

Supporting Information

Stimulating Electrocatalytic Oxygen Reduction Activity on Nitrogen doped Graphene through Noncovalent Molecular Functionalisation

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Synthesis of Graphene Oxide (GO): Graphene oxide (GO) was synthesized by a modified Hummer's method.^{1,2} 1 g of graphite flakes (Sigma-Aldrich) was grounded with 20 g of NaCl (Himedia) in a mortar pastel for 30 minutes. The excess NaCl was washed by rinsing repeatedly with water through vacuum-filtration. The above washed graphite flakes were dried in oven for 30 minutes at 70 °C. 23 ml of 36N H₂SO₄ (Rankem) was added to the dried graphite flakes in a 250 ml round bottom flask and stirred for 24 hours at room temperature. Then the temperature was raised to 40°C and 100 mg of NaNO₃ (Himedia) was dissolved in the solution. This step is followed by slow addition of 500 mg of KMnO₄ (Himedia) into the reaction mixture, keeping the reaction temperature below 45°C. Subsequently, 3 ml of water was added to the flask, followed by another 3 ml after 5 minutes. After next 5 minutes, 40 ml of water was added slowly to it. After 15 minutes the flask was removed from the oil bath and 140 ml of H₂O and 10 ml of 30% H₂O₂ were added. Then the flask with the reaction mixture was stirred at room temperature for 10 minutes. Then reaction mixtures were washed by centrifugation with 5% HCl and then further with excess of water. The final precipitate was dispersed in 100 ml of water and ultrasonicated for 30 minutes. Graphite particles in the dispersion were separated by centrifugation at 5000 rpm for 5 minutes and a brown homogeneous supernatant was collected. Then pure GO was collected from the above supernatant solution by centrifugation at 15000 rpm for 30 minutes and re-dispersed in 100 ml of ethanol (~2 mg/ml).

Synthesis of rGO, NrGO, PB-rGO, PB-NrGO & BA-NrGO: Reduced GO (rGO) was prepared by simple polyol reduction method, in which 5 ml of GO dispersion (2 mg/ml in ethanol) was added to 20 ml of 1, 4-Butandiol (Himedia) in a round bottom flask. Then the solution was heated in oil bath to 140⁰C with constant stirring. The colour of the dispersion gradually changes from brown to black showing reduction of GO to rGO. The reaction was allowed to continue for 4 hours and then the solution was brought to room temperature. The resulting rGO was collected by centrifugation and further washed with excess amount of water followed by subsequent washing in ethanol and acetone. For synthesis of NrGO 5ml of 30% NH₄OH was added to the above mentioned reaction mixture and the same method as discussed for rGO was followed for the reaction and purification.

To prepare PB-rGO, 5 ml of GO dispersion (2mg/ml in ethanol), 25 mg of 1-Pyrenebutyric acid (Sigma-Aldrich), 16 mg of NaOH (Rankem) were added to 30 ml of 1,4-Butanediol (Himedia) in a round bottom flask and ultrasonicated for 15 minutes. Then the solution was heated in oil bath to 140⁰C for 4hr with constant stirring. Similar purification method was followed as discussed for rGO.

To prepare PB-NrGO, 5 ml of GO dispersion (2mg/ml in ethanol), 5ml NH₄OH (30% solution), 25mg of 1-Pyrenebutyric acid (Fisher scientific), 16 mg of NaOH (Rankem) were added to 30 ml of 1, 4-Butanediol (Himedia) in a round bottom flask and ultrasonicated for 15 minutes. Then the solution was heated in oil bath to 140⁰C for 4hr with constant stirring. Similar purification method was followed as discussed for rGO.

In a typical reaction to prepare BA-NrGO, 10 mg of GO dispersion, Benzoic acid (0.2 mmol), NaOH (0.4 mmol) and 5 ml 30% NH₄OH solution was thoroughly mixed in 30 ml of 1,4-butanediol and reaction was carried out at 140⁰C for 4 hr. Similar purification method was followed as discussed for rGO.

