Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2017

Electronic Supporting Information

Gram-scale production of nitrogen doped graphene using a 1,3-dipolar organic precursor and their utilisation as stable, metal free oxygen evolution reaction catalysts

Mustafa K Bayazit,[a, b]* Savio J.A. Moniz[b]* and Karl S. Coleman[c]

[a] Department of Chemistry, Imperial College London, London SW7 2AZ, UK
[b] Department of Chemical Engineering, University College London, Torrington Place, London, WC1E 7JE, UK
[c] Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK

Experimental Section

Preparation of 3-phenyl-phthalazinium-1-olate and its carbonization to *N*-doped graphene nanosheets: All chemical were purchased from Sigma-Aldrich and used as-received. 3-Phenyl-phthalazinium-1-olate was prepared following a modified literature procedure.[1,2] In a typical procedure, phenylhydrazine (0.04 mol) in $CHCl_3$ (10 mL) and phthalic anhydride (0.04 mol) in $CHCl_3$ (100 mL) was stirred at 20 °C for 3 h. The formed anilinophthalamic acid was filtered off, air dried, and heated at 175 °C in a well-ventilated oven for 1 h with occasional mixing to give *N*-anilinophthalimide (yield~80%) as yellow powder. Resultant *N*-anilinophthalimide (0.01 mol) in THF (80 mL) was reduced by $NaBH_4$ (1.0 g, 0.2 mol) in THF (20 mL) in the presence of distilled water (5 mL) at 20 °C. After 2 h, the excess of $NaBH_4$ was decomposed with a large excess of acetone. The solution was stirred for 1 h more, filtered, and evaporated under vacuum. The oily residue was heated at 130-140 °C for 1 h to give a solid 3-Phenyl-phthalazinium-1-olate which was re-crystallized from ethanol (yield~70 %) and characterized by FTIR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy. The 1,3-dipolar compound (4 g) was placed in an alumina boat and annealed at 480 °C for 1.5 h in air for conversion to *N*-doped GNSs. Carbonized material was washed with ethanol repeatedly

until no coloured impurities were detected. The resultant *N*-doped GNSs were finally dried at 80 °C overnight.

Electrode preparation

Carbon paper and nickel foam were used as susbtrates. Nickel foam substrates were rinsed with 10% HCl prior to use. *N*-doped GNS (2 mg) in DMF (10 mL) was ultrasonicated for 3 hr. The supernatant after 30 min settling was decanted and added to a 1:1 water isopropanol mix (3 mL) containing 50 μL 5% Nafion perfluorinated resin. The mixture was sonicated for a further 30 min, then 1 mL of this solution was drop-cast directly onto the substrates. These were then dried at ambient temperature then heated at 150 °C in air for 2 hours. RuO_2 electrodes on Ni foam were synthesised using a modified literature procedure. Briefly, a 10mM solution of ruthenium chloride with 10% butanol was drop-cast onto a Ni foam substrate which was placed on a hotplate at 70 °C. Following evaporation of the liquid the samples were heated in air at 450 °C for 2 hours.[3]

Oxygen evolution reaction:

Oxygen evolution reaction (OER) measurements were conducted using a gas-tight single compartment three-electrode electrochemical cell (Adams-Schittenden Co, USA) linked to a potentiostat (Ivium technology). The samples, deposited on Ni foam, were attached to a stainless steel alligator clip (RS components) with the non-exposed area coated with ultra-resistant ATACS epoxy resin and used as the working electrodes (exposed area = 0.5 x 0.5 cm). Pt mesh and Ag/AgCl (3 M KCl) were used as counter electrode and reference electrode, respectively. The scan speed was 20 mV s^{-1} and the electrolyte was 1M KOH (pH 14) purged with argon gas for 1h.

Characterization. Raman spectra were recorded using a Jobin Yvon Horiba LabRAM spectrometer in a back-scattered confocal configuration using He/Ne (632.8 nm, 1.96 eV) laser excitation. All spectra were recorded on solid samples (using as-produced powder) over several

