Supporting Information

Plasma-assisted Simultaneous Reduction and Nitrogen Doping of Graphene Oxide Nanosheets

Nanjundan Ashok Kumar,[‡§] *Hugo Nolan,*[‡§†] *Niall McEvoy,*[‡ §] *Ehsan Rezvani,*[§†] *Richard L. Doyle,*[†] *Michael E. G. Lyons*[†] *and Georg S. Duesberg**[§†]

[§]*Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN),*
[†]*School of Chemistry, Trinity College Dublin, Ireland*

* Address correspondence to: Duesberg@tcd.ie

Experimental Methods and Materials:

Materials and Reagents

Flaky graphite powder was obtained from Aldrich. Sulfuric acid (95-97%), hydrogen peroxide (30 wt. %), potassium permanganate, sodium nitrate, were obtained from commercial sources and used as received. All other solvents were used as received unless otherwise stated.

Material Synthesis:

Synthesis of graphite oxide (GO): Initially graphite oxide (GO) was prepared by a modified Hummers and Offeman's method as described previously.[1] Briefly, graphite (3g) was mixed with 1.5 g of NaNO3 and 75 mL of concentrated H_2SO_4. The mixture was cooled down to 0 °C in an ice bath and stirred for 2h. Then, 9 g of $KMNO_4$ was added slowly (temperature was maintained at <5 °C throughout the mixing), and continuously stirred for another hour. The cooling bath was then removed and the mixture was brought to room temperature. To this, ~100 mL of distilled water was added (gas evolved) and the temperature was increased to 90 °C in an oil bath. After reaching 90 °C, 300 mL of water was added again and continuously stirred for another hour and a half. The color of the mixture turned to mud brown. This mixture was then treated with 30 mL of 30% H_2O_2 and ~3 liters of hot water was added and diluted. The mixture was further washed with excess water until the pH of the filtrate was nearly neutral. Finally, the mixture was vacuum filtered and dried under reduced pressure overnight to yield GO.

Plasma Reduction and doping:

Plasma treatments were performed using a R^3T TWR-2000T microwave radical generator at room temperature. Experimental conditions involved an output power of 500W, a gas mixture of H_2 and NH_3 with gas flow rates of 50 sccm each, with an exposure time of 1 hour and a pressure of 1 Torr. Samples were positioned ~30 cm downstream from the plasma source. In this position the plasma generated ions were energetically relaxed upon arrival at the sample and thus the plasma could be considered remote, minimising surface damage.

Characterisation:

The morphology and microstructures of the samples were investigated by High resolution transmission electron microscopic (HR-TEM) using a FEI Titan 80–300 at an acceleration voltage of 300 kV and a high resolution (<1nm) Field Emission SEM with a Gemini® column was used for Scanning Electron Microscopy. For the preparation of TEM samples, 25 mg of material was dispersed in deionised water (50 mL) and exposed to mild sonication. Microlitre volumes of this dispersion where then dropped on Lacey carbon grids and dried in air before analysis. The chemical composition was analysed by XPS with an Omicron ESCA system with an EA 125 Analyser and XM1000MK II monochromatic x-ray source. The Al Kα x-ray line was used with a spot size of ~2 mm. The analyser was operated with pass energy (Ep) of 50 eV. For wide scans a step size of 0.2 eV was employed, while fine scans had a step size of 0.1 eV. For these measurements, the samples were mounted by pressing mg amounts of the powder into indium foil with a clean glass slide. For the insulating GO samples, charge neutralisation was achieved using an Omicron CN 10 charge neutraliser. The crystallographic structures of the materials were determined by a wide-angle X-ray diffraction (WAXD) system (Philips diffractometer) equipped with a Ni-filtered Cu Kα radiation (40 kV, 100 mA, λ=0.15418 nm). Changes in the surface chemical bonding were recorded by Fourier transformed infrared spectrophotometry (FT-IR, Perkin-Elmer Spectrum GX, s100, USA) in the frequency range of 4000-400 cm^{-1}. Raman spectra were obtained using a Witec Alpha 300R with an excitation wavelength of 532 nm. Low power (< 1 mW) was used to avoid sample damage.

Transmission Electron Microscopy:

TEM analysis with associated Selected Area Electron Diffraction (SAED) patterns showed some flake to flake variation of the N-doped graphene. Fig. S3 shows three flakes of N-doped graphene as viewed by TEM and their associated SAED patterns. All three samples show discrete diffraction spots embedded in a diffuse diffraction ring indicative of few-layered graphitic materials with differing levels of crystalline quality. This clearly illustrates that the plasma treatment partially restores the graphitic lattice. Crystalline defects observed in the SAED pattern are attributed to the functionalisation of the N-doped graphene flakes.

