Microwave assisted facile synthesis of N-doped Graphene Oxide

A dissertation

submitted in the partial fulfilment of the requirement for the award of degree of

MASTER OF SCIENCE

in

PHYSICS

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Certification

I hereby certify that this thesis entitled **"Microwave assisted facile synthesis of N-doped Graphene Oxide"** in partial fulfillment for the requirements for the award of Degree of Master of science in Physics submitted to School of Physics and Materials Science, Thapar institute of Engineering and Technology, Patiala is an authentic record of my own work and is carried under the supervision of **Dr. Loveleen Kaur Brar**. The matter submitted via this thesis report has not been submitted for the award of any other degree to the best of our knowledge.

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This is to certify that the above statement made by the candidate is correct and true to the best of my knowledge.

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Dedicated

to my

Family

and

Friends

for their love.

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Shubham

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ABSTRACT

Graphene oxide (GO) described as a graphene sheet consisting of hydroxyl, epoxide, carbonyl, carboxyl functional groups. GO modifies its physical and chemical properties based on oxygen inclusions. This permits a broad range of applications. N-doped GO finds applications in energy devices such as metal-air batteries and fuel cells. In this study we synthesize the GO with modified Hummer's method at room temperature. The formed GO was further doped with nitrogen using Urea by microwave technique using open container and Teflon Autoclave. XRD, TGA and Raman Spectroscopy indicated the successful preparation of graphene oxide and nitrogen doped-GO samples. FTIR reveals the presence of N-containing functional groups for the doped samples. DC resistivity measurements show that the conductivity is enhanced for the nitrogen doped samples with maximum conductivity for the sample synthesized in Teflon autoclave (1.66 S/m). SEM and EDX measurements were done to know the morphology and presence of elements. All the samples show flake like morphology with sharp edges with EDX confirming the presence of N in the doped-GO samples. The samples were characterized for their use for supercapacitor applications. The samples synthesized in Teflon autoclave showed multi fold enhancement in specific capacitance (147.79 F/cm^2) as compared to undoped (13.82 F/cm^2) and doped sample synthesized in open container (19.67 F/cm^2).

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Chapter 1

Introduction to the synthesis of Graphene Oxide and its Nitrogen doping

1.1 Graphite

Graphite which also known as plumbago and black lead, exist as a crystalline form of carbon. It is basically referred as a mineral element, a semimetal and is one of the famous known carbon's allotropes. Under some standard conditions, Graphite is one of the most stable form of carbon. So, there is a wide range of applications present. Due to its good electrical conductivity, used as electrodes in arc lamps. Graphite is mainly used as self-lubricate and dry-lubricate at industries levels. The graphite lubricating properties exists due to loosen bonding between the sheets.

Fig.1.1 Specimen of Graphite

Category	Mineral element
Chemical Formula	C
Crystal System	Hexagonal
Crystal class	Dihexagonal dipyramidal
Colour	Steel-grey, Black
Tenacity	Non-elastic but very flexible
Cleavage	Perfect on (0001)
Characteristics	Greasy, conducts, strongly anisotropic

There are basically three ways of occurrence of natural Graphite.

- Graphite flakes which are crystalline and occurring as plate like, flat and isolated particles having hexagonal edges.
- Amorphous graphite having very fine flakes.

- Vein graphite which is also known by name lump graphite, has fractures and appears fibrous. This graphite fibre is referred to carbon fibre. [1]

1.2 Introduction to Graphene Oxide and its synthesis

Now days, Graphene as well as its derivatives have immense attention of researchers because they have a wide range of applications due to its optical, mechanical, thermal and electrical properties. Graphene is basically a form of carbon with single atomic layer of carbon atoms having honeycomb like appearance & 2-D lattice. This single atomic layer has sp^2 hybridisation and it has thickness in nanometres. [2] Graphene oxide (GO) is explained as a graphene sheet having carboxyl, hydroxyl, epoxy, carbonyl functional groups. It forms sp^2 and sp^3 hybrid orbitals which help to modify its chemical & physical properties. Graphene oxide is a water-soluble compound which can be ready using strong chemicals or strong oxidising agents just to introduce oxygen containing groups which discussed above. [3]

