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Synthesis and Characterization of Heteroatom Doped Graphene as a Novel Non Precious Catalyst for ORR

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Abstract

Oxygen reduction reaction (ORR) is a fundamental reaction for energy storage and conversion systems. It has relied on Pt based electrocatalysts but chemical doping of carbon based materials proved to be promising strategy for preparing non precious and metal free alternatives. First part of this work involved synthesis of few layers of graphene oxide nanosheet from graphite by improved Hummers method. This was followed by conversion into nitrogen doped graphene using one-pot microwave assisted method. The X-ray Diffraction (XRD), Fourier Transform Infra-red (FTIR) and Raman spectroscopy characterization results show the confirmation of reduction, the functional groups present in the sample, and the surface defects in the samples respectively. The electrochemical studies revealed the oxidation reduction potential and the onset potential of the material by cyclic voltammetry, linear sweep voltametry (LSV), Rotating Disk Electrode (RDE) and Rotating Ring Disk Electrode (RRDE) experiments. This material showed promising results needed by ORR electrocatalyst for application in energy system like Fuel cell.

Keywords: Graphene;Defect; Doping; Electrocatalyst; Voltammetry.

1. Introduction

Graphene is an abundant allotrope of carbon with several interesting properties. It has excellent mechanical strength, elasticity, thermally and electrically conductive and its chemically inert. Hence graphene is considered as replaceable alternative material in existing energy and storage applications [Sui *et al* (2017); Quinson *et al* (2018); Qazzazie *et al* (2015); Steele *et al* (2001); Zhang *et al* (2011)].

In 1859, Brodie synthesized graphene oxide by using $KMnO_4$, sodium nitrate, potassium chlorate. In 1898, Stadenmair group also synthesized using $KMnO_4$, pottasium nitrate and the graphite. In 1958, Hummers synthesized GO by using the mixture of graphite and $KMno_4$, Sulphuric acid and Phosphoric acid. All these methods involve generation and release of toxic by product into the environment (as shown in figure 1). Hence, there is a need for better environmentally friendly alternative [Ji *et al* (2015); Zhang *et al* (2017); Yao *et al* (2016); Winter *et al* (2004)].

Tour method's provide this needed scheme for chemical exfoliation and oxidation of graphite by improving the Hummers method of synthesizing GO

using increased ratio of H_2SO_4 and H_3PO_4 (9:1). This research adopts this method with little modification. It is worth mentioning that introduction of hetero atom such as Nitrogen, Boron, and Fluorine increase the electronic activity of graphene oxide [Sudhakar *et al* (2018); Wang *et al* (2018); Patel *et al* (2015); Hu *et al* (2019); Liang *et al* (2017); Yi *et al* (2019)]. Thus, making it a good defect-control electrocatalyst for ORR. Hydrogen Evolution Reaction (HER) and Oxygen Evolution Reaction (OER).

Hetero atom doped graphene is used in various applications such as energy conversion, energy storage, biomedical and other applications. Here, our aim is to use doped-graphene as electrocatalyst in fuel cells and otherwise in supercapacitors.

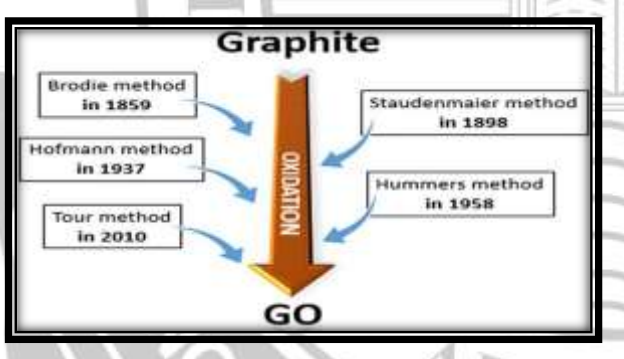

Fig. 1: Synthesis of Graphene Oxide

2.0 Materials and Methods

2.1 Materials

Graphitic flakes powder (Sigma Aldrich,<20 µm), Pottassium Permanganate (Rankem), Sulphuric Acid (Acros Organics), Phosphoric Acid(Sigma Aldrich), Hydrogen Peroxide (Merck), Hydrochloric acid (Fisher Scientific), ethanol(Burgyon and Deionized water is obtained from Millipore water system. All chemicals were used as received without further purification.

