

Supplementary Information

Nano Ceria supported Nitrogen Doped Graphene as Highly Stable and Methanol Tolerant Electrocatalyst for Oxygen Reduction.

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Synthesis of GO, rGO, CeO₂, NrGO and CeO₂/rGO:

The Graphene oxide (GO) was prepared from graphite flakes (Sigma-Aldrich) using a modified Hummers method and dispersed in deionised water.^{1,2}

To prepare CeO₂, about 20 ml of 1,4-butanediol (spectrochem, India) and 250 mg of ceric ammonium nitrate (Fisher Scientific, India) were mixed together in a 60ml of teflon container and shaken well to form homogeneous mixture. Teflon container was fixed in a autoclave tightly and placed inside microwave system (MDS-60 Made of Sineo, China). Autoclave was kept under microwave radiation for 30 minutes at 180 °C (maximum 800 watts). The obtained products were washed with doubled distilled water, ethanol and acetone for 3 times and finally dried at 80 °C for 1 hr.

To prepare reduced graphene oxide (rGO), 0.05 g of dispersed graphene oxide in doubled distilled water was mixed in 20 ml of 1,4-butanediol using ultrasonication and the solution was treated with microwave radiation in a similar condition as in case of CeO₂. The product formed was washed with deionised water, ethanol and acetone repeatedly by centrifugation and then dried in oven at 100 °C.

To prepare NrGO, 0.05 g of graphene oxide (dispersed in doubled distilled water) and 2 ml of 6.4M NH₄OH was mixed with 20 ml of 1,4-butanediol using ultrasonication and then solvothermally treated under microwave radiation at 180 °C for 20

minutes. The product formed was washed in a similar manner as mentioned above during the synthesis of rGO.

To prepare CeO₂/rGO nanocomposite, a mixture of 250 mg ceric ammonium nitrate, 50 mg Graphene oxide, and 20 ml 1, 4-Butanediol were ultrasonicated for 15 minutes and then solvothermally treated under microwave radiation at 180 °C for 20 minutes. The product formed was washed in a similar manner as discussed above.

Physical Characterisation: For XRD measurements about 1 gm of grinded samples were kept in a sample holder and was fitted inside Rigaku Advance X-ray Diffractometer operating at 40 KV (radiation source Cu K_α (wavelength=1.5418 Å). FTIR analysis was carried out with the help of Thermo Fischer iS5 FTIR instrument. The XPS measurement was done using DESA-150 electron analyzer (Staib Instruments, Germany) having Mg-K_α (1253.6 eV) as radiation source. Raman analysis of the samples were carried out on Horiba HR 800UV confocal Raman spectrophotometer with λ=632.8 nm and He-Ne laser as excitation source. Transmission Electron Microscope (TEM) images were obtained by the Model FEI Technai G2 S – Twin.

Electrode Preparation: For electrochemical studies homogeneous ink of the catalysts were prepared by following 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 disk (GCD) electrode was repeatedly polished with alumina powder (size 0.05 µm) and washed with distilled water, then dried in N₂ flow. About 12 µl of catalyst ink (~0.17 mg/cm²) was dropped onto the GCE using micropipette and allowed to dry for 3 hours in desiccator before electrochemical analysis.

Rotating disk electrode (RDE) Measurements: 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. All the measurements were conducted in a three-electrode cell system having Platinum wire as counter electrode, catalyst coated GCD electrode (Metroham Instrument Co.) as working electrode and Ag/AgCl (3M KCl) as

reference electrode. For ORR studies, the electrolyte was initially bubbled with O₂ for 20 minutes and during RDE experiments a continuous flow of O₂ was maintained over the electrolyte. All the ORR measurements were conducted at room temperature in oxygen saturated 0.1M KOH solution.