Electrode Preparation:

For electrochemical studies homogeneous ink of all the catalysts were prepared by a single procedure. About 5mg of the catalyst was added to 5ml of 3:2 (v/v) water/isopropanol mixtures, followed by addition of 25 µl of 5wt% Nafion solution (Sigma-Aldrich) as binder. Then the solution was sonicated for 15 minutes to achieve homogeneous ink. For electrode preparation a 3 mm diameter glassy carbon electrode (GCE) was repeatedly polished with

alumina powder (size 0.05 μm) and washed with distilled water, then dried in N_2 flow. About 12 μl of catalyst ink ($\sim 170 \mu\text{g}$ of catalyst/ cm^2) was dropped onto the GCE using micropipette and allowed to dry for 3 hours in desiccator before electrochemical analysis.

Electrochemical Measurements:

Cyclic voltammetry (CV): The cv measurements were performed by a computer-controlled Autolab potentiostat/galvanostat (PGSTAT204, The Netherlands) with a three-electrode cell system having Platinum wire as counter electrode, catalyst coated GCE as working electrode and Ag/AgCl (3M KCl) as reference electrode. All the measurements were conducted at room temperature in 0.1M KOH solution. The working electrode was cathodically scanned in electrolyte saturated with N_2 between 1.1 V to 0.1 V at a scan rate of 100 mVs^{-1} for at least 5 times before data were recorded. For ORR studies, the electrolyte was initially bubbled with O_2 for 15 minutes and during the CV experiments a continuous flow of O_2 was maintained over the electrolyte.

Rotating disk electrode (RDE): The RDE measurements were carried using an Autolab potentiostat/galvanostat (PGSTAT204, The Netherlands) in combination with a rotating disc electrode rotator (Autolab RDE-2, The Netherlands) and a speed control unit. A glassy carbon disc electrode of 3mm diameter from Metroham Instrument Co. was employed in the RDE measurements. The same catalyst inks with constant mass loading were used to conduct RDE measurements as in case of CV. The three-electrode cell system was used having Platinum wire as counter electrode, catalyst coated glassy carbon disk electrode as working electrode and Ag/AgCl (3M KCl) as reference electrode. All the ORR measurements were conducted at room temperature in oxygen saturated 0.1M KOH solution.

The observed disk current density and rotation speed in RDE measurements is related by Koutecky–Levich equation given as:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

Where, $B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6}$ and $J_K = nFkC_0$

J is the disc current density, J_K and J_L are the kinetic- and diffusion-limiting current densities, ω is the angular velocity, n is electron transfer number per O_2 molecule, F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$), C_0 is the bulk concentration of O_2 ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$), D_0

is the diffusion coefficient of O_2 in 0.1 M KOH solution ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν is the kinematic viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$), and k is the electron-transfer rate constant. The constant 0.62 is adopted when the rotation speed is expressed in radian s^{-1} . Koutecky–Levich plots (J^{-1} vs. $\omega^{-1/2}$) were analysed at various electrode potentials. The slopes of their best linear fit lines were used to calculate the number of electrons transferred (n) on the basis of the Koutecky-Levich equation.²

Chronoamperometric measurements: For all the Chronoamperometric measurements a three-electrode cell system having a Platinum weir as counter electrode, catalyst coated glassy carbon disc as working electrode and Ag/AgCl (3M KCl) as reference electrode was taken and the electrode preparation was similar to that of RDE measurements. For all the measurements the working electrode was rotated at 1000 rpm and at a fixed potential of 0.65 V in O_2 saturated 0.1 M KOH electrolyte.

Reversible Hydrogen Electrode (RHE) calibration: In all electrochemical measurements, we used Ag/AgCl (3M KCl) as the reference electrode. It was calibrated with respect to RHE. The calibration was performed in the high purity H_2 -saturated 0.1M KOH electrolyte with a Platinum wire as the working electrode.³ Cyclic Voltammetry was run at a scan rate of 1 mV s^{-1} , and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reaction. The result is given in figure S1.

