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Supporting information

Facile and Economical Mass Production of Graphene Dispersions and Flakes

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Experimental

Synthesis of graphene materials

In a typical procedure, 1 g pristine graphite powder (~2 μm), 5 ml NPE(≥98% purity) and 10 ml deionized water were placed into an agate jar (Φ15 cm) containing 6 mm and 11 mm agate balls as grinding media. The capsule was then fixed in a planetary ball mill and agitated with 400 rpm for 12 h to obtain few-layer graphene (FLG) flakes. The resultant products were transferred into 100 ml water. The obtained dark dispersion was then centrifuged at 5000rpm for 20 min to remove any large particles including partially exfoliated pristine graphite and unexfoliated residual pristine graphite, giving a dark homogeneous colloidal suspension of graphene sheets in water. The suspension was vacuum-filtrated through a PVDF membrane (with pore size of 200 nm) and washed with absolute ethanol. The yield of the exfoliated FLG flakes is estimated about 10 wt% of the pristine graphite. The FLG flakes were redispersed in water to make a stock solution with concentration of 0.96 mg/ml.

Comparison on the Production Cost

Table 1 Comparison on the production cost for mass production of FLG

	Chemically Derived Graphene from Graphite Oxide[1]	Epitaxial Graphene and Chemical Vapor Deposition[2,3]	Ball Milling
Product quality	Low quality with defect	Very high quality	High quality
Apparatus	Refrigerator, Hot type magnetic stirring water bath pot, mechanical agitator, supercentrifuge, ultrasonic cleaner	G-CVD (380,000 yuan)	Planetary ball mill
Time	Two weeks for one cycle	Several days for one cycle	13h for one cycle
Manpower, material	Lots of manpower and material, Dialysis membrane	Transfer process consumes lots of manpower and material， metal etching	~12h of electricity, agate jar
Experiment condition	Harsh oxidants, corrosive acids and toxic reductive agent	High temperature and high pressure	NPE, normal temperature and pressure

Since 2004, various preparation processes of graphene have been developed, while there are only two methods potentially capable of quantity production of few-layer graphene (FLG) flakes, i.e. oxidation-reduction of pristine graphite and epitaxial growth on silicon carbide or metal substrates using chemical vapor deposition (CVD).

In this work, our ball-milling method is also potentially capable of quantity production of FLG. And the cost is much lower than the above-mentioned two methods, taking account of the product quality, manpower and material resources, and apparatus and time cost.

Characterization of graphene materials

High-resolution Transmission Electron Microscope (TEM, JEOL, JEM-2100F) was used to investigate the number of layers of the samples, and the morphology and size of graphene is observed by low-resolution TEM. The dilute sample suspension was directly dropped on lacy carbon-coated Cu grid for TEM observation without any ultrasonic treatment. The graphene dispersion was washed with ethanol to remove the NPE at a centrifugal speed of 10,000rmp, and then the sediment was dispersed into N, N-dimethyl formamide (DMF) for the test of AFM by dropping the new solution on fresh mica sheet. Fourier-transformed Infrared (FT-IR) spectra were taken on a Nicolet 6700 FT-IR Spectrometer by using pressed KBr pellets. Raman spectra were recorded on a LabRAM HR800 Raman spectrometer using a 532 nm excitation laser. RST-9 4-Point Probes Resistivity Measurement System (Guangzhou four-probe Technology Co., Ltd., China) was used to measure the sheet resistivity of samples. The graphene sample films (Φ42mm, 8.6 mg, Figure S5) of Raman, XPS and Resistivity measurements were fabricated by vacuum filtration of the graphene dispersion through the PVDF membrane followed by washing with ethanol and drying at room tempertature in air. UV-visible spectrophotometer (UNICO 3802) was used to evidence that NPE can disperse graphene into water.

