Electronic Supplementary Information for

Non-templated ambient nanoperforation of graphene: A novel scalable process and its exploitation for energy and environmental applications

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Contents

1. Experimental Section

1.1. Materials

Graphite (500 mesh), Sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30 %), sodium hydroxide (NaOH), tetraethyl orthosilicate (TEOS) are purchased from M/S Merck. Cetyltrimethylammonium bromide (CTAB) is purchased from Loba Chemie. Hydrazine hydrate (78-82 %) is purchased from Sigma-Aldrich. Rhodamine B (RhB) is purchased from Himedia. The deionized (DI) water is produced using a Millipore Mili-Q grade, with a resistivity of 18.5 MΩ cm^{-1}. All chemicals are used without further purification.

1.2. Synthesis of holey graphene

1.2.1. Preparation of graphene oxide. Though commercial GO can directly be used to avoid this step, graphene oxide (GO) is prepared in our laboratory from natural graphite powder (mesh 500), based on modified Hummers method as originally presented by Wang et al.[S1,S2] Graphite (2g, 500 mesh) and sodium nitrate (1 g) are added to 250 ml flask at 0 °C. Concentrated H_2SO_4 (50 ml) is added slowly with stirring below 5 °C. The mixture is stirred for 30 min and 0.3 g of $KMnO_4$ is added in small portions below 10 °C. The reaction mixture is stirred for an additional 30 min and 7 g of $KMnO_4$ is added to the mixture in 1 h below 20 °C. After the mixture is warmed to room temperature and stirred for 2 h, 90 ml of water is slowly dripped into the paste, causing a spontaneous increase in temperature due to exothermicity and the diluted warm suspension is stirred for another 15 min. Then, it is further treated with a mixture of H_2O_2 (30%, 7 ml) and water (55 ml). The resulting suspension turns bright yellow and the warm suspension is filtered, resulting in a yellow-brown filter cake. The cake is washed three times with a warm solution of 3 % aqueous HCl (150 ml). The GO is exfoliated to generate GO nano sheets by sonication in water for 1 h. Finally, the GO is separated by centrifugation and drying in vacuum oven for 24 h.

1.2.2. Sol-gel process to get graphene silica nanohybrid (SGO):
GO based nano hybrid is prepared via hydrolysis of TEOS. In a typical experiment, as-synthesized GO (15 mg) is firstly suspended in an aqueous solution containing a cationic surfactant CTAB (500 mg) and NaOH (20 mg), and then ultrasonicated (Equitron ultrasonic cleaner, 53 kHz, 75 W) for 3 h. After stirring for 2 h at room temperature TEOS (2.5 ml) is slowly added to the above mixture. After reaction for 12 h, graphene nano-hybrid is separated by washing with ethanol, followed by drying in oven for 6 h.

1.2.3. Holey graphene by surface etching of SGO

Above synthesized graphene silica nano hybrid (120 mg) is mixed with 30 ml of aqueous 1M NaOH solution and stirred for 1 h at room temperature. Resultant product is washed with warm ethanol, separated by centrifugation and dried. This treatment produces holey GO sheets (hGO). In order to increase the conductivity of hGO, above material is reduced by using the method reported by Stankovich et al.[9] Briefly, the fully dried hGO (100 mg) is mixed with 100 ml of DI water and 1 ml hydrazine hydrate. The mixture is subjected to reduction by heating under reflux conditions for 24 h. The product (hG) is separated by centrifugation and washed several times with methanol. Finally it is dried in oven for 6 h. To test the scalability, the recipe is fine-tuned with no serious hurdles to get a yield of up to 10 g of hG in single batch.

1.2.4. Synthesis of reduced graphene oxide (rGO)

For synthesis of rGO (without holes), GO is used instead of hGO. Dried GO (100 mg) is mixed with 100 ml of DI water and 1 ml hydrazine hydrate. The mixture is subjected to reduction by heating under reflux conditions for 24 h. The product (rGO) is separated by centrifugation and washed several times with methanol. Finally it is dried in oven for 6 h.

