Supporting Information

Nanoporous graphene by quantum dots removal from graphene and its conversion as potential oxygen reduction electrocatalyst *via* nitrogen doping

Thangavelu Palaniselvam, Manila Ozhukil Valappil, Rajith Illathvalappil and Sreekumar Kurungot*

Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Pune- 411 008, India. Email: <u>k.sreekumar@ncl.res.in</u>

1. Experimental Method

1.1. Preparation of graphene oxide (GO)

GO was synthesized by improved Hummer's method. Briefly, a mixture of potassium permanganate (KMnO₄) and graphite powder (6:1 g ratio) was added slowly to the acid mixture of con. H₂SO₄ and H₃PO₄ (9:1 ratio) with mechanical stirring at 0 °C. Further, the temperature of the reaction mixture was allowed to increase up to 45 °C for 1 h followed by increasing the temperature up to 55 °C and maintaining the same temperature for 12 h. Subsequently, 3 ml of 30 % H₂O₂ in ice water was added to the reaction mixture to stop the oxidation of the reaction. The mixture was subjected to centrifugation at 12000 rpm and the supernatant solution was decanted away. The resulting material was subjected to multiple washings with water, ethanol, acetone and polyether in sequence and conserved for further use.

1.2. Preparation of graphene (Gr) from graphene oxide (GO)

Gr was prepared by the pyrolysis of GO at high temperature in inert (Ar) atmosphere. Briefly, GO was loaded in an alumina boat, which was placed in the quartz tube. Further, the tube was kept in a tubular furnace under inert atmosphere by purging Ar by maintaining a flow rate of 0.5 sccm. Subsequently, the temperature of the furnace was increased up to 900 °C and thereafter the same temperature was maintained for 3 h. This was allowed to cool down to room temperature after pyrolysis with Ar flow. The pyrolysed product was then preserved for further studies.

1.3. Preparation of porous graphene (pGr) and graphene quantum dots (GQDs) by hydrogen peroxide (H_2O_2) oxidation of Gr.

The pGr and GQDs were prepared simultaneously by H_2O_2 oxidation of Gr. Briefly, 100 mg of Gr was dispersed in 100 ml of H_2O_2 (30 %) with the aid of sonication for 10 min at room temperature and temperature of the reaction mixture was increased to 70 °C and maintained for 72 h. Subsequently, the resulting mixture was filtered by a filter paper having a pore size of 0.44 µm (Rankem Chemicals) and the filtrate (*i.e.* pGr-72) was dried at 50 °C for 3 h and preserved for further analyses. The filtrate collected in the previous step was allowed for dialysis in a dialysis bag for 3 days. The resulting aqueous solution (GQD-72) was conserved for further analysis. For effectively comparing the influence of the time of oxidative treatment on the formation of both GQD and pGr, we have collected more samples by maintaining the times of reaction as 24 and 48 h. The samples prepared at 24 h are designated as pGr-24 and GQD-24, whereas at 48 h, the samples are designated as pGr-48 and GQD-48.

1.4. Preparation of nitrogen doped porous graphene (NpGr-72)

NpGr-72 was prepared by the pyrolysis of pGr-72 with 1,10 phenanthroline mixture at 900 °C for 3 h in Ar atmosphere. Briefly, 50 mg of pGr-72 in ethanol solution was mixed with 100 mg of 1,10 phenanthroline (phen) in ethanol and the reaction mixture was kept for mechanical stirring for 24 h to attain effective diffusion of phen into the cavity of pGr-72. Further, the solvent was evaporated by thermal evaporation at 50 °C for 3 h. Subsequently, the resulting composite material was loaded on alumina boat

which was placed in the quartz tube. Followed by this, the tube was kept in a tubular furnace and an inert atmosphere was maintained with the help of Ar at a flow rate of 0.5 sccm. Further, the temperature of the furnace was increased up to 900 °C and the system was maintained at this condition for 3 h. Thereafter, the furnace was allowed for cooling to room temperature without disconnecting the Ar flow. Thus obtained pyrolysed product (NpGr-72) was then washed with ethanol and preserved for further studies. For the effective preparation, the non-porous nitrogen doped Gr (NGr) was also prepared by similar method while using Gr as the substrate.

