Electronic Supplementary Information

Facile Fabrication of High Quality Graphene from Expandable Graphite: Simultaneous Exfoliation and Reduction

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Experimental Methods:

All chemical reagents were obtained from commercial sources without further purification. Expandable graphite (EG) bought from Qingdao Tianyuan Company (140 mesh), hydrazine hydrate (80%), concentrated ammonia (28%) were obtained from Beijing Chemical Co. Ltd. Experimental solutions were prepared using deionized water.

Our single- and few-layer graphenes were synthesized from EG by quenching method. Generally, a long quartz tube was heated to 800 °C within 2 min. A nitrogen inlet was inserted the quartz tube. EG (0.1g) was placed into the quartz tube. EG rapidly expand within 10s in the tube. Then, the samples were quickly quenched to low temperature in the cool hydrazine hydrate (20%) or concentrated ammonia (28%). During quenching process, part of hydrazine hydrate or concentrated ammonia would be decomposed into a large amount of obvious pungent gas. After transient quenching, the resulting dispersion was subjected to 30 min of centrifugation at 3,000 r.p.m to remove any unexfoliated bulk graphite. The top dispersion was separated by filtration and washed with a large amount of water several times. The final products were dried under ambient condition. The sediment remaining of no entirely exfoliation after quenching can be recycled. When the heating again, the dried sediment release obvious gas in like manner, which help to improve the total yield of graphenes.

Characterization:

SEM: Scanning electron microscopy (SEM) micrographs were taken using a Hitachi S-4800 instrument operating at 10kV.

TEM: Transmission electron microscopy (TEM) experiment was performed on a JEM-2100 electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. Carbon-coated copper grids were used as the sample holders. We disperse few as-prepared products ethanol. After mild sonication, the solution of graphenes was dropped onto the TEM grids for following TEM measurement.

AFM: The morphology and thickness of different graphenes were characterized by atomic force microscopy (AFM, Digital Instruments NanoScope IIIa, operating in tapping mode). The samples were dispersed in the ethanol. After mild sonication, the solution of graphene was spin coated onto the surface of mica for following measurement.

XPS: X-ray Photoelectron Spectroscopy (XPS) analysis was performed on a VG ESCALAB MK II with an Mg Kα (1253.6eV) achromatic X-ray source.

Raman: Raman measurements were performed with a Jobin Yvon HR800 micro-Raman spectrometer at 457.9 nm. The laser intensity at the sample was kept below the threshold for any laser-induced changes in the Raman spectra and electrical transport characteristics. The powders of graphenes including single- and multi-layer graphene were placed on a clean SiO₂/Si substrate for the Raman measurement.

Electrical conductivity measurement: The electrical conductivity of graphene was measured using conductive-AFM (Seiko SPA 400 with a Nanonavi Probe Station) within an atmospheric environment. The used tip of conductive-AFM was coated with gold. In addition, the gold was covered evenly on Si substrate, exposing the nearly atomically smooth gold surface, for conductive-AFM measurements. Then, the solution of graphene was spin coated onto the gold surface for the electrical conductivity measurement. One terminal of the conducting cantilever, defined to be the cathode for bias voltage, was connected to ground; the other was connected to the layer of the sample. Nano-scale *I-V* characteristic and current were measured in the contact mode. To get the reliable electrical conductivity data, the *I-V* curves were recorded using the same tip at five different sites of each sample on the gold substrate, which show the similar high conductivity.

In-situ IR measurement: The in-situ IR were used for the analysis of the decomposition process of intercalation compounds in the EG. The typical procedure as follow: EG (0.1g) was placed into the sealed quartz tube with a pipe on the port of tube. Then, the quartz tube was rapidly heated to 800 $^{\circ}$ C. EG rapidly expand in the tube, releasing a large quantity of gas. Finally, the gas was imported in the FT-IR (Nicolet, IS10) by the pipe under nitrogen environment for the in-situ IR measurement. The in-situ IR was collected every 18s, which can provide detailed information about decomposition process of intercalation compounds based on the different time IR data.