2.2 Synthesis Methodology

The scheme of synthesis is shown in fig 2. A brief summary is as follows. 3 g of graphitic flakes powder and 18 g of $KMnO_4$ were grinded together. 360 mL of Sulphuric acid, 40 mL of Phosphoric acid were added and stirred for 15 minutes. The mixture of graphitic powder and $KMnO_4$ was added slowly into the beaker containing H_2SO_4 and H_3PO_4 while stirring. Then the solution was kept stirring at 70 °C for 14 hours. Then the reaction was terminated by placing the solution in an ice bath, while adding 11 mL of H_2O_2 drop wise. A yellow colour aliquot was formed. The solution was kept for 3 hours and 500 mL of distilled water was added. The upper layer was decanted after 2 hours and another 500 mL of water was added. This process was repeated 3 times and the solution was later washed with 5% of HCl for 10 times. It was centrifuged with water 22 times and 10 times with ethanol at 4000 -5000 rpm. The precipitate was kept for drying in hot air oven at 80° C for 24 hours at 5° per minute. A black coloured Graphene Oxide (GO) sample was obtained and this was crushed and grinded to fine powder.

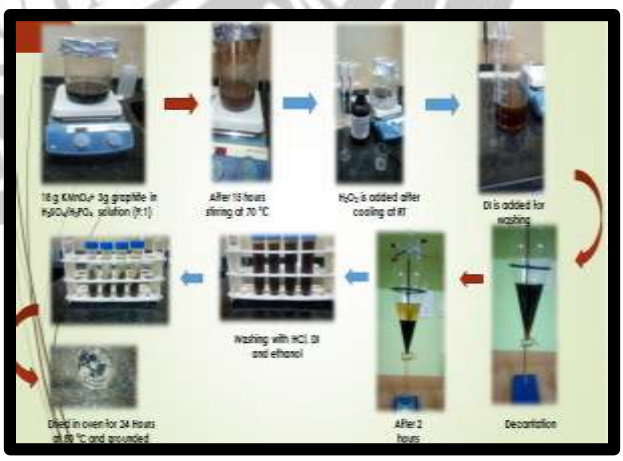

Fig 2: The schematic of synthesis process of GO

2.3 Synthesis of Nitrogen doped graphene

Nitrogen doped graphene (NG) was synthesized via one pot Microwave assisted method. 0.1 g of the as-synthesized graphene oxide (GO) was dissolved in a beaker containing 10 mL of distilled water. The solution was sonicated for 30 minutes and 0.01 g of Melamine along with 10 mL of distilled water was added to this, followed by 30 minutes sonication. Afterwards, the above two solutions were mixed and kept for for another 30 minutes sonication.

The solution was heated in microwave oven for 10 minutes. It was cooled to room temperature and then centrifuged with distilled water and ethanol 3 times each at 4000-5000 rpm. The remaining precipitate is collected and kept for drying in Vacuum air oven at 150° C for 5 hours.

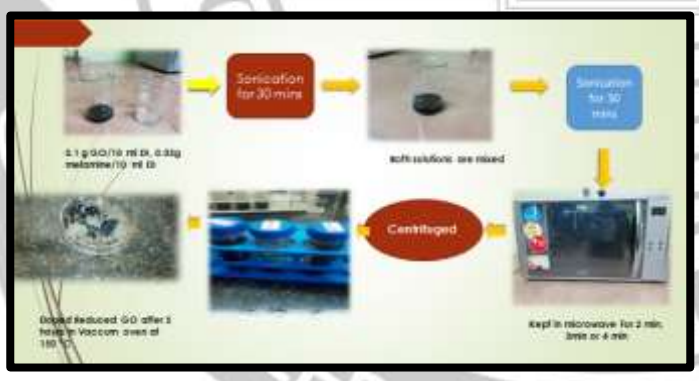

Fig 3: Schematic diagram of synthesis of N-doped Graphene

3.0 Results and Discussion

3.1 Material characterization

XRD is used for determining the crystalline nature of the materials. X-ray diffraction measurements were done by using BRUKER D8 ADVANCE X-ray Diffractometer with Cu Kα radiation (=1.5418 A) for the 2Θ ranging from 10° to 80° at 0.02° steps. Fourier Transform Infrared Spectra were measured in TENSOR 27 spectrometer (BRUKER) by KBr pellet technique with wavenumber ranging from 400 to 4000 cm^{-1}. The chemical nature and structure defects in N-doped graphene were determined using Laser Raman Spectrometer

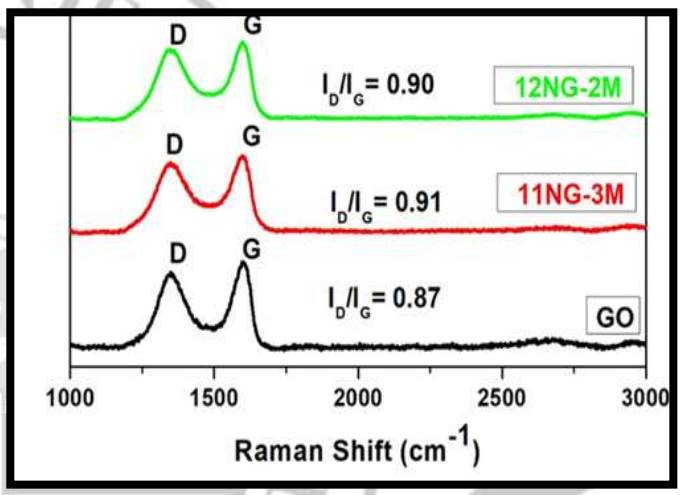

Fig 4: Raman spectrum of GO, 11NG, 12NG for 3 and 2 minutes of microwave heating.

