conductivity of the products. Secondly, the dimension distribution is so wide that separation of small sheets becomes very difficult to achieve. Tab. 1 shows that high-speed centrifugation and filtration are often required to remove the large sheets, which makes the process high cost and time-consuming. Thirdly, many chemicals involved are either expensive or toxic, leading to environmental pollution. Additionally, various surfactants and polymer molecules have been extensively utilized in exfoliation of GNSs, but they are difficult to be removed from the products, which significantly reduces the properties of GNSs.

As shown in **Tab. S1**, most methods currently employed have the above-mentioned limitations and drawbacks. Pan et al., He et al. and Park et al. prepared GNSs by chemical oxidation and then separated small nanosheets or nanodots by filtration and centrifugation. During these chemical cutting processes, graphene lattice was attacked because of the introduction of oxidants and reductants, inevitably leaving residual surface species. Meanwhile, although liquid-phase exfoliation of GNSs by long-time sonication is a simple and practical way, this method typically results in graphene with sizes ranging from dozens of nanometers to several micrometers, which causes a consequent issue of separation. Lotya et al., Coleman et al. and Torrisi et al. prepared GNSs and separated them by centrifugation at different rates, but the small sheets (less than 1 μm) only constitute a small proportion. Afterwards, Green et al. successfully realized size and thickness control by density gradient ultracentrifugation at a rate of 15 krpm, but this method is quite expensive and inefficient. To achieve high concentration or yield of small GNSs, Secor et al. and Liang et al. sonicated graphite particles in ethyl cellulose-ethanol, but this means results in a low yield (~0.2%) and excessive ethyl cellulose needs to be removed. Interestingly, Knieke et al. peeled GNSs from graphite particles in a stirred media mill and achieved high concentration of small GNSs (less than 1.5 μm in lateral size), while the average thickness is about 2.7 nm. Similarly, Shang et al. detached GQDs (average 9-29 nm large for different time) by ionic liquid-assisted grinding, but this research relied on manual work and needed to remove the ionic reagents from GQDs. Above all, the mean size of nanosheets prepared by mechanical forces is much smaller than that prepared by sonication method, indicating that methods based on mechnical forces have more advantages in terms of GNSs and GQDs production. Therefore, one can say that we provide a novel way to prepare GNSs in IPA-water mixtures, which mainly depends on hydrodynamic forces.

Table S1. Details on our work and other published works. ethyl cellulose (EC), sodium dodecyl sulfate (SDS), sodium cholate (SC), isopropanol (IPA), deionized water (DI water), graphene quantum nanodots (GQDs), reduced graphene oxide (RGO)

References	Method (experimental procedure)	Product	Solvent	Size	Thickness	Yield	Applications
Pan et al. *Adv. Mater.* **2010**, *22*, 734[1]	1. Modified Hammer method 2.Thermal reduction 3.Sonciaition 4. Filtration 5.Hydrothermal approach	GQDs	DI water	5–13 nm	1-2 nm	~5 %	Blue-Luminescent Graphene Quantum Dots
Park et al. *J. Ind. Eng. Chem.* **2011**, *17*, 298[3]	1.Modified Hummers method 2.Sonication 3.Filtration 4. Further oxidization 5. Filtration	RGO	DI water	less than 200 nm	No data	No data,	water soluble graphene
He et al. *Adv. Funct. Mater.* **2012**, *22*, 2542[2]	1.Modified Hummers method 2. Sonication 3.Reduction in the autoclave 4.Centrifugation at 10000 rpm	RGO	DI water	No data,	~0.75 nm	No data,	Graphene-Based Ultraviolet Absorbers
Secor et al. *J. Phys.* Chem. *Lett* .**2013**, *4*, 1347[8]	1. Probe sonication 2. Centrifugation at 7500 rpm 3. Adding of NaCl 4. Centrifugation at 7500 rpm 5. Filtration	GNSs/ EC	EC-ethanol	~50×50 nm^2	~2 nm	Exceed 0.2%	Flexible Graphene Patterns
Liang et al. *J. Am. Chem. Soc.* **2010**, *132*, 17661[9]	1. Sonication 2. Centrifugation at 7500 rpm	GNSs/ EC	EC-ethanol	50~400nm	1.6-1.8nm	~0.2 %	highly concentrated solutions
Torrisi et al. *Acs Nano*. **2012**, *6*, 2992[4]	1. Sonication 2. Centrifugation at 10000 rpm 3. Filtration	GNSs	NMP	less than 1 μm	No data	~0.11 mg ml,	Inkjet-Printed Graphene Electronics
Green et al. *Nano Lett.* **2009**, *9*, 4031[7]	1. sonication 2. Density gradient ultracentrifugation at 15 krpm	GNSs	SC/water	50 nm~ hundreds nm	80% less than 1.2 nm	~0.9 mg ml^{-1}	Separation of GNSs with different size
Lotya et al. *ACS nano*. **2010**, *4*, 3155[5]	1. Sonication 2. Centrifugation at 500-2000 rpm	GNSs	SC/water	Length~1 μm,Width~400 nm	~4 layers	~6 % for 1500 rpm	Production of GNSs
Coleman et al. *J. Phys.* Chem. *C.* **2011**, *115*, 5422[6]	1. Sonication 2. Centrifugation at 2000 rpm	GNSs	IPA	~1 μm length	Less than 5 layers	~15 % for 500 rpm	Production of GNSs
Knieke et al. *Carbon*. **2010**, *48*, 3196[10]	1. Preparing in a stirred media mill	GNSs	SDS/ water	100 nm-1.5 μm	Less than 3 nm	~25 mg ml^{-1}	Production of GNSs
Shang et al. *Chem. Commun.* **2012**, *48*, 1877-1879.[11]	1. Mechanical grinding 2. Centrifugation at 3000 rpm 3. One-day sedimentation	GNSs and GODs	Ionic liquid	9-29 nm for different times	1-16 nm for different times	~20 %	Production of GNSs and GODs
Our work	1. Exfoliation by high shear mixer 2. Centrifugation at 500 rpm	GNSs And GODs	IPA-water	0-1μm	Less than 2 nm	~5.4 %	Production of GNSs and GODs