regions and were referenced to the silicon line at 520 cm^{-1}. X-ray diffraction (XRD) was carried out on a Bruker D8 Advance X-ray diffractometer (40 kV, 30 mA) with CuKα radiation (λ=1.54 Å) equipped with a PSD LynxEye silicon-strip detector. Materials were tested in powder form prepared from ethanol dispersions of as-produced N-doped GNSs. High-resolution XPS was performed using as-produced *N*-doped GNSs by a Thermo Scientific K-alpha photoelectron spectrometer with monochromatic Al-Kα radiation; peak positions were referenced to the C 1s line at 284.5 eV and the CasaXPS software was used for data processing. Transmission electron microscopy (TEM) was performed using JEOL-2010F coupled with an EDS detector (Oxford Instruments) instrument. Stable dispersion of *N*-doped GNSs was prepared by sonication in *N*-Methyl-2-pyrrolidone (NMP) using an ultrasonic bath (Ultrawave U50, 30-40 kHz) for 15 min. Produced dispersion was left a side for 30 min to remove big particulates. Supernatant was used for microscopy analysis. TEM samples were prepared from stable dispersions of as-produced *N*-doped GNSs by dropping onto carbon coated copper grids. Samples for AFM analysis were produced by drop deposition onto freshly cleaved mica. Samples were dried in air before imaging in tapping mode using a Digital Instruments Multimode AFM instrument with a Nanoscope IV controller. Infrared (FT-IR) spectra were recorded from as-produced *N*-doped GNSs using a Perkin-Elmer Spectrum 100 equipped with a Pike ATR fitted with a Ge crystal. TGA data were recorded on 1-3 mg of sample using a Perkin-Elmer Pyris I coupled to a Hiden HPR20 mass spectrometer. Data were recorded in both flowing Air (50 mL min^{-1}) and Helium at (50 mL min^{-1}) a ramp rate of 10 °C min^{-1} to 900 °C after being held at 120 °C for 30 min to remove any residual solvent. All graphs were obtained by OriginLab software (Origin9.1).

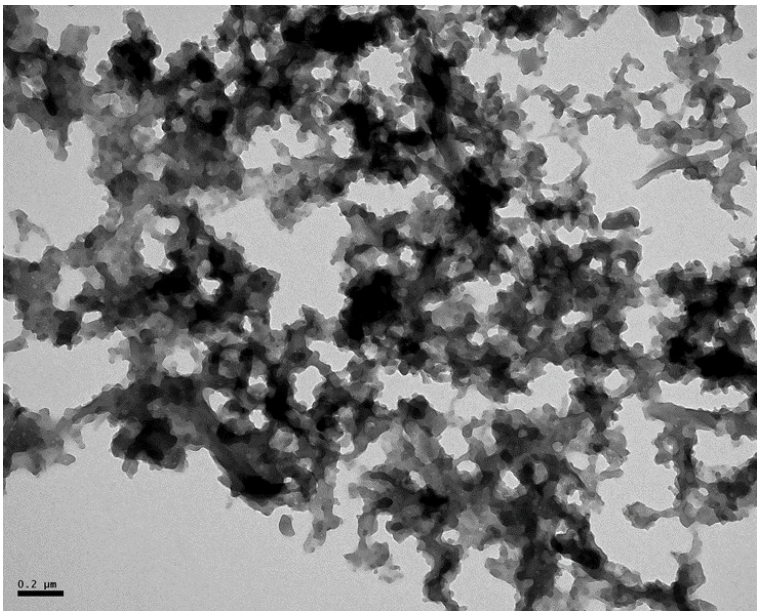

Figure S1 TEM image of *N*-doped GNS dispersed in NMP. Image shows the evidence of 3D-network like structure formation.

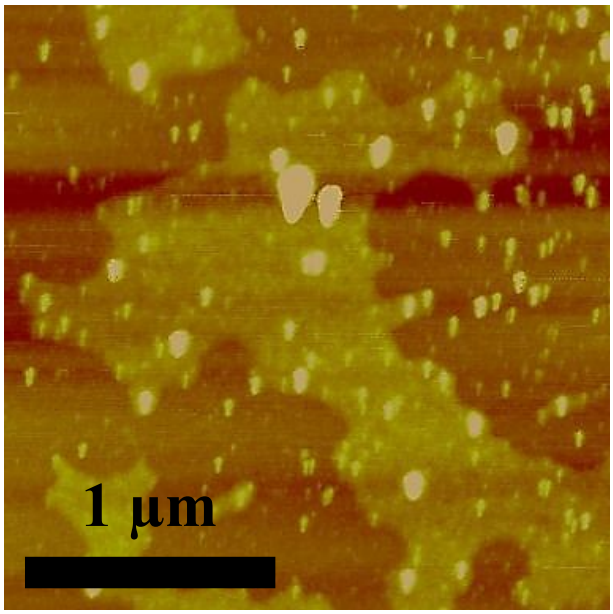

Figure S2 AFM image of *N*-doped GNS dispersed in NMP. Image shows a flake with lateral dimension of ~2.5 µm. It is also worth noting that there are larger (~100 nm) and smaller (10-20 nm) particulates that may be formed by sonication induced decomposition of *N*-doped GNSs.