$$E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.92 \text{ V}$$

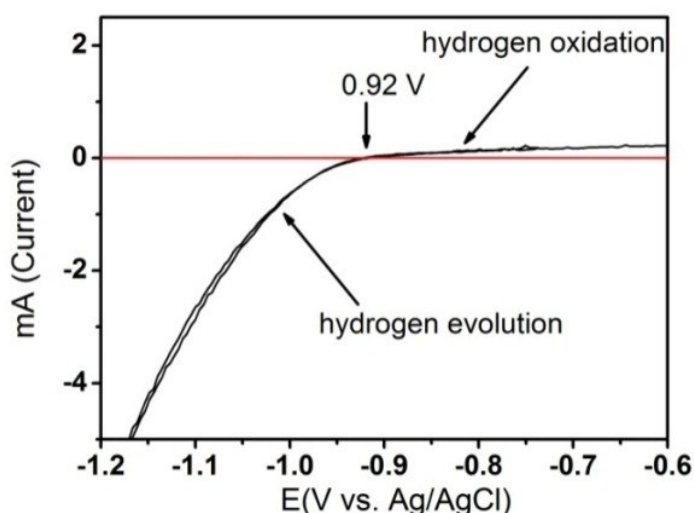


Figure S1: The RHE calibration curve

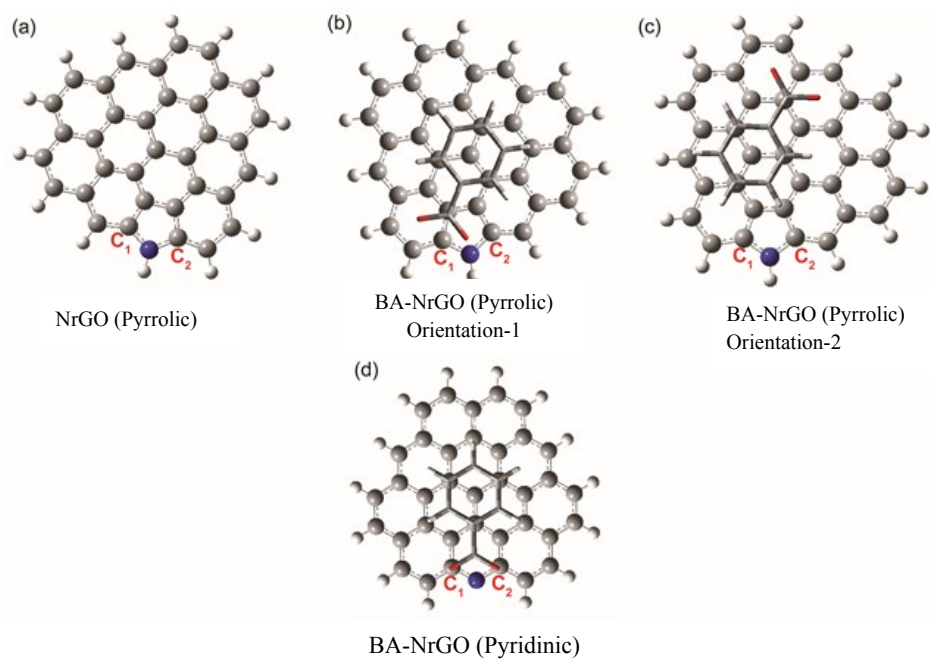


Figure S2: DFT studies on NrGO (pyrrolic) and BA-NrGO (pyrrolic) has been performed to investigate the charge density on carbon atoms adjacent to N-atom before and after functionalisation.

Table-S1

Graphene Samples	Charge Density (Mulliken Scale)	
	C ₁	C ₂
NrGO (Pyrrolic)	0.31	0.33
BA-NrGO (Pyrrolic)-1	0.36	0.37
BA-NrGO (Pyrrolic)-2	0.29	0.31
BA-NrGO (Pyridinic)-2	0.26	0.26