1.3. Preparation of supercapacitor electrodes and setup

Supercapacitor electrodes are prepared by coating nanocomposites on carbon paper using a simple brushing technique. The composition used for electrode preparation is 80:15:5 (weight percentage) for measurement of capacitance where 80% stands for active material mass (hG), 15% stands for *super-p* (conducting additive) and 5% stands for the binder (Kynar). The above mentioned composition is thoroughly mixed with N-methyl pyrrolidone in an agate mortar and then coated on a carbon paper homogeneously. Carbon paper is weighed before and after coating and drying the material to get the correct value of loading of sample at each electrode. These coated papers are readily used as electrodes for measuring capacitance properties. The supercapacitor setup for testing its capacitance consists of two such carbon electrodes coated with slurries made as mentioned above and 1 M H_2SO_4 as an electrolyte. It may be noted that the weight of active mass is used for the calculation of specific capacitance (C_s) and the specific capacitance (C_s) is calculated according to 3-electrode system with the relation as seen in literature that C_s measured from 3-electrode system is double the capacitance obtained by 2-electrode system.[33]

1.4. Dye adsorption and material regeneration

Rhodamine B (RhB) is chosen as the dye for the adsorption test. A known quantity of GO, SGO, hGO and hG are dropped into the four different aliquots of dye solutions of

same concentration. The mixtures are stirred for 1h, and sediment is collected and removed by filtration. The concentration of residual dye solution is analyzed by UV-Vis spectroscopy by measuring the absorbance at the maximum absorption wavelength. The residual concentration of dye left in the mixture after adsorption is determined from the standardized calibration curve. For the removal of adsorbed dye and regeneration of the material, the material is extracted from solution through filtration, and mixed with ethanol followed by 5 min sonication. Though in a single step all the dye is removed, this step is repeated to ensure complete removal. Then powder is dried under vacuum for 2 h for next use.

1.5. Characterizations

Several characterization techniques are used to investigate structure and properties of the materials as synthesized above. Surface morphology of these materials is examined by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM). An FEI TECNAI F20 electron microscope operating at 300 kV is used for recording transmission electron microscopic (TEM) images of all materials. Samples are powdered and dispersed in methanol before depositing onto a carbon coated copper grid. Scanning electron microscopy (SEM) analysis is done using FEI SEM instrument model quanta 200 3D. The samples in suspension are dried on Si wafers prior to the analysis at a temperature of 35 °C. AFM images are obtained from XE-100 atomic force microscope of PSIA on tapping mode. The samples for AFM measurements are prepared by ultrasonic (Equitron ultrasonic cleaner, 53 kHz, 75 W) treatment of GO (in water) and SGO nanohybrid (in Methanol) dispersions of 0.25 mg ml^{-1}. The samples are drop casted on a clean silicon wafers surface. FT-IR spectra are recorded by using Perkin-Elmer FT-IR spectrometer in the range 500-4000 cm^{-1} using KBr pellet. Raman Spectra are recorded from 800 to 3000 cm^{-1} on LabRAM Horiba JY HR-800 micro Raman spectrometer coupled with a microscope in reflectance mode with a 632.8 nm excitation He-Ne laser source. The dry samples are loaded on glass slide. Powder X-ray diffraction (PXRD) data of synthesized materials are collected using a PANanalytical X'pert Pro dual goniometer diffractometer. The data are collected with a step size of 0.008° and a scan rate of 0.5° min^{-1}. The radiation used is Cu K$_\alpha$ (1.54 Å) with a Ni filter and data collection is carried out using a flat holder in Bragg–Brentano geometry. UV-visible spectra are obtained from UV-visible spectrometer of Agilent/Varian CARY 50 UV-Vis spectrophotometer. Solid state ^{13}C MAS NMR and ^{29}Si MAS NMR spectra are recorded on a Bruker ASX-300 solid state NMR spectrometer operating at 300 MHz frequency with spinning rate of 8 KHz. An Autolab electrochemical workstation [PGSTAT30 (Eco-Chemie)] is used for carrying out the CV and charge-discharge measurements.