Electrochemical measurements of graphene electrode

The graphene stock solution was 100-fold diluted with water and vacuum filtrated to form graphene film on the PVDF membrane. The graphene-coated membrane was cut into 1×1 cm^2 sheet and served as the working electrode. A 2×2 cm^2 platinum foil was used as the counter electrode. The reference electrode was an Ag/AgCl electrode with saturated KCl aqueous solution. The electrochemical measurements were performed on a CHI660D electrochemical workstation (Shanghai Chenhua Instruments, China). The specific capacitance is calculated from the galvanostatic charge/discharge curves at a constant current density using the formula:

$$C = \frac{I}{m\frac{\Delta u}{\Delta t}} = \frac{I_s}{\frac{\Delta u}{\Delta t}}$$

where I is the constant current applied, $\Delta u/\Delta t$ is the slope obtained by fitting a straight line to the discharge curve, m is the net mass of FLGs on one electrode, I_s is the current density.

Graphics

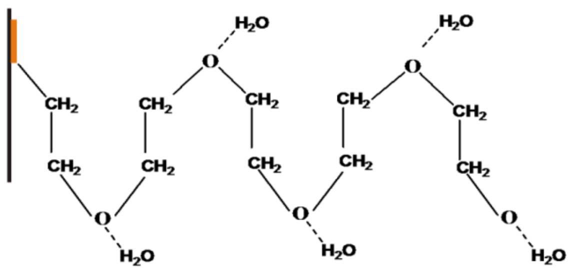

Figure S1 NPE arrangement style in graphene dispersions.

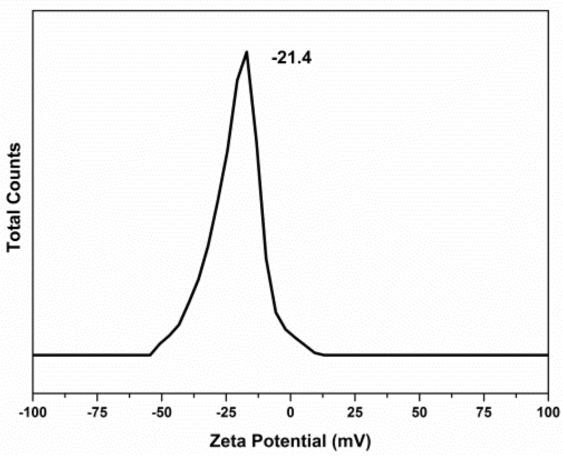

Figure S2 Zeta potential of as-prepared graphene despersions

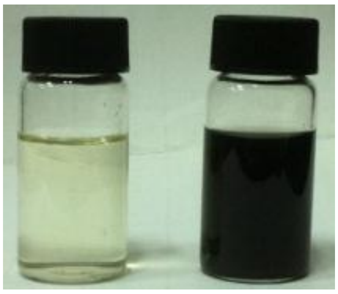

Figure S3 Digital graphs of graphite/NPE/ethanol solution (left) and graphite/NPE/water (right).

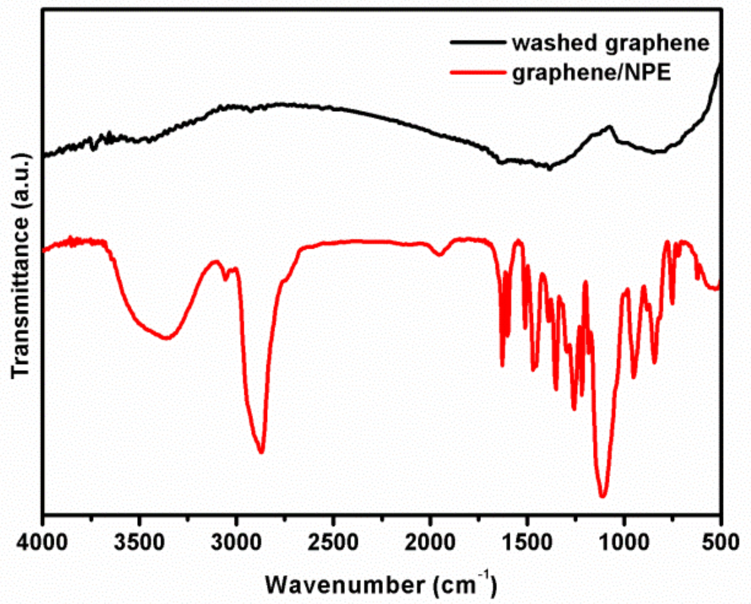

Figure S4 FT-IR spectra of washed graphene (solid black) and unwashed graphene (solid red).

