Supporting Information

Rapid room temperature chemical route for the synthesis of graphene: Metal-mediated reduction of graphene oxide

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Experimental section

1. Reagents and materials.

Graphite powder (<45 micron, >99.99%), was obtained from Sigma-Aldrich and used as received. All other chemicals used in this investigation were analytical grade (99.9%). Phosphate buffer solution (PBS, 0.1M) of pH 7.2 was used to measure the capacitance. All the solutions used in this investigation were prepared in Millipore water (Milli-Q system). Zn filings (size: ~0.5 cm with thickness of ~1 mm).

2. Preparation of graphene oxide (GO)

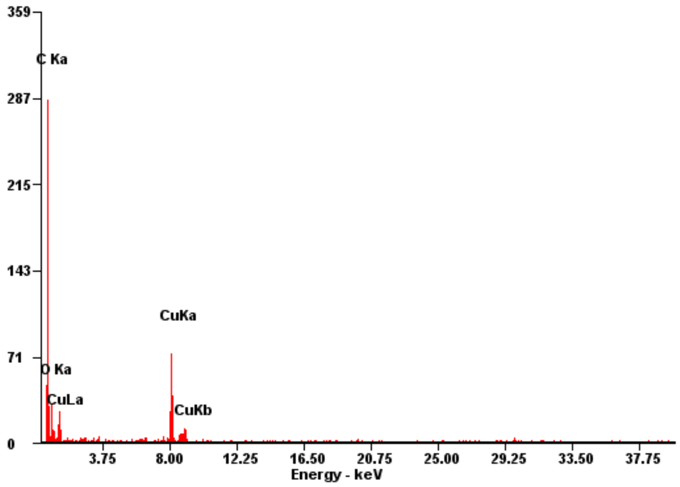
Graphene oxide was prepared using modified Hummer's method by exfoliation of natural graphite. In a typical method graphite (1g) and $NaNO_3$ (1g) was slowly mixed with 50 ml of concentrated H_2SO_4 in a round bottom flask at 0 °C. Solid $KMnO_4$ (6 g) was slowly added to the reaction mixture at 0 °C and stirred continue for 1 h at room temperature. Then, 200 ml of water was slowly added to the reaction mixture and the stirring was continued for another 30 m. H_2O_2 solution (30%) was added to the reaction mixture until gas evolution was ceased to convert the residual permanganate and MnO_2 to $MnSO_4$. The resulting suspension was centrifuge with an ultracentrifugation to remove the unexfoliated graphite and oxidizing agents. The yellow-brown GO residue was then washed repeatedly with 5% HCl solution until the washing solvent gave a negative test for sulfate ion with $BaCl_2$ solution. The residue obtained after repeated washing was further washed with small amount of Millipore water and dried under vacuum for 24 h to get the yellow-brown powder of GO.

3. Instrumentation

FTIR measurements were performed with Perkin-Elmer FTIR spectrophotometer RX1. Raman spectral measurements were carried out with a Renishaw Raman System RM 1000B coupled with a Leica DMLM microscope equipped with a peltier-cooled CCD detector. The samples were excited with an air cooled argon ion laser of wavelength 785 nm with power 20 mW and filtering of the Rayleigh scattering was achieved through an edge filter at 200 cm^{-1} cut off that allows study of Raman scattering only on the Stokes side of the spectrum. AFM measurements were performed with a dicp – II (model no AP0100) scaning probe microscope (Veeco instruments). Imaging was done in non-contact mode using P-doped Si cantilever (frequency f_c = 245 kHz, spring constant k = 20-80 N/m). Transmission electron microscopic (TEM) measurements were carried out with a JEOL JEM2010 electron microscope operating at 200 kV. Carbon-coated copper grids (400 mesh) were used in the sample preparation. Energy dispersive spectroscopic (EDS) measurement was performed with FEI TECNAI-G^2-20S-TWIN instruments with EDAX-EDS attachments (Model No. 942409761751, Standard-2). Carbon-coated copper grid (400 mesh) was used for the sample preparation. TGA analysis was performed on NETZSCH/STA 409 DC thermal analysis with Al_2O_3 crucible under N_2 atmosphere at 5 ºC min^{-1}. The UV-vis spectra of the colloidal GO and reduced GO solutions were recorded using CARY 5000 UV-vis-NIR spectrophotometer. Electrical conductivity of GO and reduced GO are measured using standard dc four-probe technique by passing 100mA constant current through the samples. The direction of the current is reversed at each measurement in order to correct the measured voltage drop for any thermo emf generated due to some temperature gradient across the sample. Electrochemical capacitance measurements of GO and nascent hydrogen reduced GO were performed with CHI643B electrochemical analyzer attached with a Faraday cage/picoampere booster (CH Instruments, Austin, TX). For the capacitance measurements, the rGO sample was heated at 100 ºC for 1 h. Nitrogen adsorption isotherm was used to measure the surface area of reduced graphene oxide with a Quantachrome instrument (AUTOSORB-1). Before adsorption measurement the sample was degassed at 100 ºC for 12 h to remove water. X-ray photoelectron spectroscopy (XPS) measurements were performed with Specs (German) using the energy source Mg (Kα, hν = 1253.6 eV). The spectra were analyzed using casaXPS software after Shirley background subtraction for evaluation of chemical shift.