1.6. DFT based computational studies

All the geometries in the study are optimized using a PBEPBE functional with *DGauss* Double Zeta Valence Polarization (DGDZVP) basis set.[S3] The convergence of geometries is based on gradient and displacement criteria with a threshold value of 10^{-3}. The criterion for the convergence of cycles is 10^{-8}. The energy minimization is performed with Berny algorithm using redundant internal coordinates. Following the geometry optimization, harmonic vibrational frequencies are computed for selected models. All the frequencies are found to be positive for the structures studied thereby, indicating them to be a local minima. Molecular dynamics (MD) is carried out using deMon 2K code at 300 K. Velocities are updated using velocity verlet algorithm and the canonical ensemble is maintained using a Berendsen thermostat. The simulations are carried out for nearly 5 ps after an equilibration of 5 ps.[S4]
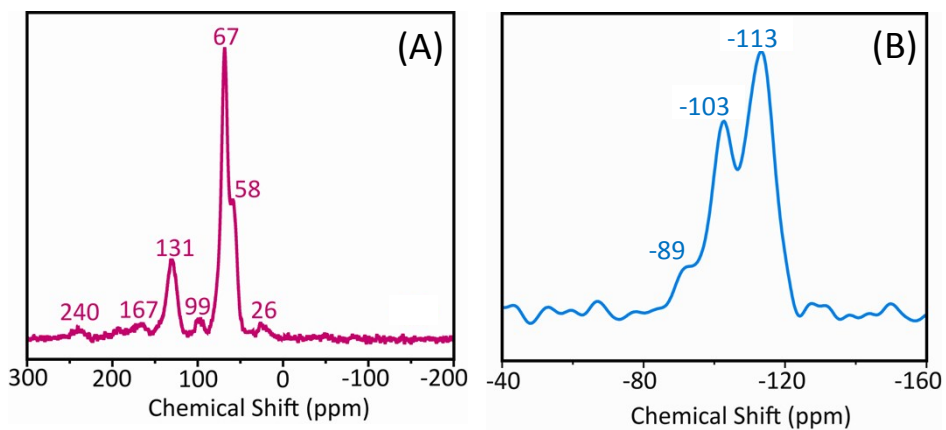
2. Supplementary Figures

Fig. S1: (A) Solid state ^{13}C MAS NMR of GO and (B) Solid state ^{29}Si MAS NMR of SGO nanohybrid
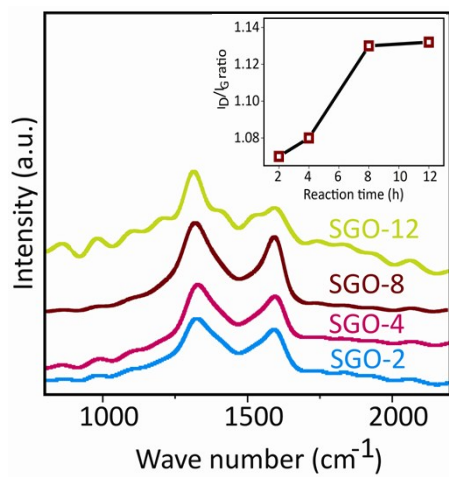