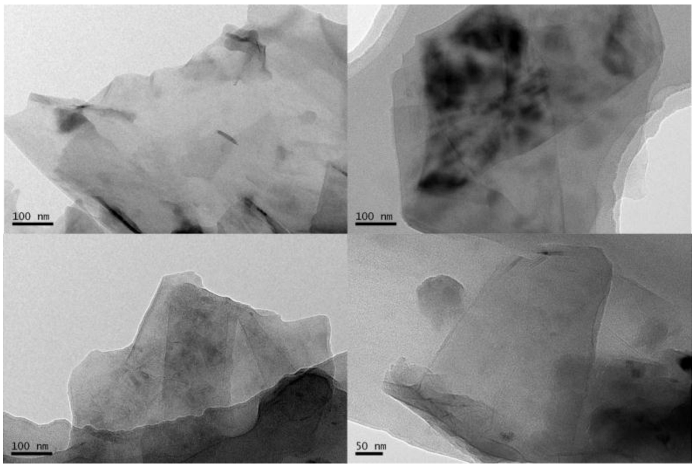

Figure S5 Low resolution TEM images of FLG flakes.

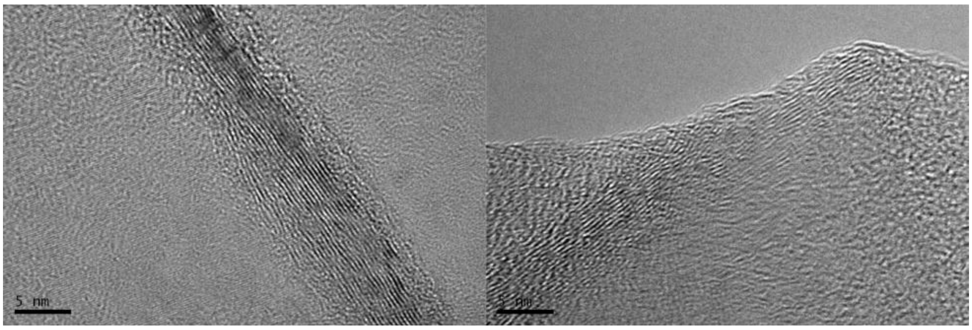

Figure S6 High resolution TEM images of FLG flakes.