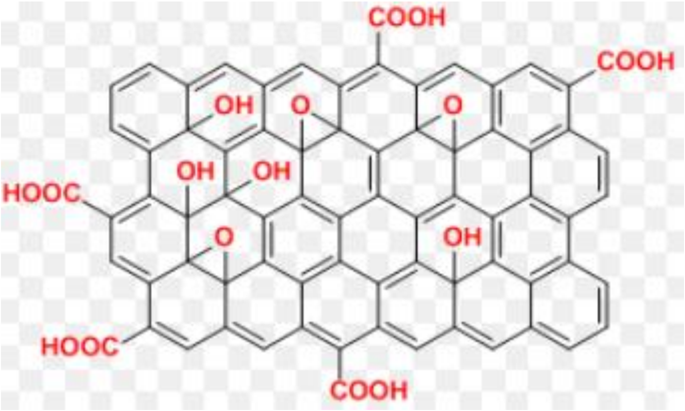

Fig. 1.2 Graphene Oxide

There are many types of methods are introduced to synthesize the graphene oxide. One of the most common method we used for synthesis is modified Hummer's method at room temperature. In this method we don't require any ice bath and $NaNO_3$ (Sodium nitrate) to form graphene oxide. [4]

Nitrogen doping of Graphene Oxide using Urea (CH_4N_2O)

Graphene has several applications in countless zones, example given is energy storage, electrocatalysis, electronics just because of its properties like specific high surface area and charge carrier mobility is high. The graphene oxide is also used in a broad way in fuel cells, electrochemical sensors, voltammetry sensors. It is worth to grow N-doped carbon materials which have tremendous durability, good catalytic activity, little cost for ORR which is compulsory for energy devices such as metal-air batteries, fuel cells. [5]

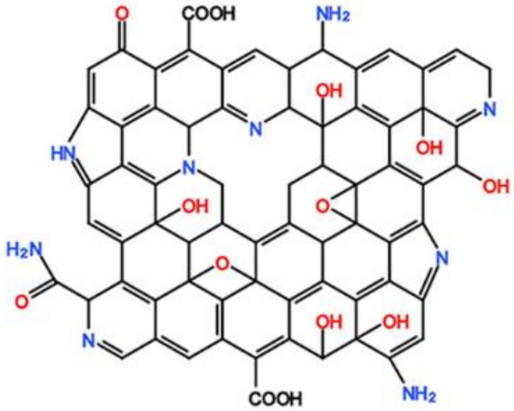

Fig. 1.3 Nitrogen functionalized Graphene Oxide

Nitrogen doping means substituting the oxygen groups with nitrogen groups in graphene lattice. This is generally done by various chemical or thermal routes involving nitrogen precursors.

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Chapter 2

Literature Review

Overview

This chapter gives the information about the research/journal papers which were studied as a part of the literature survey. The first zone represents the mandatory research papers for the basic familiarity of Graphene and Graphene Oxide. This also includes the different ways of synthesis of Graphene Oxide and involved the characterization also. The second section gives knowledge about the nitrogen doped graphene oxide and synthesis of Nitrogen doped graphene oxide and its electrochemistry.

2.1 Introduction & Synthesis of Graphene Oxide

J. F. Shen et al 2009 (1). Graphene is basically a single layer of carbon atoms having a closed packing honeycomb structure having two-dimensional lattice. The basic policy for preparation of graphene oxide using graphite through reaction with strong oxidising agent Benzoyl Peroxide. The graphene oxide's mechanism involves the formation of oxygen holding groups on graphene sheets. This functional groups decline the Van der Waals interaction amongst the layers of graphene oxide and make them hydrophilic. This suggest that raw graphite, when treated directly by suitable chemical, gladly forms graphene oxide.

J. Chen et al 2013 (2). An improved Hummer's method in which we don't use $NaNO_3$ and ice bath to obtain graphene oxide which is closely to similar as prepared by straight Hummer's method. This variation does not decrease the harvest of material, eliminating the evolution of N_2O_2 and NO_2 toxic gasses. The exclusion of $NaNO_3$ do not affect the harvest of overall reaction. By using improved Hummer's method, we can prepare GO in huge scale. Raman spectroscopy, TGA and FTIR indicated the fruitful preparation of graphene oxide. X-ray diffraction demonstrated the mechanism of intercalation and exfoliation of graphite.

L. Stobinski et al 2014 (3). The layered graphene oxide which are formed by the oxidation reaction are structurally, chemically examined by XRD technique, TEM (transmission electron microscopy) and XPS (X-ray photoelectron spectroscopy). The Scherrer's equation using a constant equal to 0.9 is applied to reflecting planes for estimating the average height of stacked layers, meant as H. These methods exposed the stacked nanostructure parameters like average height, diameter, number of layers, spacing between layers and chemical bonds of oxygen groups.