Fig. S1 (a) TEM image of Graphene 1 prepared by quenching in pure water. (b) Raman spectra of Graphene 1. (C) XPS spectra of Gaphene 1.



Fig. S2 SEM image of unexfoliated EG sediment after quenching.



Fig. S 3 Enlarged images with fitting curves of 2D-band of quenching products including Graphene 2 (a) and Graphene 3(b).

In this paper, we fit 2D-band of products using the non-linear least square fit program (Gauss–Lorentzian). After deconvolution, the objective results with high correlation (R^2 =0.9995) are shown in Fig. S3. We can see three clear fitting peaks. For Graphene 2, the first peak (2689 cm⁻¹) should belong to monolayer graphene. The bilayer graphene play the main contribution for the second peak (2710 cm⁻¹). However, the third peak (2748 cm⁻¹) is attributed to few-layer (3~5 layers) graphene in products. Meanwhile, we can obtain similar results from Graphene 3. Three peaks can be seen at 2688 cm⁻¹, 2713 cm⁻¹, and 2749 cm⁻¹, which are attributed to monolayer graphene, bilayer graphene and few-layer (3~5 layers) graphene, respectively.

	Atomic composition (%)	
	С	0
EG	87.7	12.3
Graphene-1	89.5	10.5
Graphene-2	98.2	1.8
Graphene-3	98.1	1.9

Table. S1 XPS atomic composition of EG and different graphenes prepared by different quenching medium.



Fig. S4 XPS spectra of EG (a), Graphenes 2 (b), and Graphenes 3 (c).

The best test for the presence of defects in samples is X-ray photoelectron spectroscopy (XPS). We have evaluated the effect of quenching reduction and exfoliation through analysis of surface atomic composition of graphene and the results are presented in Table. S1 (ESI[†]). The C/O ratio remarkably increased from 7:1 for EG to 55:1 for Graphene 2 and 52:1 for Graphene 3 after the

quenching, suggesting hydrazine hydrate or concentrated ammonia-assisted quenching process almost entirely remove the hydroxyl groups, epoxide groups, carboxylic and carbonyl groups. In addition, high resolution XPS spectrum (Fig. S4) of EG shows the presence of abundant C-C, C-O, C=O and C(O)O chemical binding states, corresponding to the peak at 284.6, 285.4, 286.5 and 289 eV, respectively. After the quenching, the peaks of C-O, C=O and C (O) O (Graphene 2, 3) become visibly weaken. This also indicates removal of groups between the inter-layers of EG.



Fig. S5 In-situ IR spectra for analysis of the decomposition process of intercalation compounds in different time 18s (a), 36s (b), 54s (c). Inset: the standard IR spectra of sulfur dioxide and sulfur trioxide.

The in-situ IR spectra are shown in Fig. S5 for understanding of the decomposition mechanism of intercalation compounds in EG. A series of IR spectra in different time can provide rich information about the decomposition process of intercalation compounds. The IR spectra were collected every 18s. As time increases, a significant enhancement of absorption peak of sulfur dioxide and sulfur trioxide can be seen corresponding to the standard IR spectra (Fig. S5 inset), indicating that the intercalation compounds can be pyrolyzed into sulfur dioxide and sulfur trioxide under high temperature. Generally, the sulfuric acid can be pyrolyzed to sulfur dioxide and sulfur trioxide at high temperature. Thus, we consider that the intercalation compounds are composed of sulfuric acid.

Additionally, a large amount of gas such as NH₃ from partly thermal decomposition of quenching media during the quenching can reacted with the residual acidic groups including sulfate and carboxylic groups in worm-like EG. The neutralization reaction between the NH₃ and acidic groups will not only encourage the inserting of NH₃ into graphite layers for expanding the layers space, but also promote the removal of residual acidic groups for the formation of high-quality graphenes.



Scheme. S1 Scheme of simultaneous exfoliation and reduction of expandable graphite by facile quenching method.