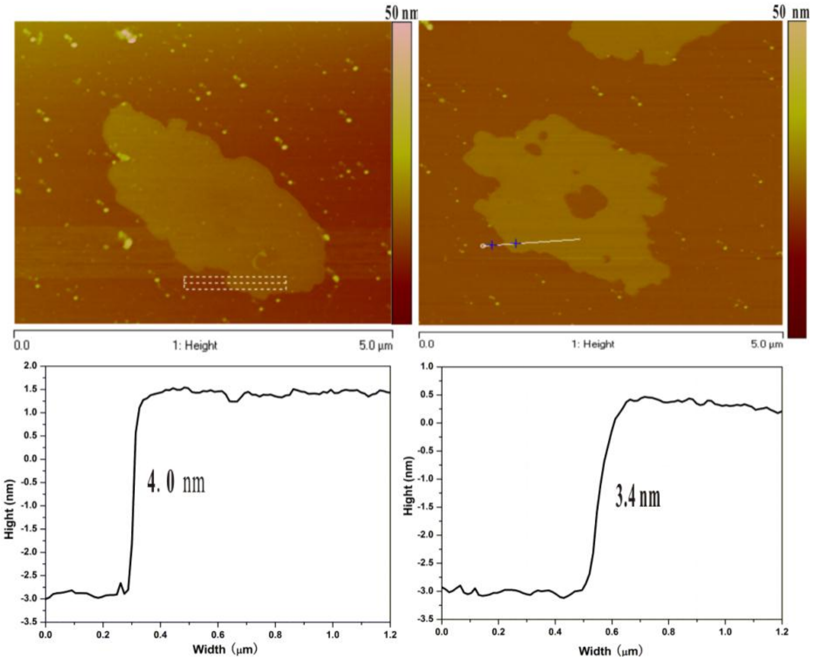

Figure S7 Atomic force microscopy (AFM) images of FLG flakes.

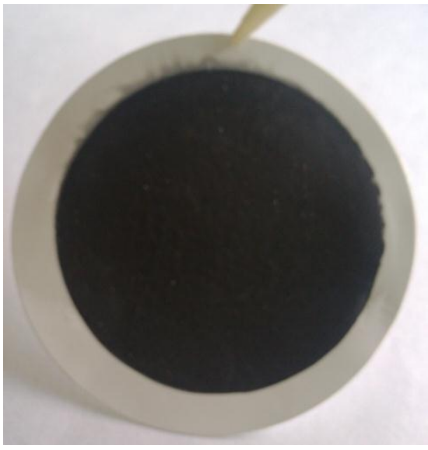

Figure S8 Graphene film(Φ42mm,8.6 mg) polyvinylidene fluoride (PVDF) membrane.

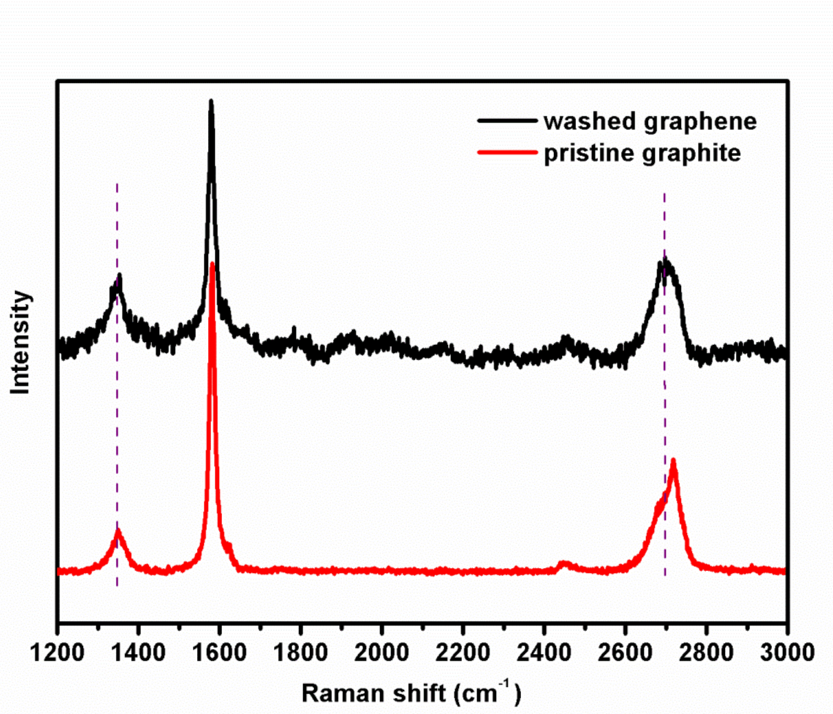

Figure S9 Raman spectra of washed graphene (black solid) and pristine graphite (red solid).