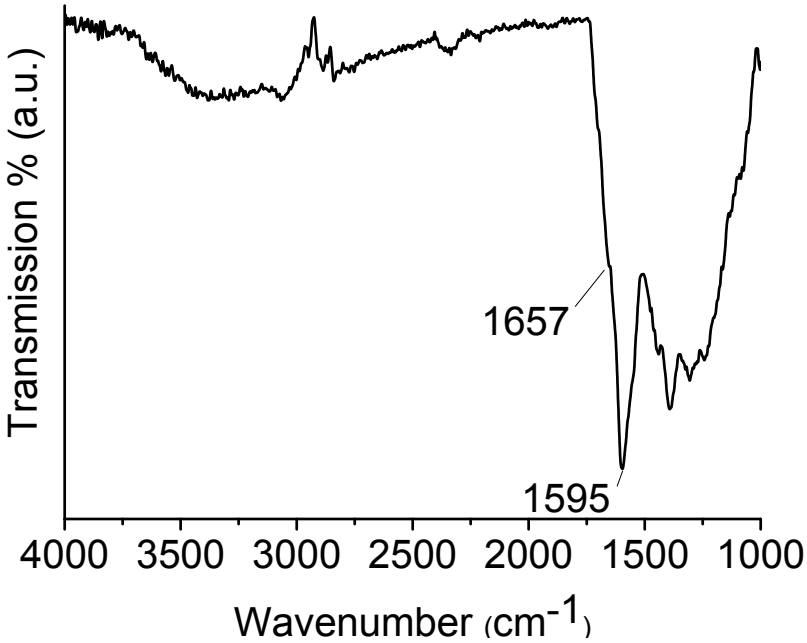

Figure S3 FTIR spectrum of as-produced *N*-doped GNS dispersed.

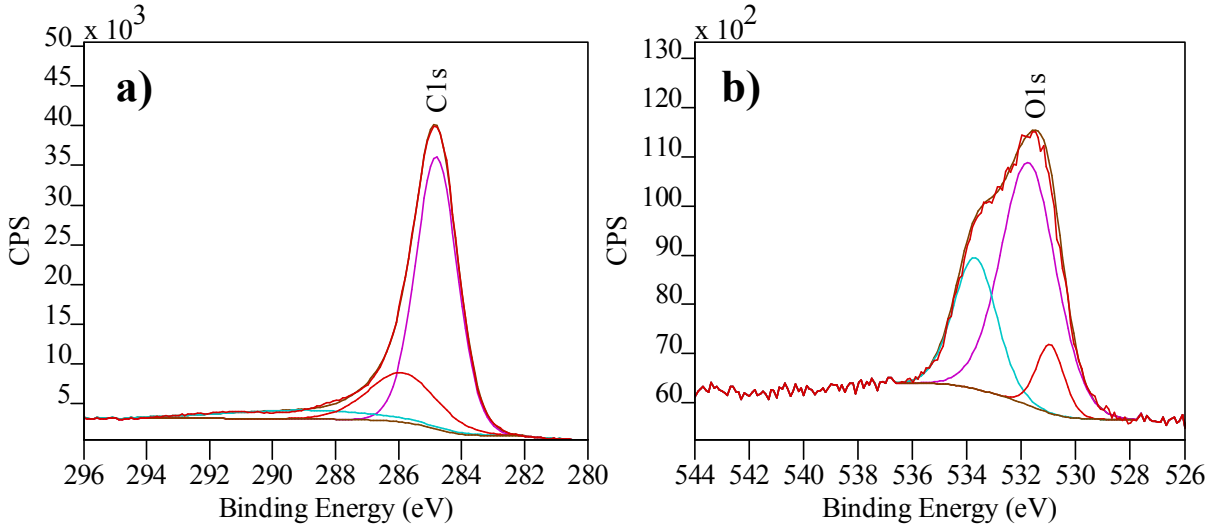

Figure S4 a) C 1s and **b)** O 1s XPS spectra of as-produced *N*-doped graphene.