The I_D/I_G provides information on the dimensions, in plane, edge defect and the disorder nature of the sample. The introduction of N atoms into grapheme can enhance the formation of a large quantity of defects, resulting in a high intensity D band due to formation of smaller nanocrystalline graphene domains by heteroatom doping. The D and G bands obtained for graphite clearly indicates the absence of disorder, while that of GO (0.87) as shown in Fig 4 reveal little or no defect.. The increase in the I_D/I_G from 0.87 to 0.90 and 0.91 indicates that structural defects have been introduced into the material due to N-doping [Li *et al* (2018); Wang *et al* (2019); Zhuang *et al* (2017); Kumar *et al* (2014)].

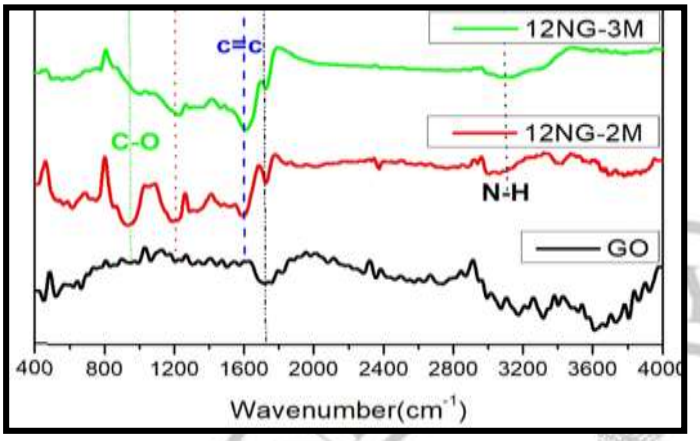

Fig 5: FTIR spectrum of GO, 12NG for 2 and 3 minutes.

Fig 5 shows the functional groups present in GO, 12NG-2M and 12NG-3M. The intercalation of GO by oxidation, resulted in the formation of graphene, NG. The absorption band around around 1380 cm^{-1} and 1570 cm^{-1} could be assigned to the presence of C=C stretching of aromatic ring and C=O stretching respectively. In addition, the two absorption bands around 1410 cm^{-1} and 1630 cm^{-1} are attributed to O-H bending and C-N stretching respectively. This confirmed the incorporation of Oxygen and Nitrogen moieties in the NG samples [Kumar *et al* (2016); Stankovich *et al* (2006); Dai *et al* (2013); Balaji *et al* (2016)].

As shown in the XRD diffractogram in Fig 6, the shift of the graphite peak around 26° to 11.08° confirmed the oxidation of graphite to graphene oxide which resulted into the interlayer spacing being increased because of the intercalation of oxygen functional groups between the lattice spacing of the various stacked graphite sheets [Va *et al* (2007); Agnoli *et al* (2016); Zhu *et al* (2016); Zhao *et al* (2017); Musico *et al* (2019); Ngidi *et al* (2019); Shao *et al* (2019)].

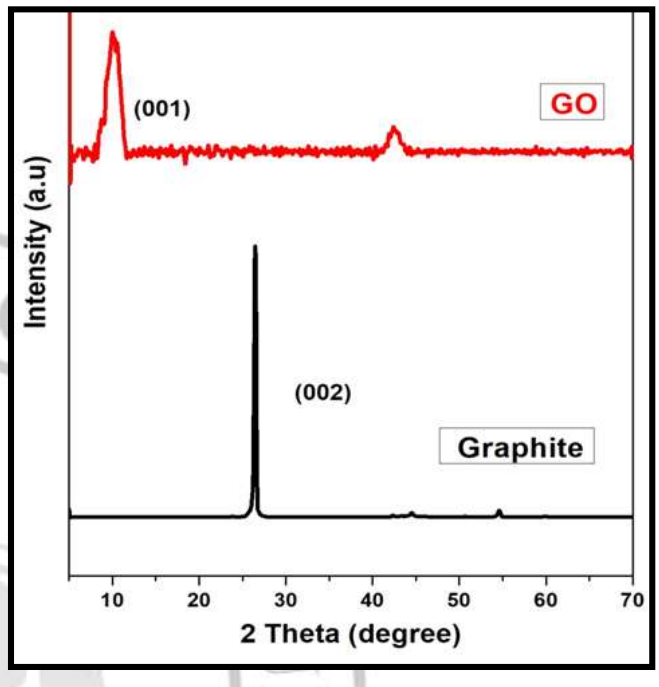

Fig 6: XRD pattern of graphite and Graphene oxide.