Electrochemistry:

The electrochemical properties of the RGO material were investigated using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) using the ferri/ferro-cyanide redox probe which was thoroughly degassed with N_2 gas prior to measurements being taken. Electrochemical analysis was performed using a Gamry Ref 600 potentiostat in a three electrode configuration. Platinum wire and Ag/AgCl were used as counter and reference electrodes, respectively. Electrodes were prepared by dispersing mg quantities of N-doped graphene material in DMF followed by sonication and drop-casting µl volumes of this dispersion on to films of as-grown Pyrolytic carbon (PyC) and dried at 80 °C. The wafer-based PyC films were mounted into a custom built holder whereby a nitrile O ring defined the region of the electrode exposed to the electrolyte (radius = 1.5 mm).

Electrocatalytic Activity Evaluation:

The ORR activity of the nitrogen-doped graphene samples was evaluated using CV and a rotating ring disk electrode (RRDE) system (Pine Research Instrumentation Modulated Speed Rotator) in conjunction with an Autolab N-series potentiostat in 1 M NaOH electrolyte. A platinum wire and Ag/AgCl were used as a counter and reference electrodes respectively.

CV was carried out first in N_2-saturated electrolyte and then in O_2-saturated electrolyte to establish the presence redox behavior in the O_2-saturated electrolyte. Linear Sweep Voltammetry (LSV) was then carried out at various electrode rotation speeds in the potential region in which the reduction peak was observed. The potential of the N-doped graphene disk electrode was varied from 0 to -0.6 V at a potential sweep of 20 mV s^{-1}; the Pt RRDE potential was set to 0.45 V, in order to detect H_2O_2. For ORR measurements, a glassy carbon (GC) electrode was used as a support for the N-doped graphene. A dispersion of N-doped graphene in DMF was prepared with a µl amount of Nafion binder to improve the mechanical robustness of the deposited film. This was then drop-coated on the GC electrode and allowed to air dry before mounting in the RDE apparatus.

References:

1. Kumar, N. A.; Choi, H.-J.; Shin, Y. R.; Chang, D. W.; Dai, L.; Baek, J.-B., Polyaniline-Grafted Reduced Graphene Oxide for Efficient Electrochemical Supercapacitors. *ACS Nano* **2012,** *6* (2), 1715-1723.