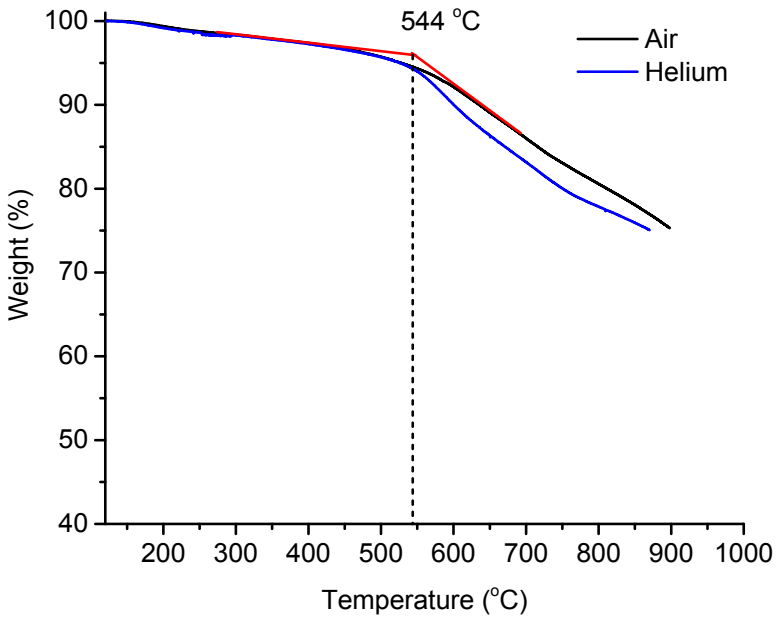

Figure S5 TGA trace of as-produced *N*-doped graphene recorded in air (black) and helium (blue). Red line shows the intersection point of tangent lines.