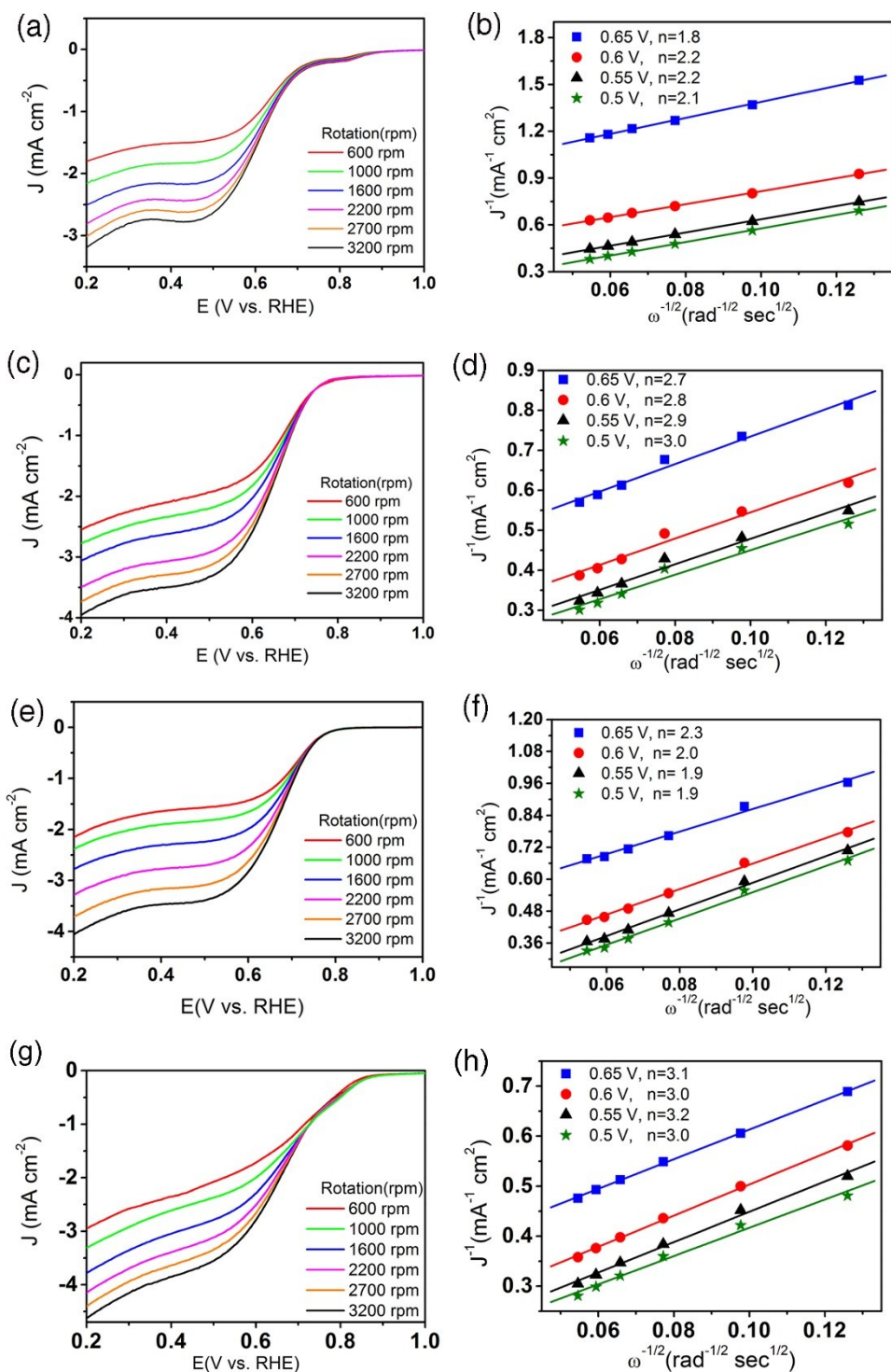


Figure S3: The oxygen reduction RDE curves on rGO, PB-rGO, NrGO and PB-NrGO electrodes at different rotation speeds are shown in a, c, e and g. The corresponding Koutecky-Levich (K-L) plots with electron transfer number (n) at different potentials shown in b, d, f and h respectively.

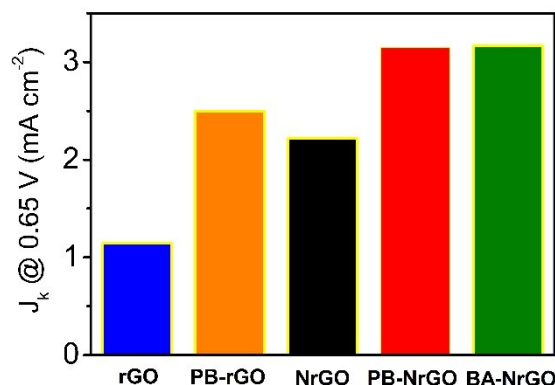


Figure S4: Electrochemical activity given as the fully diffusion-limited current density (J_k) at 0.65 V for rGO, NrGO, PB-rGO, PB-NrGO and BA-NrGO.