N. I. Zabba et al 2017(4). Single atomic plane layer of graphite called graphene. Graphene can produce from graphite using by chemical vapor deposition, mechanical or chemical methods. As compared to other carbon materials, graphene contains higher mobility, young modulus and thermal conductivity. The influence of different solvents on the structure and electrical properties of graphene oxide was obtained using raw graphite by using modified Hummer's method without sodium nitrate and ice bath at room temperature. Ethanol is more advantages than that of acetone
in form of conductivity of electrical and solubility of Graphene Oxide. These finding is confirmed by the SEM, XRD result, FTIR spectre and I-V curves.

T. F. Emiru et al 2017(5). Graphene based constituents have many potential applications like light weight, flexible, strong display screens, thin, super capacitors and electric circuits. graphene oxide was synthesized by treating graphite powder with $KMnO_4$ and a blend of concentrated H_2SO_4 & H_3PO_4. The prepared GO is characterized using UV–Visible spectroscopy, FT-IR spectroscopy, and XRD. The results displayed that treating graphite powder with $KMnO_4$ at 40°C for 12 h, resulted in better degree of oxidation.

2.2 Synthesis of Nitrogen doped graphene oxide and its Electrochemistry

S. Sarma et al 2017(6). In this we studied that nitrogen doped graphene oxide is gained using urea. For this we take 80mg of graphene oxide powder and make its solution of 50ml by ultrasonication. Then 80mg of urea is added in this solution and microwave it for 100 seconds. Again, this process is repeat and then this solution put in microwave for 400 seconds. The solution obtained after 400 seconds gives higher magnetization, examined by M-H hysteresis loop. The characterization performed for NGO is XPS, UV-VIS, Raman spectroscopy. This study provides information about graphitization, electronic properties, basic properties of NGO. This has attractive applications for the optoelectronic, FET and junction devices.

B. Ghosh et al 2018(7). Due to its specific high surface area and charge carrier mobility of graphene oxide, it discovers for potential use in many applications such as catalysis, electronics, energy storage and magnetic. In this study we found that the synthesis of NGO is synthesize with four types of nitrogen contained precursors like $C_6H_{12}N_4$, NH_4OH, CH_4N_2O, and C_2H_3N. Between these four precursors $C_6H_{12}N_4$ only gives the higher magnetization. On further doping with Fe_2O_3, its ferromagnetism is increased and study its structure as well as bonding properties. Which help in many magnetic devices and electronic devices applications.

M. Vikkisk et al 2014 [8] – In this review, nitrogen doped graphene Nano sheet were made with the help of precursor nitrogen and GO which is made by modified hummer method. Nitrogen precursor used are dicyandiamide and urea at temperature 800°C. The characterization used are X-ray photoelectron spectroscopy and SEM in which X-ray is the most successful method to reveal nitrogen doping. With the help of XPS it is observed that the level of nitrogen is 5%. Alkaline medium is used to characterise the NG materials.

H.M. Yusoff et al 2016 [9] – in this review, N-RGO is prepared from GO then both the materials i.e. GO and N-RGO were characterised by many characterisations like FTIR, SEM, TEM to observed the difference between chemical structure, their morphology and chemical bonds. With the help of SEM results it is observed that both the materials are defected but FTIR shows that the results of SEM are corroborated because of absence of OH- and C-O bond.

T. Jin et al 2018 [10] – According to this review NGOM can be formed when there is crosslinking of GO with four different aliphatic amines like EDA, DMPDA, IPEDA and TETA. After this crosslinking, it is observed that these NGOM generated have different morphology, d spacing layer and morphology size. The characterization like FTIR and XPS shows that there is covalent bond C-N or C=N form. When GO is crosslink with primary amine like DMPDA and IPEDA then the steric structure is formed. When two crosslinks are attached then heterocyclic N-compounds help the formation of crosslinked structure.

A.Z Moghaddam et al 2019 [11] – To remove the chromate from the surface of GO and NGO, a magnetic nanocomposite was prepared having best adsorbent properties i.e Glutaraldehyde cross-link coated Fe_2O_3. This composite has low cost and also eco-friendly. The method used to increase the efficiency is RSM. The time taken to achieve equilibrium stare is 60 min. and 45 min. for MCC@NGO and MCC@GO. The MCC@NGO is better than the MCC@GO.