TC2. Additional photographs of different stators

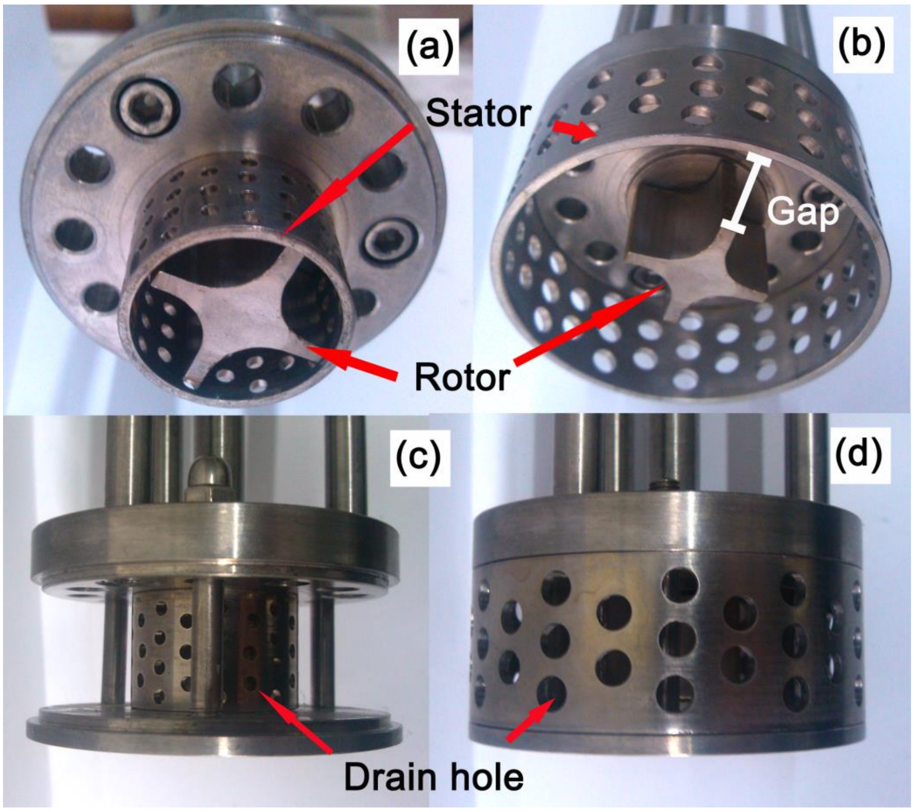

Fig. S1. Photographs of high shear generators with (a, c) the small stator and (b, d) the large stator.(a, b) The partially installed high shear generator and (c, d) the assembled high shear generator.

TC3. HSP values for solvents and graphene

Tab. S2 HSP value for solvents and graphene[12, 13]

Substance	δ_D(MPa$^{1/2}$)	δ_P(MPa$^{1/2}$)	δ_H(MPa$^{1/2}$)
Water	18.1	17.1	16.9
Isopropanol	15.8	6.1	16.4
Graphene	18	9.3	7.7

Tab.S2 lists the estimated HSP values of the solvents and graphene involved in this work. HSP values contain dispersion component (δ_D), dipolar component (δ_P), and hydrogen-bonding component (δ_H).[12, 14] The HSP of solvent mixture can be calculated by using equation (1).

$$\delta_{\mathrm{mix}} = \sum \emptyset_{\mathrm{n,comp}} \delta_{\mathrm{n,comp}} \tag{1}$$

where $\emptyset$ is the volume fraction for each composition. The precise HSP values of the graphene have yet been reported, therefore the HSP distances between graphene and solvent mixtures can then be calculated using Eq. 2.

$$R_a = \left[4\left(\delta_{D,mix} - \delta_{D,graphene}\right)^2 + \left(\delta_{P,mix} - \delta_{P,graphene}\right)^2 + \left(\delta_{H,mix} - \delta_{H,graphene}\right)^2\right]^{1/2} \tag{2}$$

The HSP distance (R_a) can be used to evaluate the solubility of solutes in solvents. The predictable solubility can increase with the decrease of R_a value under the same conditions.