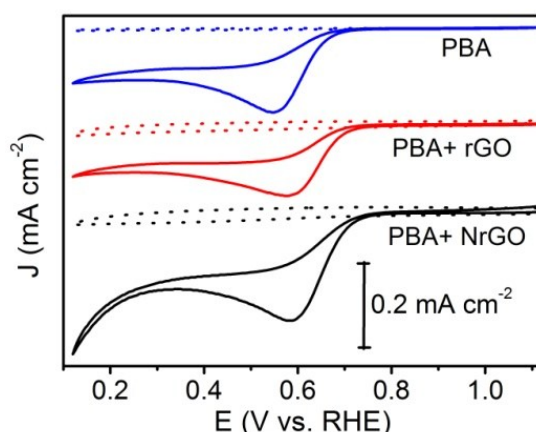


Figure S5: CV curves of PBA, mixture of PBA & rGO (PBA+rGO), mixture of PBA & NrGO (PBA+NrGO) in oxygen (solid) and nitrogen (dash) saturated 0.1M KOH.

The CV measurements on PBA alone do not show any significant ORR activity. It clearly reveals the synergistic ORR catalytic activity in PB functionalized rGO and NrGO. CV measurements were also done on physical mixture of PBA with rGO or NrGO. The onset potential and peak potential on these mixed electrodes for oxygen reduction is almost same as that of rGO and NrGO. It indicates that the presently employed polyol based method effectively establish intimate π - π interaction of PB on graphene, which is instrumental in enhanced ORR activity.

UV-VIS Spectrum: UV-Vis absorbance spectra of PB-rGO, PB-NrGO and pure PBA were obtained using G9821A Cary UV-Vis spectrophotometer with a quartz cuvette having path length of 1 cm and ethanol as solvent. PBA molecule in ethanol showed characteristic uv-visible absorption peaks at 242, 264, 275, 325 and 342 nm. Similar absorption peaks were also observed for PB-rGO, PB-NrGO which confirms the successful functionalization of PBA on rGO and NrGO respectively.

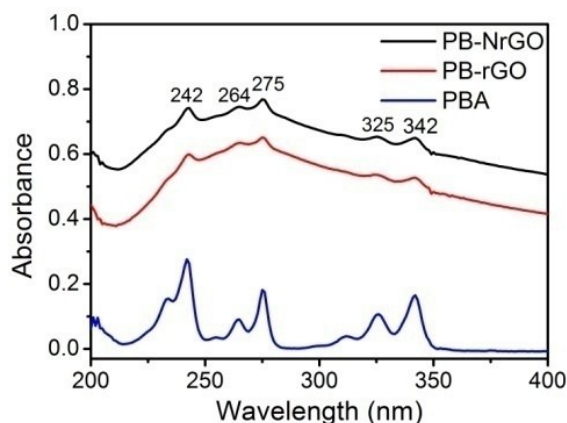


Figure S6: Shows the UV-Vis spectra of PBA (1.25 mg L^{-1}), PBA-rGO (12.5 mg L^{-1}), and PBA-NrGO (150 mg L^{-1}) in ethanol.

Fluorescence spectroscopic data:

The fluorescence spectra were recorded using G9800A Cary Eclipse Fluorescence Spectrophotometer for pure PBA, PB-rGO and PB-NrGO in ethanol. The excitation wavelength was set at 342 nm and emission was measured in a range of 352-550 nm. For all fluorescence measurements a glass cuvette having path length of 1 cm is used. In fluorescence spectra characteristic emission bands at about 376, 396 and 416 nm was observed for PBA, which is extensively quenched in PB-rGO and PB-NrGO, which suggest a charge transfer process occurring between PB and rGO or NrGO.⁴