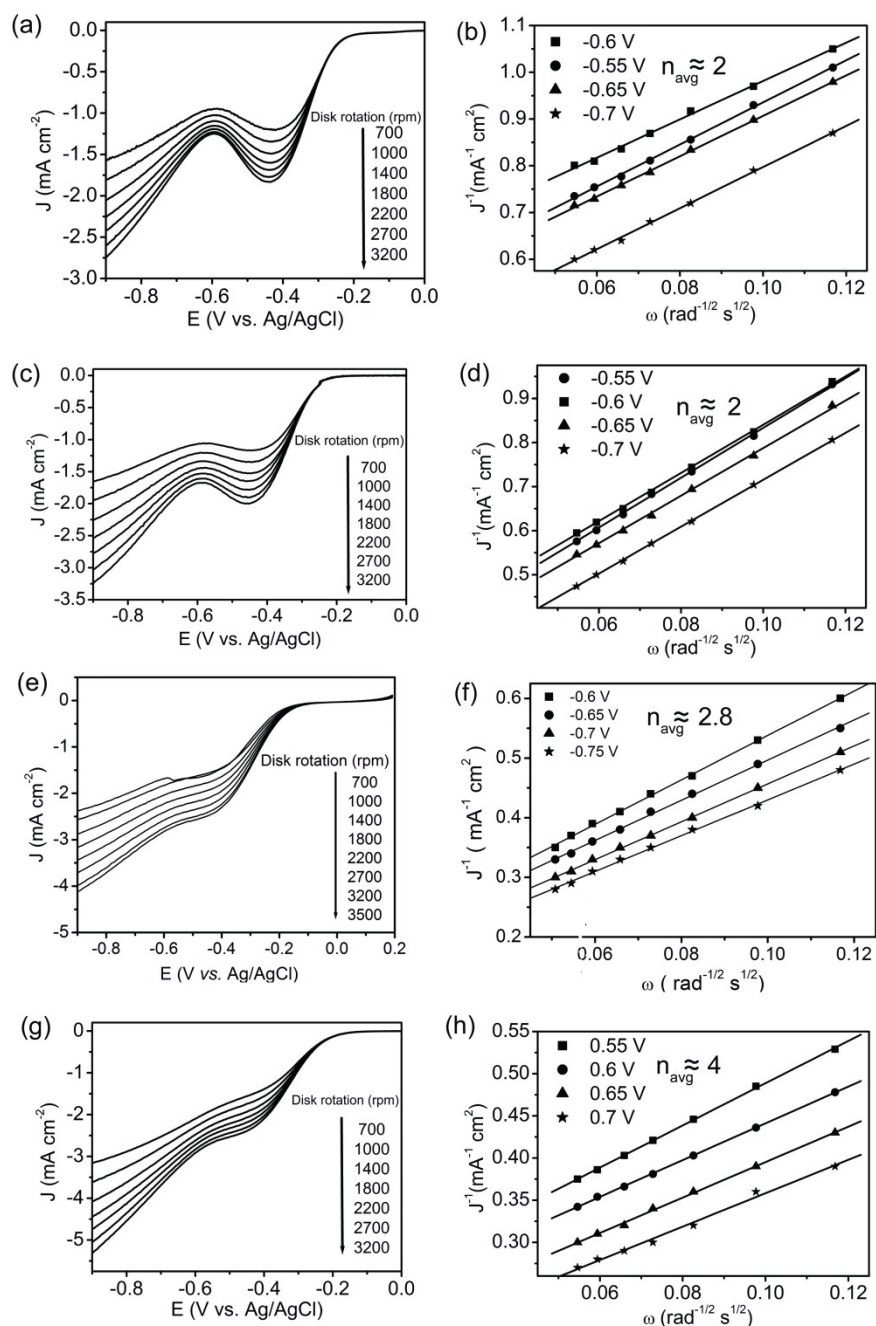


Figure S1: Graphs a, c, e and g represents oxygen reduction RDE curves on CeO₂, rGO, NrGO and CeO₂/rGO electrodes respectively. The graphs b, d, f and h represents corresponding K-L plot for the above mentioned catalysts at different potentials with average electron transfer number (n_{avg}).

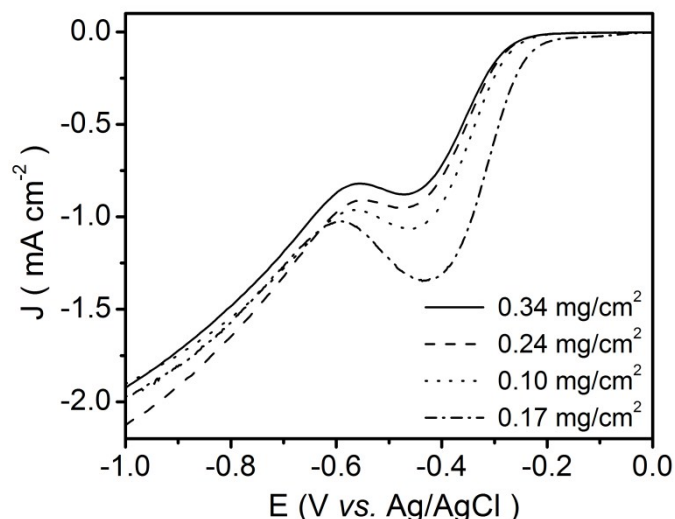


Figure S2: Shows ORR linear sweep voltammetry on electrodes supporting different amount of CeO_2 (Conditions; 0.1 M KOH electrolyte, rotation 1000 rpm, scan rate 10 mVs^{-1}).

In Figure S2, it is observed that 0.17 mg/cm^2 loading amount is optimum to get high onset potential and high current density. Therefore in case of all other catalyst the same amount of catalyst loading is made.

Chronoamperometric measurements: For the Chronoamperometric stability measurements a three-electrode cell system having a Platinum weir as counter electrode, catalyst coated glassy carbon disc as working electrode and Ag/AgCl (3 M KCl) as reference electrode was taken and the electrode preparation was similar to that of RDE measurements. Initially, cathodic cycles (0.2 to -0.8 V) were performed for removal of adsorbed gases and stabilization of electrode surfaces. For all the measurements the working electrode was rotated at 1000 rpm and at a fixed potential of -0.35 V in O_2 saturated 0.1 M KOH electrolyte. All the chronoamperometric data's for methanol tolerant test are recorded after 500 sec of ORR to avoid initial rapid fall in current density.

References:

1. Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 1339.
2. Liang, Y.; Li, Y.; Wang, H.; Zhou, J.; Wang, J.; Reiger, T.; Dai, H. *Nat. Mater* **2011**, *10*, 780.