3.2 Electrochemical studies:

To scrutinize the oxygen reduction reaction potential of the prepared N-doped graphene, it was dropped cast as the working electrode, the electrochemical activity was performed via conventional three electrode arrangement using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) using 1M KOH electrolyte [Paul *et al* (2019); Du *et al* (2017); Latiff *et al* (2017); Marcano *et al* (2018); Sheng *et al* (2011); Alam *et al* (2017); Oskueyan *et al* (2019); Lewandowska *et al* (2019)].

The electrochemical setup consists of glassy carbon electrode (geometric area: 0.0071 cm^2) as working electrode, coated with NG sample (O2 saturated) in 0.1 M KOH solution as an electrolyte. Pt electrode and Saturated calomel Electrode (SCE) was as counter electrode and reference electrode respectively. The scan rate of 50 mV/s was applied on the system. The study revealed the oxidation

reduction peak is around 0.0.1 to 0.8V as seen in Fig. 7.

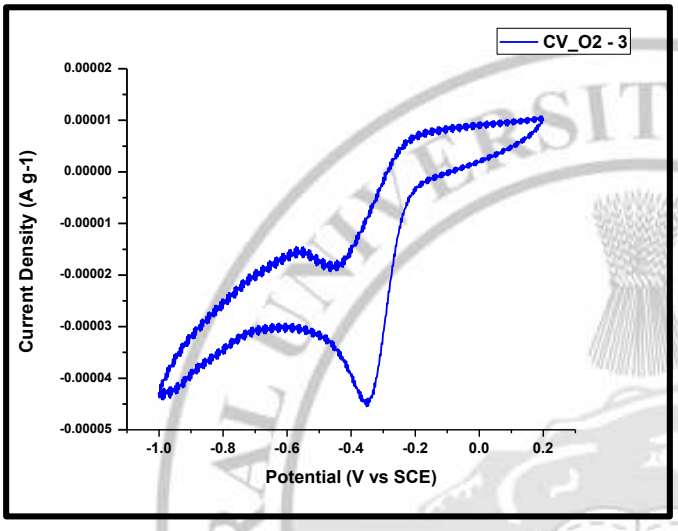

Fig 7: Cyclic voltammetry of the NG sample showing oxygen reduction potential between -0.2 and -0.8 V

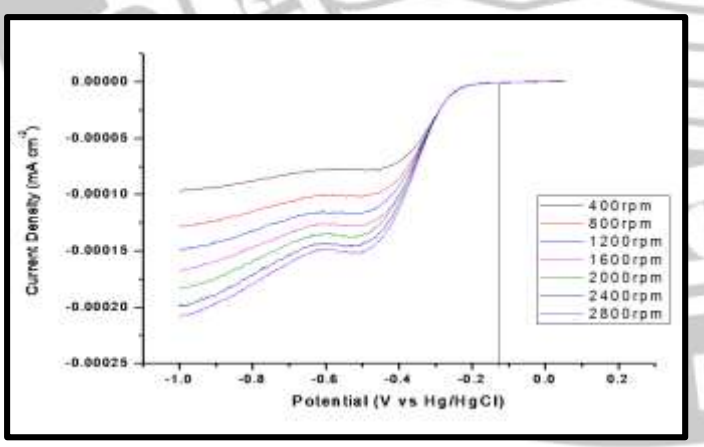

Fig 8: LSV of the NG sample showing onset potential at -0.17 of sample.

The linear sweep voltammetry, Fig. 8 was used for determining the onset potential of the catalyst as well as the electrocatalytic electron transfer system. A comparable onset potential of -0.17V which is closer to the commercial Pt/C 20%wt was obtained. This suggest the high potential of our NG sample as sustainable and low cost alternative in Fuel cell application [Lewandowska *et al* (2019); Tang *et al* (2010)].

4.0 Conclusion

In the current research, heteroatom doped carbon based metal free ORR catalysts have been developed as alternatives to Pt-based catalysts. Among them doped graphene is the best electrocatalyst due to its high ORR activity and sustainability of some precursors. N-doped graphene is synthesized using one-pot microwave assisted method. XRD and Raman results revealed that GO has been reduced to graphene and doped with Nitrogen atom. FTIR results revealed the incorporation of N atom in the graphene carbon network confirming the simultaneous doping with N-atoms and reduction of GO. CV and LSV studies showed the promising catalytic activity of the NG system. This type of heteroatom doped graphene oxide will provide an opportunity to develop efficient ORR catalysts which are essential applications in several fields.

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