Electronic Supporting Information

A Scalable, Solution-Phase Processing Route to Graphene Oxide and Graphene Ultralarge Sheets

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Experimental Details

Oxidation of graphite: The oxidation of graphite was carried out following the Hummers method. In a typical procedure, KNO_3 (1.2 g) and graphite (1.0 g) was added into 46 mL of concentrated H_2SO_4 (98%) under stirring. After 10 mins 6.0 g of $KMnO_4$ was added slowly. The mixture was then heated to 35 ^oC and stirred for 6 hours. Subsequently, 80 mL of water was added dropwise under vigorous stirring, resulting in a quick rise of the temperature to ~80 ^oC. The slurry was further stirred at this temperature for another 30 mins. Afterwards 200 mL of water and 6 mL of H_2O_2 solution were added in sequence to dissolve insoluble manganese species. The resulting graphite oxide suspension was washed repeatedly by a large amount of water until the solution pH reached a constant value at ~4.0, and finally the suspension was diluted to 600 mL with water.

Delamination of graphite oxide: 200 mL of the diluted graphite oxide suspension was transferred into a conical beaker with a volume of 500 mL. Then the suspension was gently shaken in a mechanical shaker at a speed of 160 rpm for ~6 hours. To remove the small amount of unexfoliated particles, the resulting viscous suspension was centrifuged at 2,000 rpm for 10 mins, producing a brown, homogeneous colloidal suspension of GO sheets. The colloidal suspension could be further concentrated by centrifugation at 8,000 rpm.

Reduction of the GO sheets to graphene: Typically, 100 mL of GO suspension (~2 mg mL^{-1}), 6 g

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of 10 wt% Brij-35 (or other nonionic polymeric surfactants such as Tween-80 and Triton-X100) aqueous solution, and 4 g of 5 wt% hydrazine solution were mixed and sealed in a conical beaker. The mixture was stirred for 5 mins and then placed in an oven at 80 ^{o}C for 8 hours. Finally produced was a black stable suspension containing ~1 mg mL^{-1} of graphene sheets.

Preparation of GO and graphene foams: The colloidal suspensions of the GO and graphene sheets were quickly frozen in liquid nitrogen. Then the frozen solids were transferred into a freeze drying equipment and evaporated in vacuum at the temperatures below 0 ^{o}C for 24-48 hours, resulting in fluffy solid foams.

Preparation of graphene paper: 20 mL of the graphene suspension with a concentration of ~1 mg mL^{-1} was filtered by mixed cellulose ester filter membrane with 150 nm pores. The thin filtration cake was dried at 60 ^{o}C for 6 hours then immersed into acetone to dissolve the filter membrane, finally leaving a black graphene/polymer composite paper. The paper was annealed at high temperatures (500 ^{o}C or 800 ^{o}C) for 2 hours under Ar to remove the polymer stabilizers.

Langmuir-Blodgett (LB) assembly of monolayer film of the GO sheets: Monolayer film of the GO sheets was fabricated using a Kibron MicroTrough X LB trough. The GO suspension of 0.1 mg mL^{-1} was poured into the trough. The compression of the solution surface was conducted at a rate of 10 mm min^{-1} until the surface pressure reached 10 mN m^{-1}. The GO sheets floating on the solution surface were transferred onto a vertical Si substrate under a constant withdrawing speed of 1 mm min^{-1}. The film was naturally dried at room temperature.

Characterizations: AFM characterization was conducted by a Veeco Dimension 3100V scanning probe microscope at ambient conditions using a tapping mode. SEM images were taken by a Hitachi S-4800 Field Emission Scanning Electron Microscope. Specially, a low accelerating voltage of 1.0 kV and high current of 20 μA were applied for the graphene oxide and graphene sheets on silicon substrates. The SEM images of bulk samples were normally captured at the voltage of 4.0 kV and current of 7 μA. TG measurement was carried out on a Perkin-Elmer Pyris Diamond Thermogravimetric/Differemtial Thermal Analyzer with a heating rate of 2 ºC min^{-1} under a nitrogen atmosphere. The conductivity of the graphene paper was determined by a Lucas Signatone Pro4-4000 Four Probe Resistivity Test System.