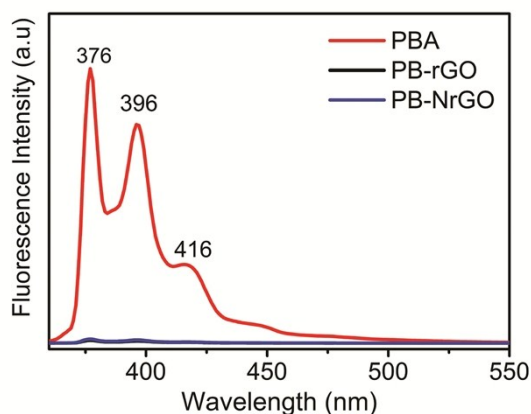


Figure S7: The fluorescence spectra of PBA (1.25 mg L^{-1}), PB-rGO (150 mg L^{-1}), and PB NrGO (150 mg L^{-1}) in ethanol.

Raman Analysis and results:

The vibrational modes of the graphene samples, rGO and NrGO, before and after functionalization with PB, have been studied using Horiba-T64000 micro-Raman spectrometer coupled with Peltier cooled CCD detector with spectral resolution as 0.8 cm⁻¹. A laser line of wavelength, 514 nm and power, 20 mW from Argon-ion source focused to a 5 μm circular spot, has been used as an excitation line for the measurements. The signal has been collected using the back-scattering geometry. The peak position of G-band, FWHM and intensity ration between 2D-band and G-band are listed in table below.

Samples	G-band	FWHM of G-band	I _{2D} /I _G
rGO	1591.43	60.19	0.44
PB-rGO	1592.41	56.57	0.13
NrGO	1581.43	48.55	0.15
PB-NrGO	1589.32	54.88	0.23
BA-NrGO	1575.69	35.44	0.36

Table-S2: The G-Band position, FWHM of G band, Intensity ratio between 2D and G band Raman modes of rGO, NrGO and PB/BA functionalized NrGO samples.

XPS Analysis: The X-ray photoelectron spectra (XPS) were recorded on VG Microtech Multilab ESCA-2000 XPS system using Mg-Kα radiation exciting source to investigate different types of nitrogen functionalities in NrGO, PB-NrGO and BA-NrGO samples. The samples were loaded on a glass slide and were set in XPS chamber.

Catalysts	Total 'N' at%	Pyridinic N %	Pyrrolic N %	Graphitic N %	Pyridinic Oxide N %
NrGO	4.1	9	46.5	24.6	19.5
PB-NrGO	2.7	42.8	27.7	4.1	25.3
BA-NrGO	6.9	32.7	45.94	21.34	0

Table-S3: The total at% of nitrogen (N) and concentration of different types of N functionalities in NrGO, PB-NrGO and BA-NrGO derived from de-convoluted N 1s XPS spectra.

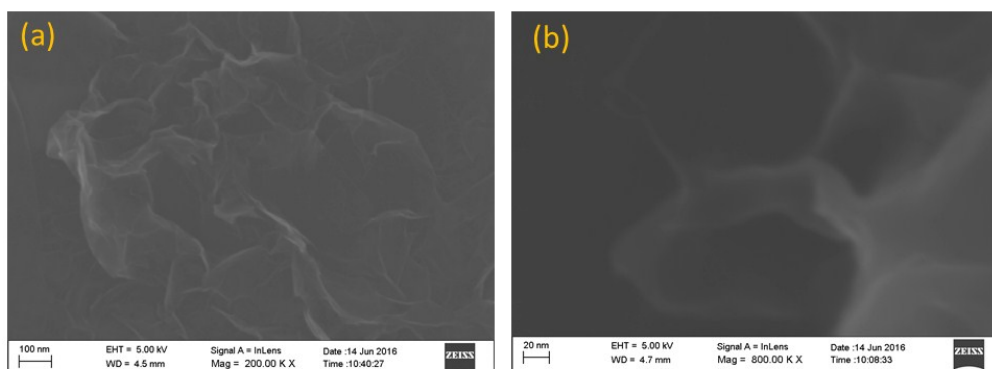


Figure-S8: SEM images of (a) NrGO and (b) BA-NrGO.

The SEM studies show that BA functionalization does not affect the morphology.

References:

1. W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* **1958**, 80, 1339.
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