Fig. S2: Raman spectra of SGO nanohybrid at different time intervals during reaction; 2h, 4h, 8h and 12 h and inset shows the corresponding variation in the I_D/I_G ratio of above mention samples
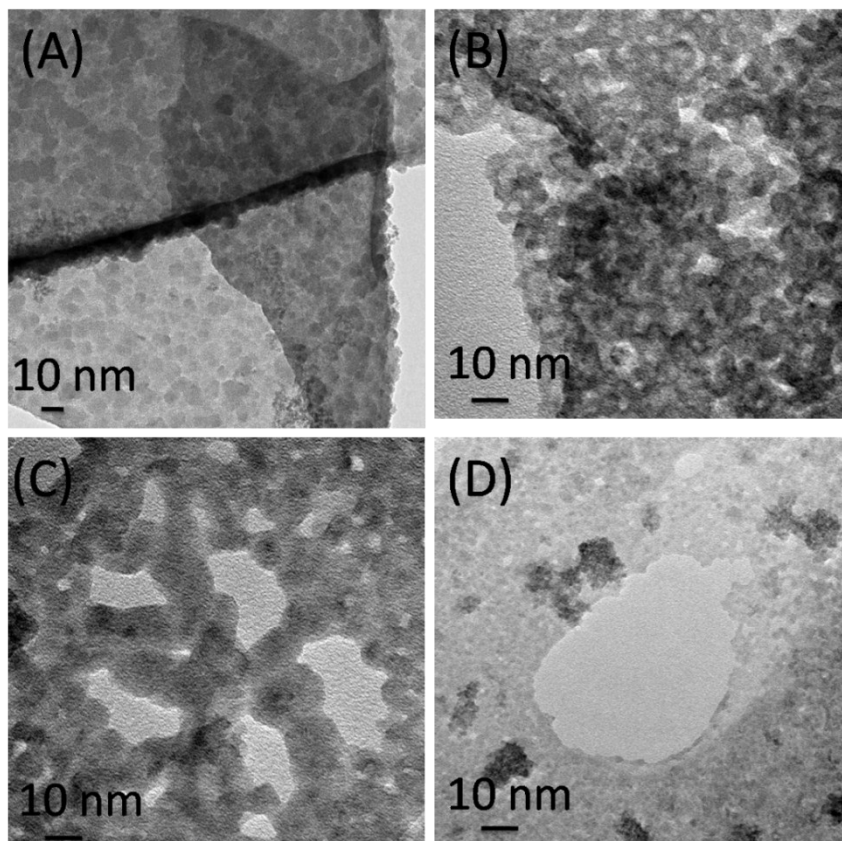
Fig. S3: TEM images showing various stages of hole formation and enlargement over the treatment (average diameter starting from ~ 5 nm to ~ 150 nm)
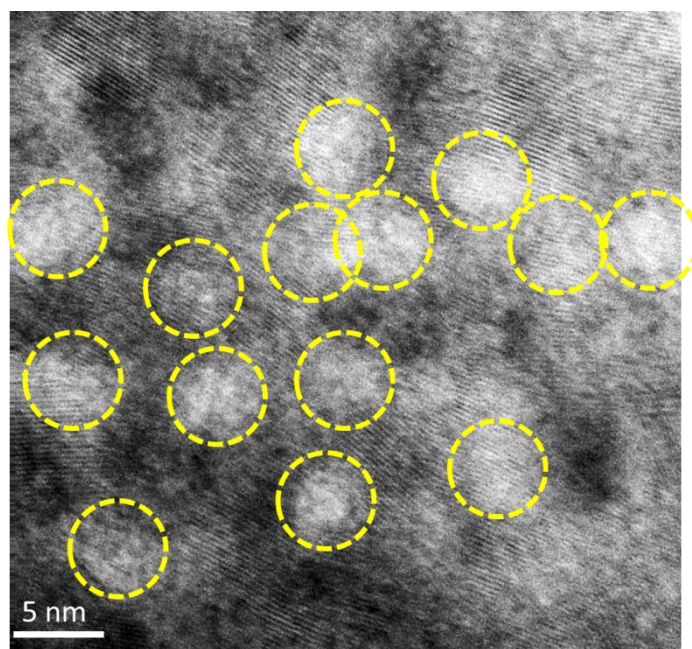