Synonyms and molecular formula/structures of nonionic polymeric surfactants used

1) *Btij35*

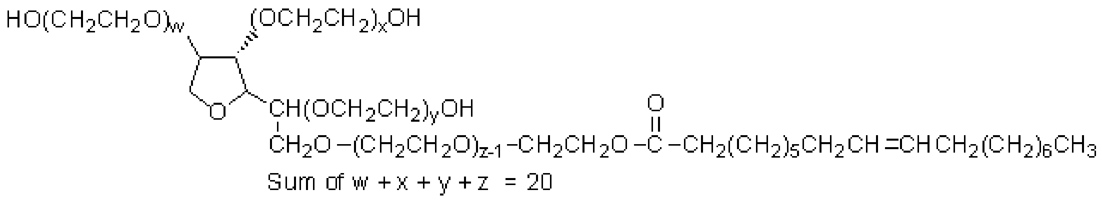
Synonyms: polyethylene glycol dodecyl ether

Molecular formula: $CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_nOH$ n~23

2) *Tween 80*

Synonyms: polyoxyethylenesorbitan monooleate

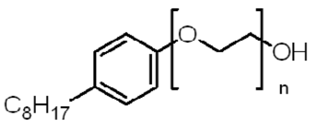
Molecular Structure:



3) *Trixton X100*

Synonyms: polyethylene glycol tert-octylphenyl ether

Molecular Structure:



n=9-10

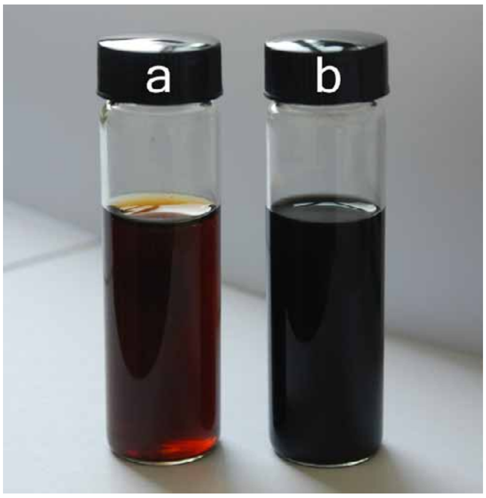


Figure S1. Digital photographs of the as-prepared colloidal suspensions of (a) GO and (b) graphene sheets. The GO and graphene contents were approximately 2 mg/mL and 1 mg/mL, respectively.

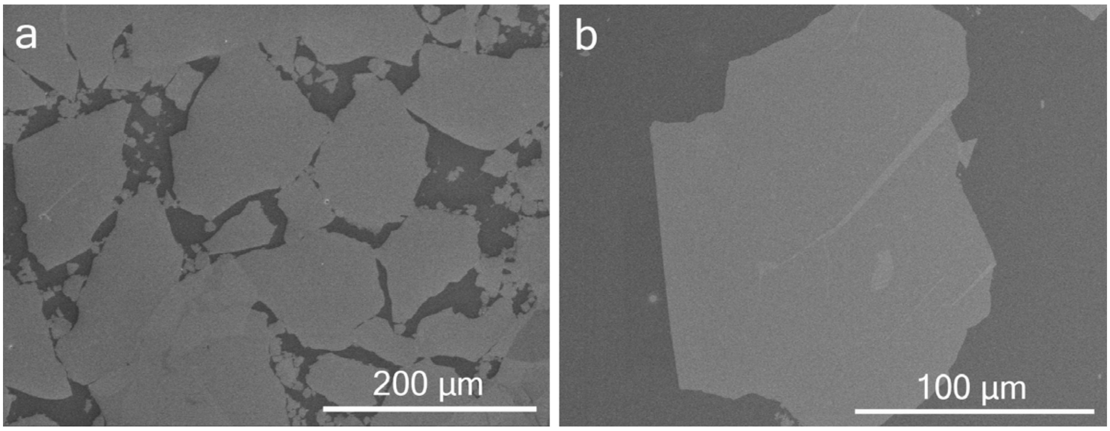


Figure S2. SEM images at different magnifications showing large sizes of graphene oxide sheets.