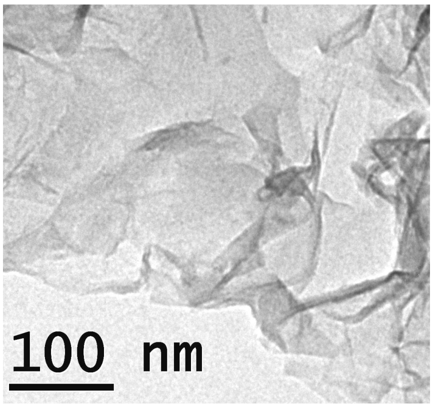
ESI-1

Energy dispersive spectra of reduced GO. The observed signature for Cu originates from the grid used for the measurement.



ESI-2

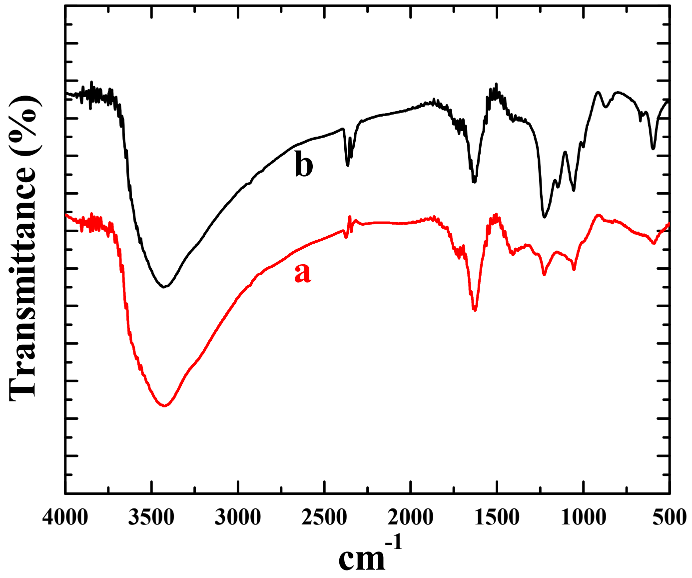
TEM image of a wrinkled graphene sheet.



ESI-3

FTIR spectral profile of GO (a) and GO after treating with H_2SO_4 for 2 h (b).

The increase in the intensity of the bands ~1220 and ~1050 cm^{-1} may be ascribed to the acid-mediated epoxide ring opening followed by the inter/intramolecular lactone/ester formation.



ESI-4

FTIR spectral profile of GO (a), GO reduced by Zn/CH_3COOH (b), Zn/HCl (c) and Zn/H_2SO_4 (d). In all cases reduction time were 2 h.

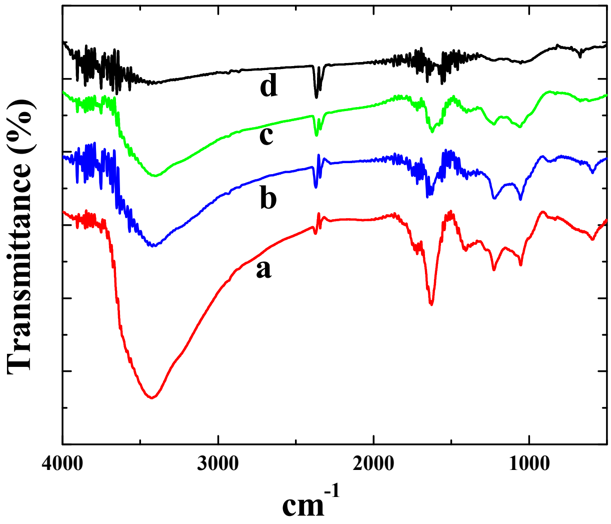
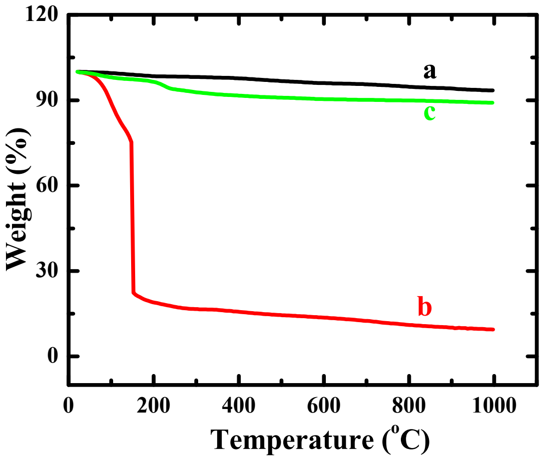


Table 1. Synthesis of rGO by different metal with different acid.