Fig. S4: High resolution TEM image showing the lattice fringes of carbon sheets and the yellow circles mark the perforations with an average diameter of ~ 5 nm during the early stages of alkali treatment
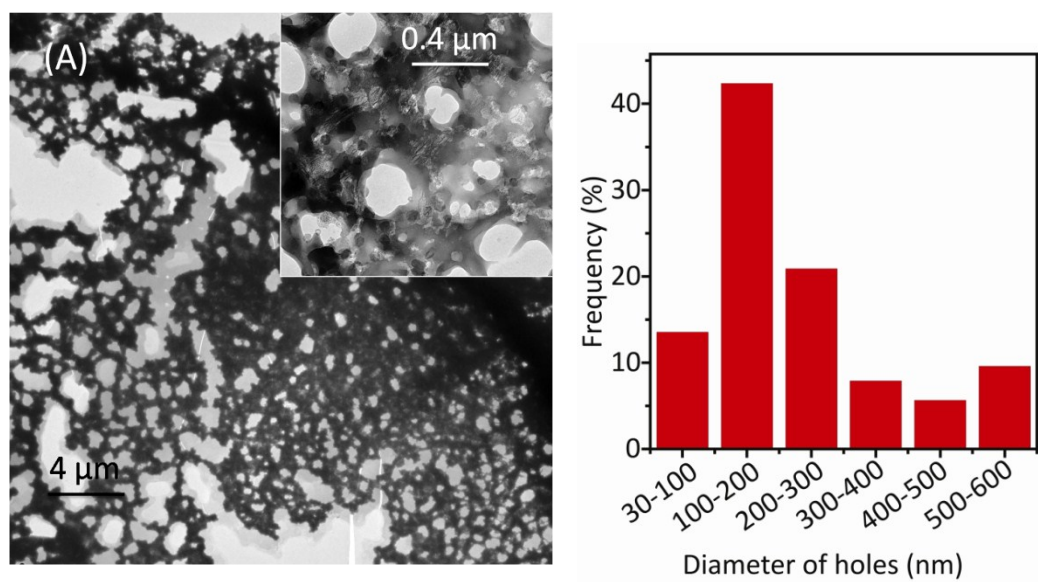
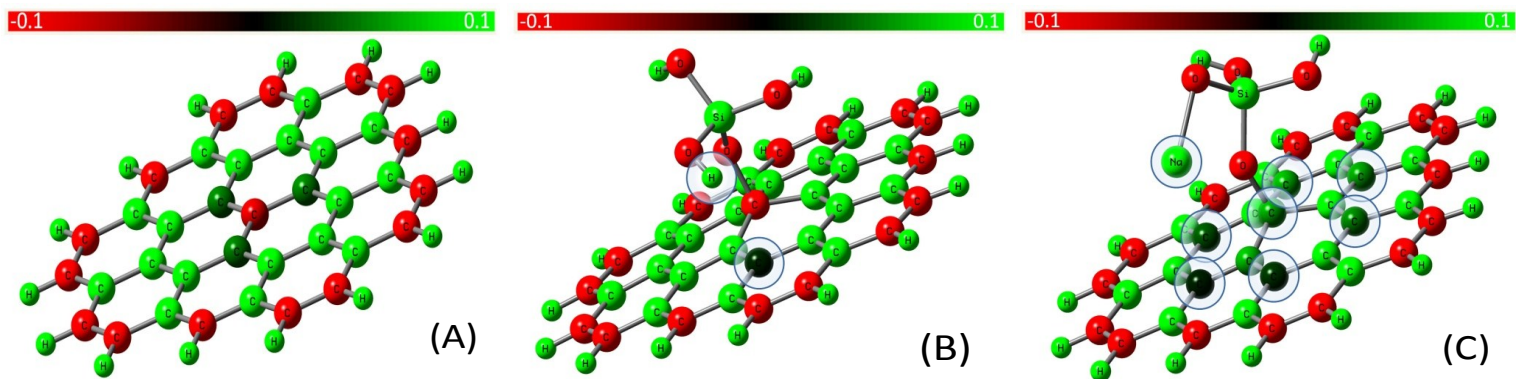**Fig. S5**: TEM Images and pore size distribution histogram of hGO