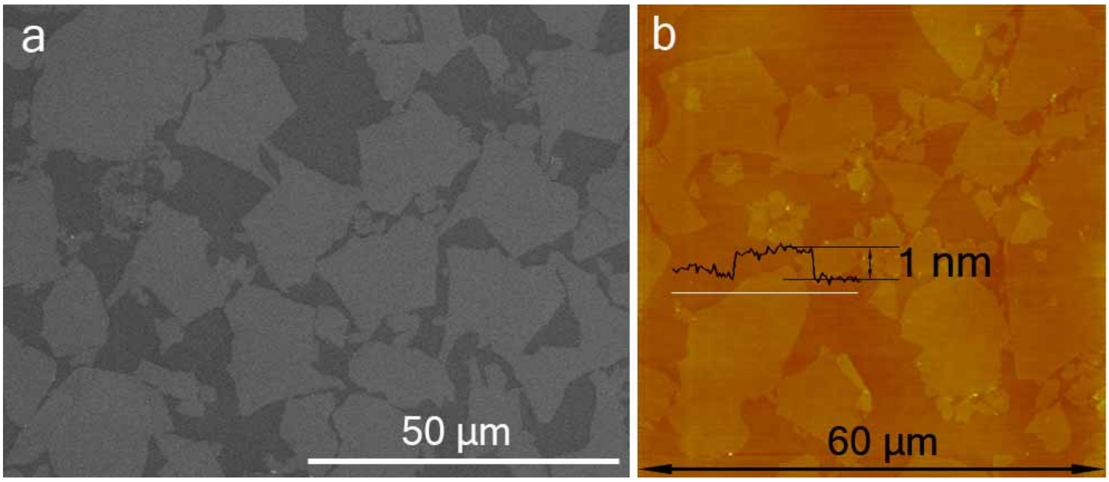


Figure S3. (a) SEM and (b) AFM images of graphene oxide sheets derived from graphite of 500 mesh size (corresponding to 25 µm in mean sizes). The height profile denoted in Figure S3b demonstrates a mean thickness of ~1 nm, indicative of the unilamellar nature of the sheets.

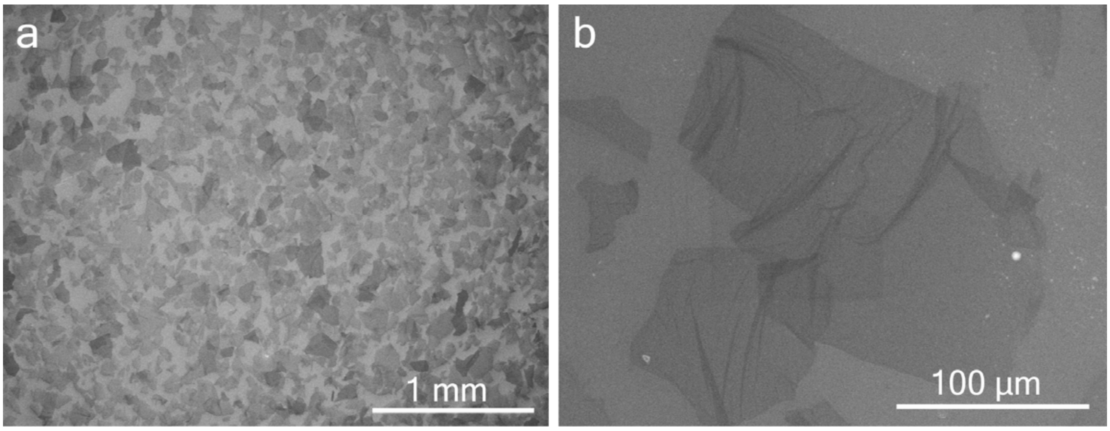


Figure S4. SEM images at different magnifications showing large sizes of graphene sheets. The sheets were deposited on a Si substrate which was precoated with one layer of polyethyleneimine.

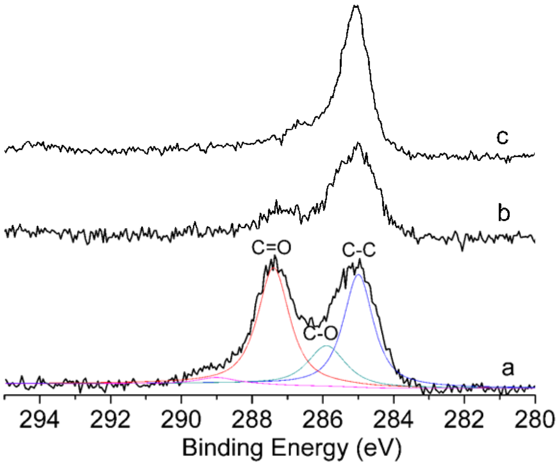


Figure S5. X-ray photoelectron spectra of a) graphene oxide, b) chemically reduced graphene and c) graphene annealed at 700 °C. It is obvious that the oxygenous groups were remarkably removed by chemical reduction and their contents further decrease after high temperature aneallling.

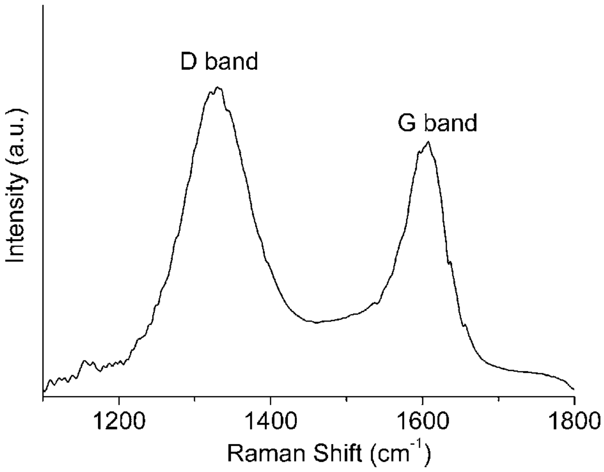


Figure S6. Raman spectrum of chemically reduced graphene deposited on PEI coated Si substrates.