1.5. Structural characterization

The high resolution transmission electron microscope (HRTEM) FEI model TECNAI G2 F30 instrument operated at an accelerating voltage of 300 kV (Cs = 0.6 mm, resolution 1.7 Å) was used to characterize the structural properties of the prepared samples. For the TEM analysis, the samples were prepared by drop casting ethanol solution of the samples on 200 mesh copper grid coated with carbon film (ICON Analytical) and dried in vacuum for overnight before loading in the electron microscope chamber. The X-ray diffraction patterns (XRD) of the samples were recorded using the PANalytical X'pert Pro instrument. In all the cases, the data was collected with the scan rate of 0.5° /min. using Cu K α (1.5418 Å) radiation. The energy dispersive X-ray (EDX) measurements were performed on FEI, Model Quanta 200 3D at an operating potential of 30 kV. A VG Microtech Multilab ESCA 3000 spectrometer equipped with an Mg K α X-ray source (hv = 1253.6 eV) was used for the X-ray photoelectron spectroscopy (XPS) measurements. Raman spectra of the prepared samples were performed on an HR 800 Raman spectrometer (Jobin Yvon, Horiba, France) using 632.8 nm green laser (NRS 1500 W). UV-VIS and photoluminescent spectra of GQDs in water were recorded using a Carry Win 50

(Agilent Tech.) instrument. Fourier transform infrared (FT-IR) spectroscopic analysis was conducted on a PerkinElmer Spectrum 2000 spectrometer. Nitrogen and hydrogen adsorption-desorption experiments were performed at 77 K using Quantachrome Quadrasorb automatic volumetric instrument. Ultra pure N₂ (99.9995%) was further purified by using calcium alumino silicate adsorbents to remove trace amounts of water and other impurities before directing into the system. A standard low-temperature liquid nitrogen Dewar vessel was used for the measurement at 77 K. Prior to the experiment, the sample was activated at room temperature (for 24 h) and at 150 °C (for 36 h) under ultrahigh vacuum (10-8 mbar) for overnight. About 40 mg of the sample was loaded for gas adsorption, and the weight of each sample was recorded before and after out gassing to authenticate the complete removal of all guest molecules including the coordinated H₂O in the pGr based samples. Prior to the hydrogen adsorption-desorption experiment, pGr-48 and pGr-72 were subjected for heat treatment at 900 °C for 3 h in Ar atmosphere to remove the oxygen functional groups to avoid the chemical interaction of H₂ with such groups.

1.6. Electrochemical studies

The cyclic voltammetric (CV) measurements were performed in Autolab PGSTAT 30 (Ecochemie) by using conventional three-electrode test cell received from Pine Instruments while rotating ring disc electrode (RRDE) measurements were performed using a Biologic electrochemical workstation coupled with a Pine RRDE system. Hg/HgO (procured from CHI instruments) and Pt wire were used as reference and counter electrodes respectively. The CV and RRDE measurements were carried out using a glassy carbon (GC) working electrode (0.19625 cm²). Before the experiments, the working electrode was polished on a polishing cloth using 0.3 μ m alumina slurry followed by washing with water and acetone. Further, 5 mg of the catalyst was

dispersed in 1 ml of ethanol in water (3:2) solution by sonication. Subsequently, $10 \ \mu L$ from the prepared slurry was placed on the GC electrode with the help of a micro syringe. Subsequently, $3 \ \mu L$ of 0.1 % Fumion in N-methyl pyrrolidone solution was coated as a binder on the surface of the catalyst layer to protect the detachment of the catalyst particles. Finally, this electrode was further dried under a lamp for 3 h and was used as the working electrode for the experiments. 0.1 M KOH was used as the electrolyte for all the CV and RRDE studies. All the CV experiments were carried out at a scan rate of 5 mV s⁻¹ whereas all the RRDE experiments, oxygen and nitrogen were used to maintain the oxygen rich and inert atmosphere, respectively and the ring potential was set to 0.6 V.