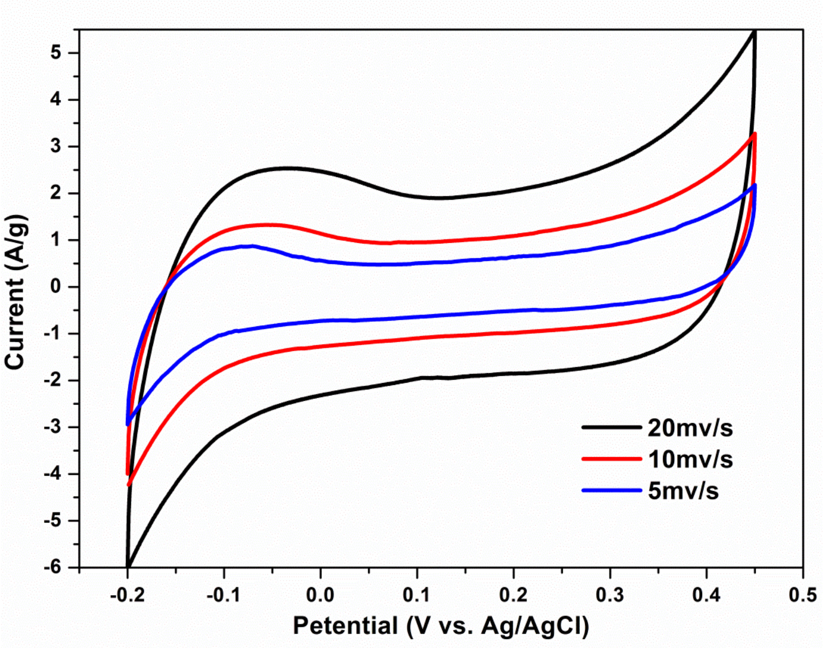

Figure S10 Cyclic voltammograms of the grpahene electrode in 1 mol/L H_2SO_4 aqueous solution at various scan rates of 5, 10, 20 mV/s, respectively.

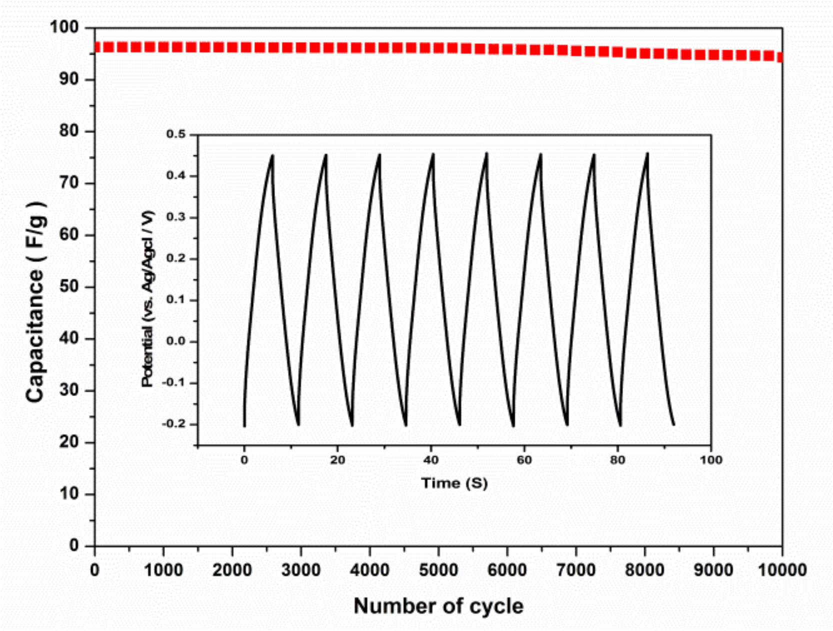

Figure S11 The capacitance retaining and charge/discharge behavior (inset) of the graphene electrode at the current density of 10A/g in 1 mol/L H_2SO_4 aqueous solution during 10,000 charge-discharge cycles.

Notes and references

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2. S. Grandthyll, S. Gsell, M. Weinl, M. Schreck, S. Hufner and F. Muller, J. Phys-Condens. Mat., 2012, **24**, 314204.
3. V. O. Ozcelik, S. Cahangirov and S. Ciraci, Phys. Rev. B, 2012, **85**, 235246.