TC4: Additional SEM images

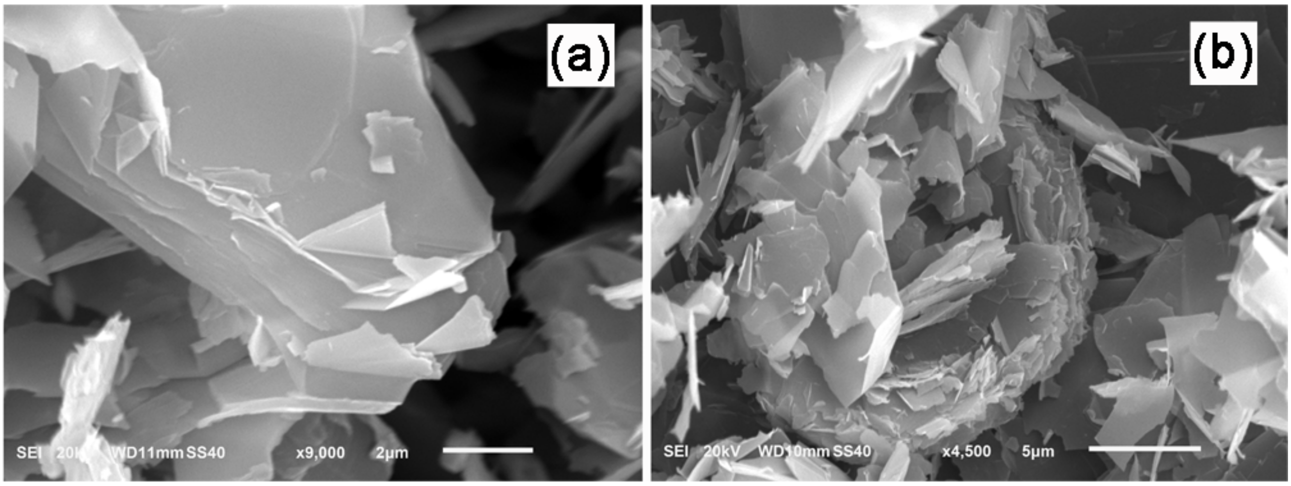

Fig. S2 Typical SEM image of the curl and loose edges of graphite particles after collision

TC4. Additional AFM images

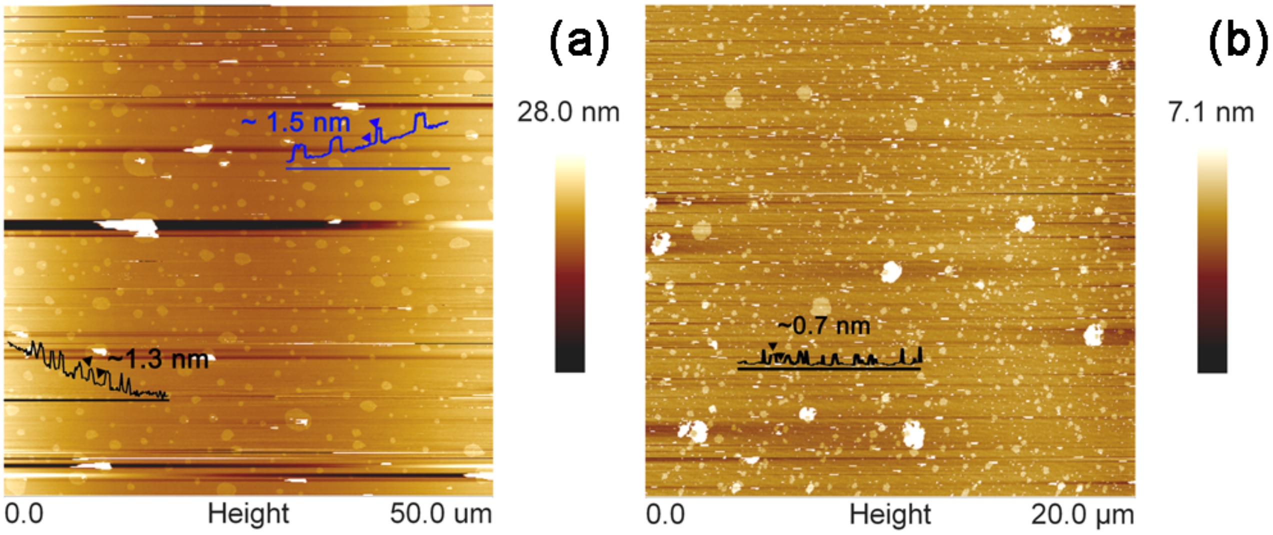

Fig. S3 Typical AFM image of GNSs prepared with the (a) large and (b) the small stators

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