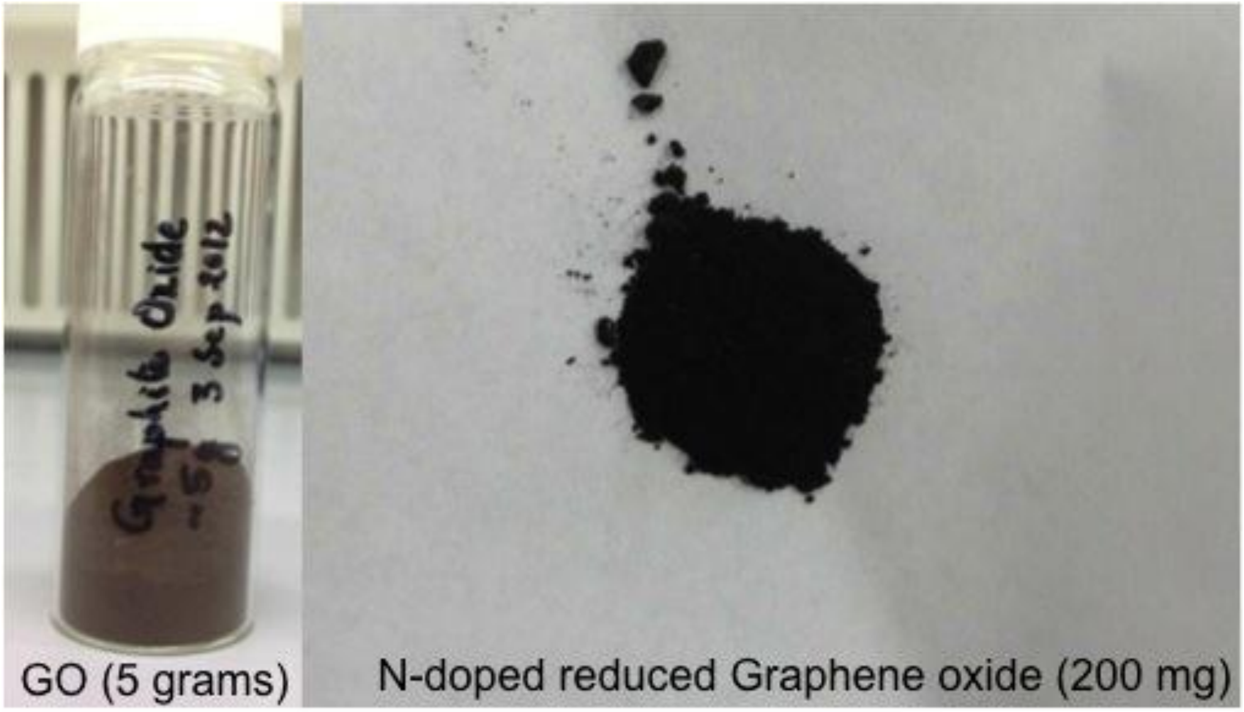

Figure S1. Digital images of (a) GO (5 grams) and (b) N-doped reduced GO. (Volume expansion and color change due to reduction and doping is represented through the above images)

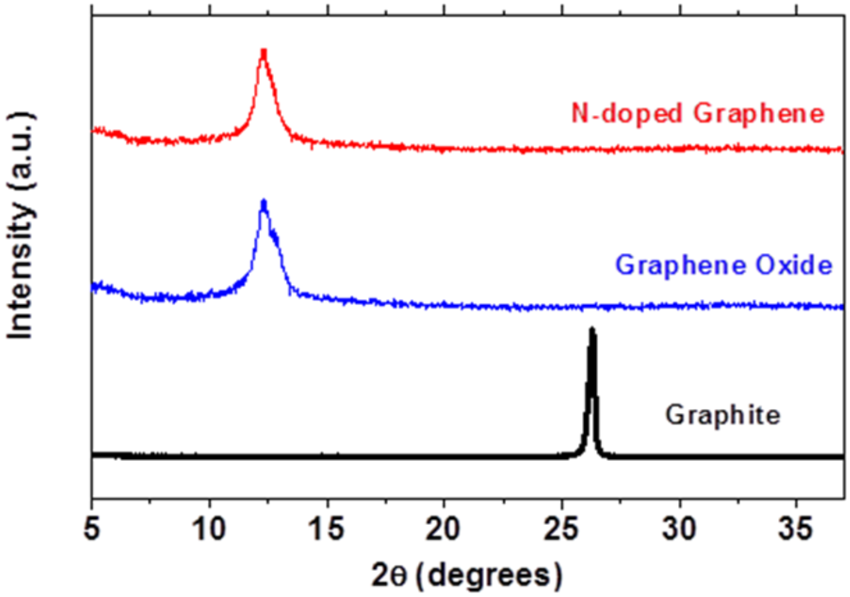

Figure S2. XRD data for graphite, graphene oxide and N-doped graphene.

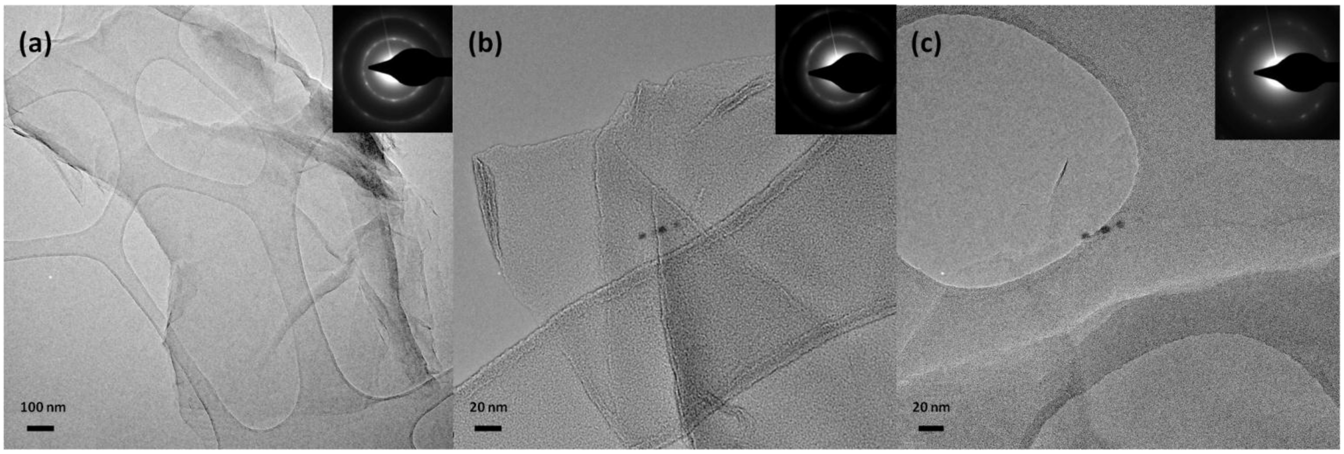

Figure S3. TEM images with associated SAED patterns illustrating the variation in graphitic crystallinity across several flakes.