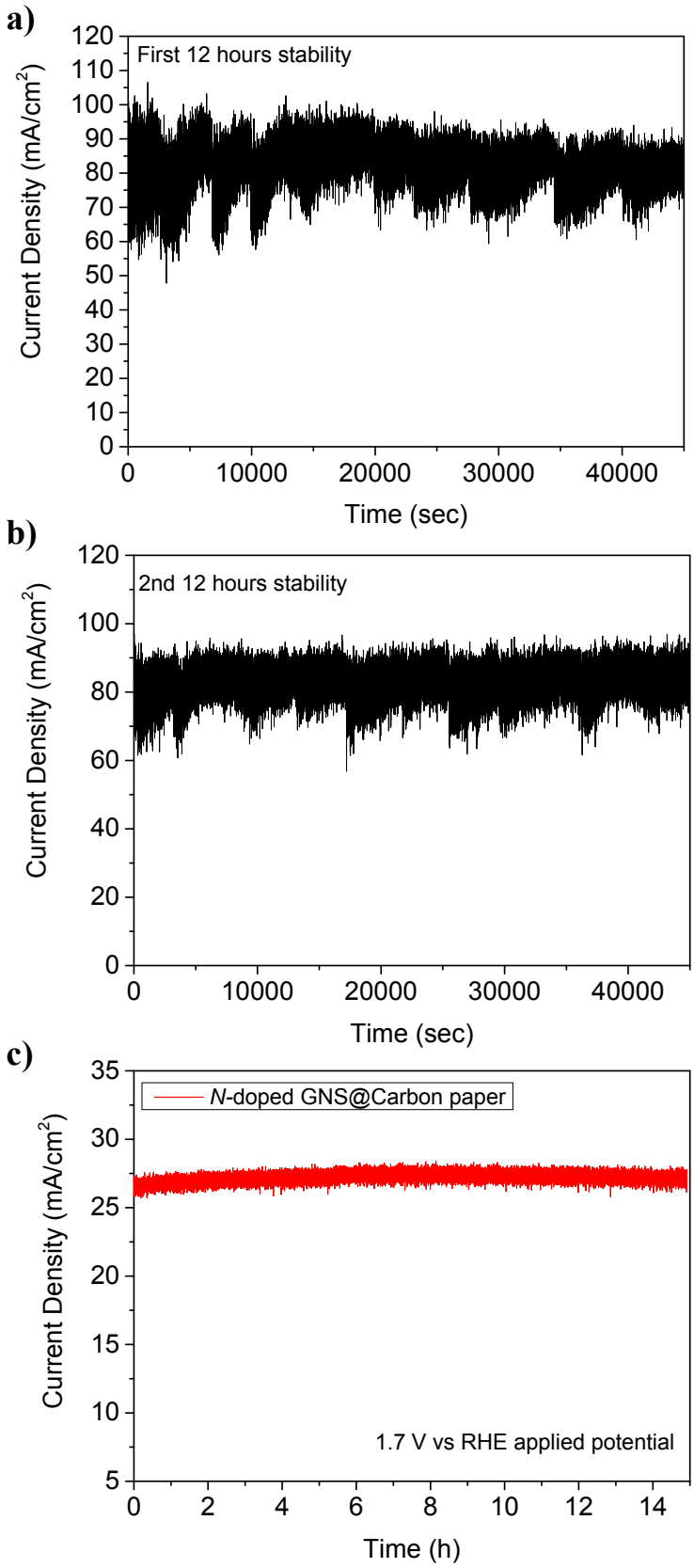

Figure S6 Electrochemical stability of N-doped graphene on Ni foam and carbon paper for OER conducted at an applied potential of 1.7 V *vs* RHE under constant stirring in 1M KOH.

a) The first 12 hours stability test of N-doped graphene on Ni foam **b)** The second 12 hours stability test of N-doped graphene on Ni foam. **c)** 15 hours stability test of the N-doped graphene on carbon paper. The noise is due to vigorous stirring to desorb oxygen bubbles away from the electrode surface together with the high sensitivity of the potentiostat.

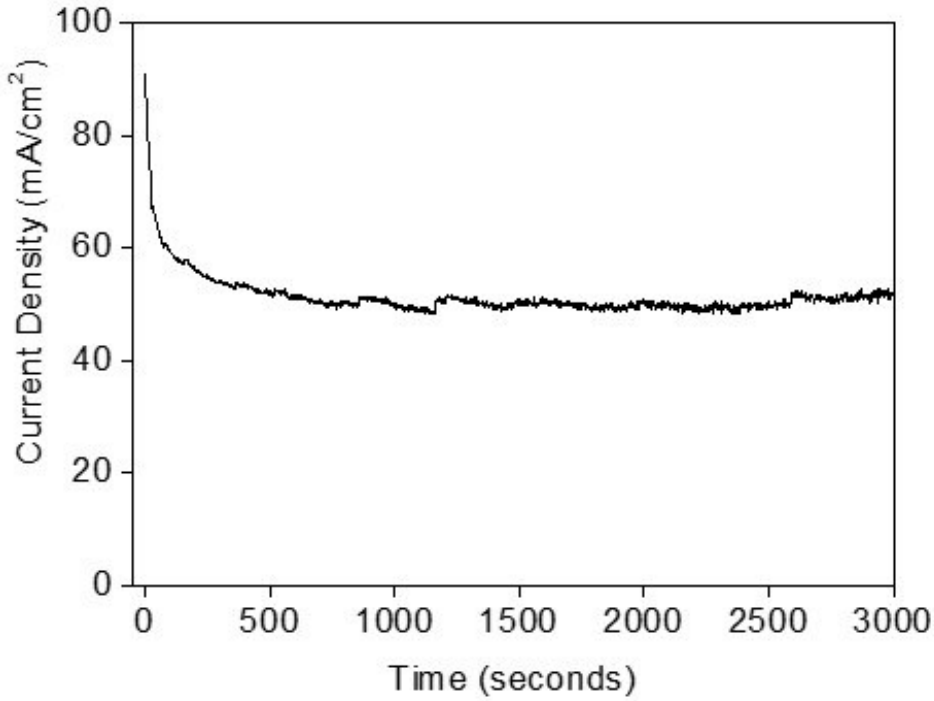

Figure S7 Electrochemical stability of RuO_2 grown on Ni foam for OER conducted at an applied potential of 1.7 V *vs* RHE in 1M KOH.

(1) Dennis, N.; Katritzky, A. R.; Ramaiah, M. 1,3-Dipolar character of six-membered aromatic rings. Part XI. 1-Oxido-3-phenylphthalazinium. *Journal of the Chemical Society, Perkin Transactions 1* **1976**, DOI:10.1039/P19760002281 10.1039/P19760002281(21), 2281.

(2) Bayazit, M. K.; Coleman, K. S. Probing the Selectivity of Azomethine Imine Cycloaddition to Single-Walled Carbon Nanotubes by Resonance Raman Spectroscopy. *Chemistry – An Asian Journal* **2012,** *7* (12), 2925.

(3) Browne, M. P.; Nolan, H.; Duesberg, G. S.; Colavita, P. E.; Lyons, M. E. G. Low-Overpotential High-Activity Mixed Manganese and Ruthenium Oxide Electrocatalysts for Oxygen Evolution Reaction in Alkaline Media. *ACS Catalysis* **2016,** *6* (4), 2408.