1.7. Membrane Electrode Assembly (MEA) Fabrication and Single Cell Test.

The active nitrogen doped porous and nonporous graphene (NpGr-72 and NGr) were tested as fuel cell cathodes to evaluate the ORR characteristics by MEA analysis under anion exchange membrane fuel cell (AEMFCs) conditions. For the catalyst slurry preparation, the prepared catalyst was mixed with commercially procured Fumion solution (10 wt %) in Nmethyl-2-pyrrolidone by ultrasonication. Subsequently, the catalyst slurry was brush coated on the gas diffusion layer (GDL) having an area of 4 cm² until the total catalyst loading of 2.5 mg cm⁻² was reached. Whereas in the case of Pt based system, commercial 40 wt % Pt/C (Johnson Matthey) was used at the anode as well as cathode with the loading of 0.8 mg cm⁻². The catalyst (40 wt % Pt/C) with a similar loading was used as the anode in the case of NpGr-72 and NGr systems. 10 wt.% Fumion in N-methyl pyrrolidone solution was used as the binder. The fumion to carbon ratio was maintained as 0.5. Finally, the MEA was prepared by sandwiching the commercial Fumapem FAA-3 pre-treated membrane (with a thickness of 55 µm in wet condition and ion exchange capacity of 2.01 meq g⁻¹ in dry form) between the anode and cathode by pressing under an applied pressure of 0.5 tone for 1 min at room temperature. Prior to the experiment, the Fumapem FAA-3 membrane was pre-treated by keeping in 1 M KOH for 24 h at room temperature to replace the bromide ions by hydroxyl ions in the polymer matrix. After the treatment, the membrane was kept in DI water for 1 h. Subsequently, the membrane was rinsed thoroughly with DI water and to make it ready to use. In order to avoid the CO₂ contamination, the pre-treated membrane was kept in closed container containing 1 M KOH. Finally, AEMFCs test was carried out in a single cell with serpentine flow channels in the monopolar graphite plates (fixture procured from Fuel Cell Technologies Inc, USA). The steady state polarization measurements were carried out by maintaining a flow of humidified (100% RH) H₂ and O₂ as 50 sccm and 100 sccm respectively at 50 °C with ambient pressure using a fuel cell test station (Fuel Cell Technologies Inc, USA).

2. Results



Fig. S1. (a) Higher magnification image of GQD-72 and (b) its lattice fringes profile.



Fig. S2. TEM images of porous graphene (pGr-72) taken under different magnifications.

The TEM images of pGr-72 under different magnifications are shown in Fig. S2. These images clearly show the presence of pores with an average size of 5 nm. The size of the pores is well in accordance with the size of the quantum dots, GQD-72, which authenticates the claim that GQDs are formed by the etching out of small portion from the Gr surface during the H_2O_2 functionalization.



Fig. S3. TEM images of graphene (Gr) taken under different magnifications.



Fig. S4. TEM images of porous graphene (pGr-48) taken under different magnifications.



Fig. S5. TEM images of GQD-48 taken under different magnifications.



Fig. S6. (a) UV-Vis spectra of GQD-48 and (b) photoluminecent spectra of GQD-72 in water. Inset of Fig. S6a shows the optical image of GQD-48 under the UV light.

Quantum yield calculation.

The quantum yield has been calculated by using the following equation. Here, the quinine sulphate in water was used as the standard material.

Where, ' Φ ' is the quantum yield of the topic of interest, 'I' is the measured integrated emission intensity, 'A' optical density and ' η ' is the refractive index of the solvent. Here '*st*' stands for the standard and '*x*' stands for the unknown material.

Table S1. Quantum yield of GQDs using Quinine sulphate as a reference material.

Sample	Integrated emission intensity	Absorbance at 340 nm	Refractive index of the solvent	Quantum yield
	(I)	(A)	(η)	(Φ) %
Quinine	77275.0	0.06	1.33	53 (known)
GQD-24	3591.2	0.3	1.33	0.49
GQD-48	11661.3	0.2	1.33	2.39
GQD-72	26851.2	0.07	1.33	15.8

Table S2. Comparison table of the quantum yields.

Author	Method	PL Quantum yield (%)
Pan. <i>et al.</i> ¹	Hydrothermal method	6.9
S. Zhu. <i>et al.</i> ²	Solvothermal method	11.4
Y .Dong. et al. ³	Carbonization of citric acid	9.0
M. Zhang. <i>et al.</i> ⁴	Electrochemical method	14.0
L.Lin. <i>et al</i> ⁵	Exfoliation of MWCNTs	6.53
Present study	H ₂ O ₂ oxidation	15.8



Fig. S7. Infra-Red spectra of (a) Gr, (b) material collected after sonication with H_2O_2 at room temperature, (c) material collected immediately after the temperature of the reaction mixture reaches to 70 °C, (d) material collected after 1 h of reaction at 70 °C and (e) material collected after 24h of reaction at 70 °C (pGr-24) (f) material collected after 72h of reaction at 70 °C (pGr-72).