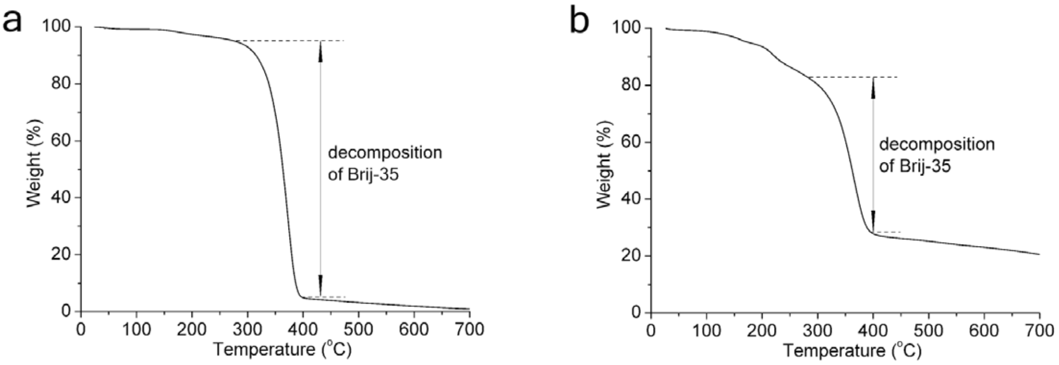


Figure S7. TG curves of (a) pure polymer Brij-35 and (b) the freeze-dried graphene/Brij-35 foam recorded under a nitrogen atmosphere. The both curves indicate that >95 wt% of Brij-35 decomposed at ~400°C and that the complete removal of the Brij-35 from the foam achieved at ~700 °C.

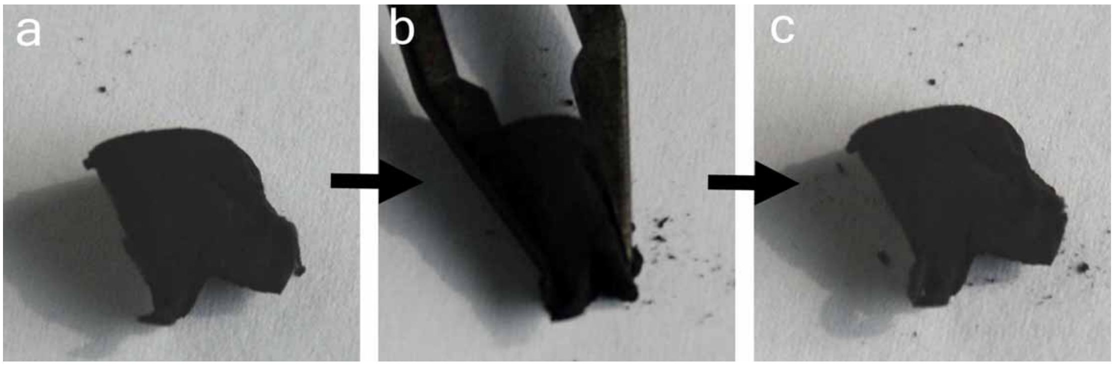


Figure S8. Series of digital photographs demonstrating the elasticity of the graphene foam annealed at 500°C under Ar. (a) a piece of foam; (b) the foam being squeezed by a tweezers; (c) the foam recovered its original shape after withdrawing the tweezers.

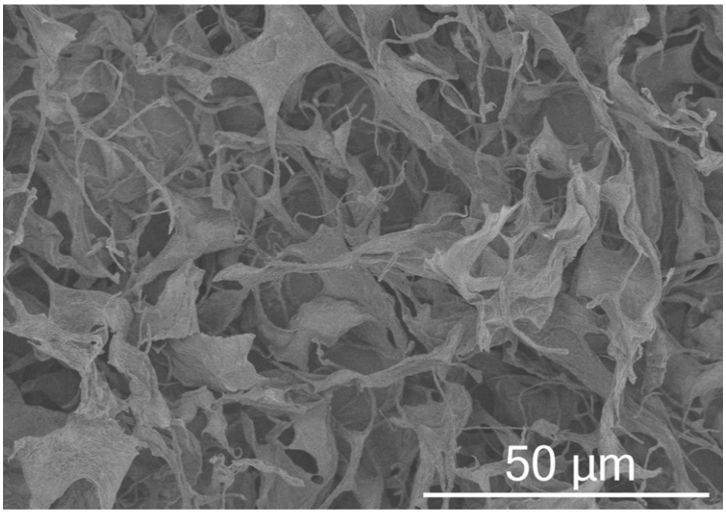


Figure S9. SEM image of the graphene foam annealed at 500 °C under an Ar flow, showing a highly crosslinked morphology.