Metal	Acid (4 M)	Time
Zn	H_2SO_4	2 h
Zn	HCl	18 h
Zn	CH_3COOH	12 h
Sn	HCl	3 h
Cu	H_2SO_4	24 h

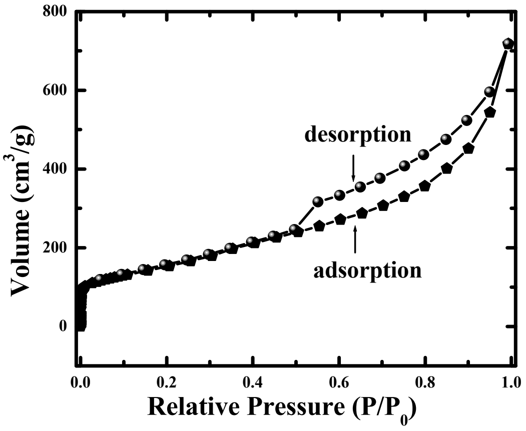
ESI-5

Normalized TGA plots of graphite (a), graphene oxide (b) and rGO (c).



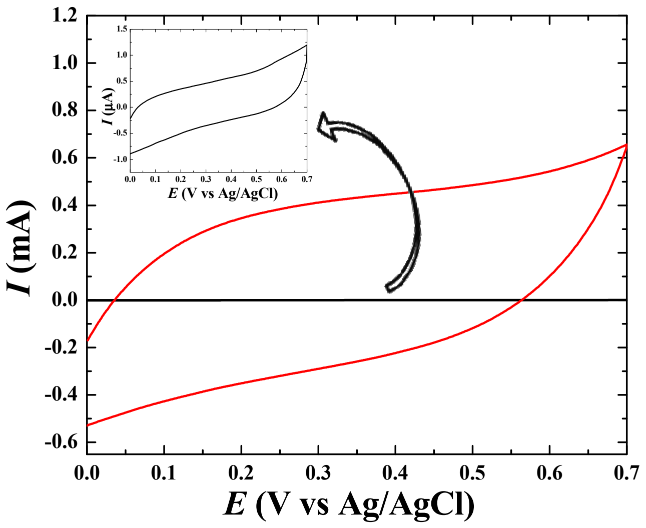
ESI-6

Nitrogen adsorption-desorption isotherm obtained for rGO.



ESI-7

Cyclic voltammetric response obtained from GO (black) and rGO (red). Inset shows the magnified version of GO.



ESI-8

Table. Synthesis of reduced graphene oxide at different experimental conditions.

Reducing agents/Methods	**Solvent**	**Temperature °C**	**Time h**	**Oxygen Content (atomic %)/ C/O atomic ratio***	**Byproduct**	**Reference**
Hydrazine hydrate	H_2O	100	24	10.3*	N_2H_2	1
Hydroquinone	H_2O	Refluxed	20	-	Quinone	2
Ascorbic acid	H_2O	RT	48	-	Guluronic acid, oxalic acid	3
Ascorbic acid + amino acid	H_2O	80	24	-	Dehydroascorbic acid	4
Solvothermal reduction	H_2O, Ethanol, 1-butanol, Ethelene glycol	120-200	4-48	6.6-16.6	-	5
Thermal reduction	DMAc + H_2O (10:3)	150	8	4.7*		6
Solvothermal reduction	NMP	205	24	13.8	Oligomers	7
Hydrazine + ammonia solution	H_2O	95	1	-	-	8
Glucose + ammonia solution	H_2O	95 RT	1 48	-	Gluconic acid	9
Sodium borohydride	H_2O	125	3	-	-	10
S-containing compound	H_2O/DMAc -H_2O	95	3	6.48*	SO_4^{2-}	11
Hydrazine hydrate/DMF	DMF	180 autoclave	12	1.5	-	12
Te nanowire	H_2O	RT	36	-	TeO_2	13
Hexamethylenetetramine	H_2O	100	12	-	$HCOO^-$	14
Fe powder	H_2O	RT	6	7.9*	Fe^{2+}	15
Zn + H_2SO_4	H_2O	RT	2	4.5	$ZnSO_4$	this work

GO was the precursor in each case.

* Represents the C/O atomic ratio of reduced grapheme oxide (atomic % oxygen content data are not available).

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