F.N. Indah Sari et al 2015 [12] – in a microwave assisted hydrothermal (HMT) method, nitrogen doped graphene can be easily synthesised. In MHT, GO is diminished using ethylene glycol to get graphene and nitrogen source used is ammonium liquid. This is an easy and proficient path for getting NDG and level of nitrogen is high. Ammonium is used as precursor and GO is graphene. Using NDG as supercapacitor electrode by which specific capacitance increase by 54%.

Z. Yu et al 2017 [13] – in this review mesoporous silica film is used to synthesize 2D nitrogen doped mesoporous carbon after that this is studied as non-precious metal for the ORR. The characterization used for this are TEM, XPS, CV and RDE and results get from shows that carbon catalyst have high electronic surface area.

B. Xie et al 2019 [14] – In this study, an NGA is prepared with the help of facial one pot assembly. To get high ORR current density, a metal free from NGA but have high quality of rich microspores in walls and large content of nitrogen due to large quantity of nitrogen atom and there is increase an adsorption of O_2 in NGA.

Y. Wang et al 2010 [15] – when a chemical doping is done with foreign atom then the properties of host material increased. Among all, the doping of nitrogen is very effective to increase the electronic properties which are used as biosensors and in biomedical. In this study, N-doped graphene is prepared with the help of chemical method.

B. Yao et al 2017 [16] – supercapacitors and Li-S batteries are the paper-based material used as energy storage device. In this study the development of paper-based material as electrode for storing energy device is done but the only problem face is that these materials are capable of controlling the mechanical and structural changes takes place during large volume change. An ideal electrolyte should be highly flexible, eco-friendly.

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Chapter 3

Materials and Methods

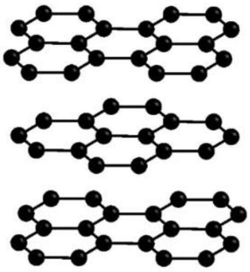
Overview

This chapter designates the materials that are used for the synthesis of graphene oxide and its nitrogen doping. Also, the characterization techniques that are necessary for the investigation of the same.

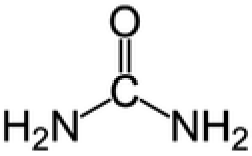
3.1 Materials

The following reagents were used for the synthesis work:

1) **Benzoyl peroxide ($C_{14}H_{10}O_4$):** BPO with 25% H_2O, Extra pure is purchased from Loba Chemie pvt. Ltd.
2) **Sulphuric acid (H_2SO_4):** This is a one of the strong acids having molecular formula H_2SO_4. It is colourless and odourless and thick liquid resolvable in water and in synthesizing reactions it is highly exothermic. The sulphuric acid used for the test was of purity 98% and bought from Loba Chemie pvt. Ltd.
3) **Phosphoric acid (H_3PO_4):** A weak acid with chemical formula H_3PO_4 with IUPAC name Orthophosphoric acid. As Phosphoric acid is not belonging to the class of strong acid but the 85% solution is enough acidic for corrosion. This was bought from Loba Chemie.
4) **Graphite (C):** Basically, graphite is a crystalline form of carbon and its atoms are organized in a hexagonal assembly. It is a semi metal, a native element mineral and one of the allotropes of carbon. Graphite powder, <20µm is purchased from Avra Synthesis Pvt. Ltd.



5) **Potassium permanganate ($KMnO_4$):** It is an inorganic compound having chemical recipe $KMnO_4$. It is strong oxidising agent. It is bought from Loba Chemie Pvt. Ltd.
6) **Hydrogen peroxide (H_2O_2):** It is a transparent liquid & a little additional viscous than water. It is used as an oxidizer and bleaching agent. It is bought from Loba Chemie Pvt. Ltd.
7) **Deionized water:** With resistivity of 18.2 MΩ, deionized water is obtained from Millipore Q3 system, used in the experiment to dilute the HCl.
8) **Hydrochloric acid (HCL):** Hydrochloric acid is a strong acid with a distinctive pungent smell. It can attack the human's skin over a wide series until it completely dissociates in aqueous solution.
9) **Urea (CH_4N_2O):** Urea is also meant as carbamide. It is an organic compound with chemical formula CH_4N_2O. It contains two $-NH_2$ groups linked by carbonyl (C=O) functional group. It was bought from Loba Chemie Pvt. Ltd.