Fig. S8. (a) N_2 adsorption-desorption profiles used for calculating the BET surfaces areas of Gr, pGr-48 and pGr-72; (b) Pore size distribution patterns of Gr, pGr-48 and pGr-72.



Fig. S9. N₂ adsorption-desorption profiles of GQDs.



Fig. S10. Comparison of the TEM images of (a-b) graphene and (c-d) porous graphene with reduced size, ensuring the gentle structural breakage of graphene sheets during the H_2O_2 oxidation.



Fig. S11. Hydrogen adsorption desorption isotherms of pGr-48 and pGr-72 at 1 atm pressure and 77 K and (b) Weight percentage of hydrogen uptake of pGr-48 and pGr-72 at 1 atm pressure and 77 K.



Fig. S12. (*a*) Long range X-ray photoelectron spectra of pGr-72 and GQD-72; C1s spectra of (b) pGr-72 and (c) GQD-72; (d) FT-IR spectra of Gr, fGr, GQD-72 and pGr-72.

Cyclic voltamogramme of 20 wt.% Pt/C



Fig. S13. Cyclic voltamogramme of 20 wt.% Pt/C (E-TEK) taken at scan rate of 5m $V s^{-1}$ in oxygen saturated 0.1 M KOH solution.

Koutecky-Levich (K-L) plot

The mathematical representation leading to the Koutecky-Levich (K-L) plot is shown in Eqn. (1).

$$1/j = 1/nFkC_{O2} + 1/0.62nFD_{O2}^{2/3}C_{O2}^{*}v^{-1/6}\omega^{1/2} \dots (1)$$

where, 'j' is the measured current density 'n' is the number of transferred electrons per oxygen molecule, 'A' is the area of the electrode, 'F' is the Faraday constant (96500 C mol⁻¹), 'D₀₂' is the diffusion coefficient of the electrolyte, 'C₀*' is the concentration of the dissolved oxygen in the electrolyte, 'v' is the kinematic viscosity of the electrolyte, ' ω ' is the

angular velocity of the electrode. In this study, the used values for D_0 , C_0^* and 'v' are 1.9 X 10^{-5} cm² s⁻¹, 1.22 X 10^{-6} mol cm⁻³ and 0.01 cm² s⁻¹ respectively.



Accelerated durability test (ADT)

Fig. S14. Accelerated durability test for (a) NpGr-72 and (b) 20 wt % Pt/C (E-TEK).



Fig. S15. Single cell polarization data by using 40 wt.% Pt/C (E-TEK) as the cathode as well as anode with loading of 0.8 mg cm⁻² and FumaTech FAA as the anion exchange membrane. Operating temperature is 50 °C; H_2 and O_2 flow rates are 50 and 100 sccm respectively and 100 % relative humidity was maintained for the H_2 and O_2 streams.

EDAX Spectra





Fig. S16. EDAX spectra with elemental quantification of (a) NpGr-72 and (b) NGr.

Authors	Preparation	N content (%)	No of electrons	Overpotential
	method		transferred	difference (mV)
Lin <i>et al</i> ⁶	Thermal	16	2	200
	chemical vapor			(vs Ag/AgCl)
	deposition			
	method			
Wong <i>et al</i> ⁷	Thermal	8.1	3.3	120
	annealing			(vs Ag/AgCl)
Kurungot et al ⁸	Thermal	9	3.2	90 (vs Hg/HgO)
	annealing			
Present study	Thermal	7.8	3.8	60 (vs Hg/HgO)
	annealing			

Table. S3. Comparison of the performance of nitrogen doped catalysts.

Table S4. Comparison of the fuel cell performances of non-Pt electrocatalysts under anion exchange membrane fuel cell (AEMFCs) conditions.

S.No.	Catalyst	Membrane	Catalyst Loading. (mg cm ⁻²)	Maximum power density. (mW cm ⁻²)	Maximum current density. (mA cm ⁻²)
1.	N-CNT ³⁵	FAA, Fuma- Tech GmbH	5	37.3	~145
2.	NpGr-72 (present study)	Fumapem FAA-3	2.5	27	~ 104

Reference number is as given in the main text.



Fig. S17. *Quantification of the types of nitrogen in their relative percentages out of the total doped nitrogen in (a)* NpGr-72 (b) NGr.



Fig. S18. Tautomerization of 2- pyridone between hydroxyl and Zwitter ion forms.

References

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