Fig. S6: Optimized models viz., (A) Gr-12R, (B) Gr-OSi(OH)$_3$ and (C) Gr-OSi(OH)$_2$ONa with the Mulliken charge distribution on atoms as seen in the color(scale bar range = -0.1 to +0.1; red to green)
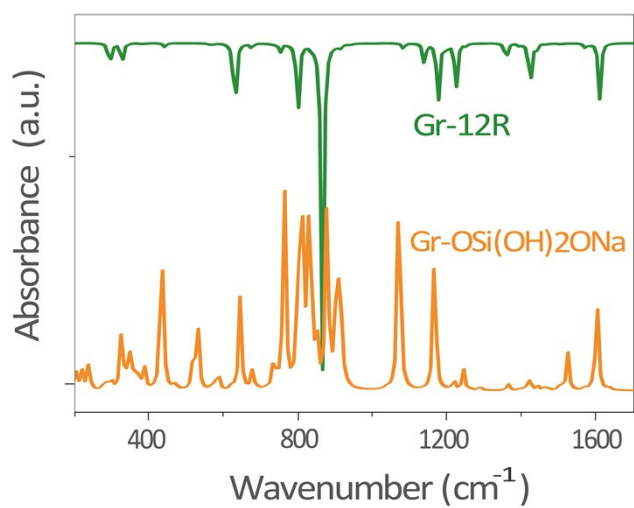
Fig. S7: Calculated IR spectra for the models of unfunctionalized and alkali treated functionalized rGO/graphene. The spectrum of Gr-12R is reversed to facilitate easier comparison of peaks.
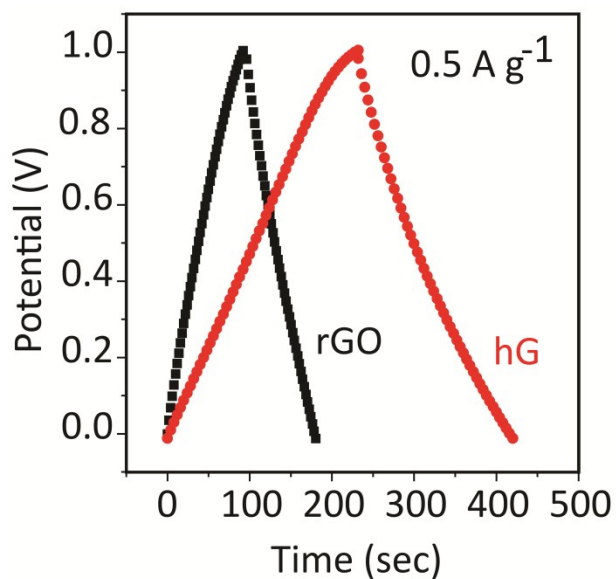

Fig. S8: Galvanostatic charge-discharge plots for hG and rGO at current density of 0.5 A g^{-1} in 1 M H$_2$SO$_4$

3. Supplementary Tables

Table ST1. Calculated vibrational frequencies of major basal vibrations and of the silicate functionality (cm^{-1})

Vibrational Mode	Gr-12R	Gr-OSi(OH)$_2$ONa
Basal breath	381 (in-plane)	374(in-plane)
In-plane stretch (C-C and C=C)	918 (sym I), 929 (assym I) 1049, 1057 (assym II) 1356 (sym II), 1389 (assym III)	914 (sym I), 921 (assym I) 1032, 1046(assym II) 1326 (sym II), 1355 (assym III)
C-O-Si bend	Not present	432
Si-O stretch	Not present	759
C-O stretch	Not present	800, 808
C-H stretch	3103 – 3107 3123 - 3125	3100 – 3107 3123 - 3126
O-H stretch	Not present	3709, 3724

Table ST2. Comparison of specific capacitance (C$_s$) of values porous carbon materials prepared using alkali treatment as reported in literature and hG prepared in present work.

Preparation method	Nature of electrode	Electrode configuration	Electrolyte	Current density (A g^{-1})	Cs (F g^{-1}).	Ref.
Hydrothermal carbonization of GO-polymer / biomass composite/ KOH activation	Porous 3D graphene	2	1M TEABF$_4$ / AN	1	202	S5
Polyacrylonitrile with KOH 700˚C	N-doped porous carbon	3	6 M KOH	1	189	S6
GO with melamine at 700 ˚C / KOH at 700 ˚C	Activated N-doped graphene	3	1 M KOH	0.1	132.4	S7
Graphene-activated carbon composite/ activation	Porous activated carbon on graphene	2	1 M KOH	0.1	122	S8
GO reduction by hydrazine hydrate	graphene	3	1 M H$_2$SO$_4$	0.5	90.9	Present work
Exfoliated graphene by silica/ NaOH at 25 ˚C	Holey graphene	3	1M H$_2$SO$_4$	0.5	250	Present work

Table ST3. Comparison of Rhodamine B dye adsorption capacities (Q_e) with various C based adsorbents reported in literature

S No.	Materials	Time (h)	Adsorption Capacity (mg g^{-1})	Ref
1	Porous graphene oxid-polyethylenimine composite	3	25	S9
2	O-Carbox-ymethyl chitosan-N-lauryl	1	38.5	S10
3	Rhizopusoryzae biomass	24	39.0	S11
4	Magnetically separable porous graphite		73	S12
5	Holey graphene	1	58.8	Present work

5. Supplementary References

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