10) **Glass wares:** Conical flask is used for proceeding the reaction having a flat bottom, a conical body with a cylindrical neck.

3.2 Methods

The following technique was followed to accomplish the experiments.

3.2.1 Fast & Facile Route for synthesis of Graphene Oxide

1) For this we used graphite of size less than 20µm. Take 5gm of Benzoyl per Oxide and 0.25 gm of raw graphite powder.
2) With the help of Agate Mortar & Pestle, grind them for 15-20 minutes to get a very fine powder without using acetone, transfer the mixture in a beaker and heat it at 110°C.

3) After the explosion and expansion of CO_2 remove the beaker from the hot plate and let the beaker to cool down.
4) Then with the help of ethanol, remove the blackish substance in to another beaker and let it drying for overnight at 80°C [1].

3.2.2 Modified Hummer’s Method

1) Take 54ml of sulphuric acid (H_2SO_4), 6ml of phosphoric acid (H_3PO_4), mix them in a conical flask and stirred for ten minutes at room temperature using magnetic stirrer.
2) Then 0.45g of graphite powder then added into the mixing solution in stirring condition. 2.64g of potassium permanganate ($KMnO_4$) is then added gradually into the solution within a time period of half an hour.
3) This mixture is stirring for 6hours until the solution become dark green.
4) To removing the excess of $KMnO_4$, 1.35ml of H_2O_2 gone dropped slowly and again stirred for 10-15 minutes. An exothermic reaction take place and left the solution for cooling at room temperature.
5) Take 20ml of HCl & 60ml of deionized water and mix them and make a solution of 80ml. this solution then added to the mixing solution. A vigorous exothermic reaction was taken place and mixing solution become very hot.
6) On the completion of reaction, the solution was cooled at room temperature and centrifuged at 12000rpm for seven minutes. Then supernatant was poured out away and residuals then again rewashed with the solution of HCl & DI water for 2 times for removing the excess of sulphate ions.
7) Then again centrifuged the sample to getting the pH of sample neutral. Then washed remaining black precipitate of GO solution was dried in oven at 80°C for overnight to yield the powder of graphene oxide [2].

3.2.3 Nitrogen doping of Graphene Oxide using Urea in microwave with open microwave safe container and with the usage of Teflon autoclave

1) 100ml of aqueous solution of graphene oxide in which 0.16g of graphene oxide powder is present, was prepared by ultra-sonicating for 50-60 minutes.
2) 0.16g of Urea (CH_4N_2O) was then added & again sonicate for another10 minutes.
3) Using Teflon autoclave & a microwave safe container, put half of solution(50ml) in the container and left half 50ml solution in the Teflon autoclave. Then firstly put the open container covered with a loose lid to allow the expansion in standard household microwave and heated for 400 sec. at maximum power output. After that, put autoclave in the microwave and again heat for 400 seconds.
4) Both the solutions were cooled at room temperature and fill that solutions in properly marked Oakridge tubes. Then centrifuged at 10,000 rpm for 10-12 minutes.
5) The clear supernatant obtained after centrifuge was separated and black precipitate were further washed in deionized water for two times by centrifuge at 10,000 rpm for again 10 minutes for both cases.
6) The final slurry was left to dry in oven at 90°C for overnight to produce nitrogen doped graphene oxide using autoclave & open beaker process [3].

3.3 Characterization Techniques

3.3.1 X-Ray Diffraction

X-Ray Diffraction is a famous technique for phase examination, atomic spacing as well as crystal structures. Its basically used to calculate average spacing in the stacked layers of material. Its principle is grounded on the constructive interference of homochromatic X-rays and the sample which are crystalline in nature. The X-rays used for this technique is created by using a CRT (cathode ray tube) which acts as filters and produce homochromatic radiations. Then this radiation is focused to fall on the sample which has to be analysed. The incident rays which interacting with the sample helps to produce constructive interference only if it satisfies the Bragg's Law.

$$2d \sin \theta = n \lambda$$

Where d is the diffracting planes spacing, θ is the angle of incidence, n is any integer and λ = 1.54Å (X-ray Wavelength)

In way to investigate proper information about the crystalline structure, number of layers and interplanar spacing, XRD plays a very prominent role for graphene oxide. So, it widely used technique for characterization. To determine the distance(d) between the layers of graphene, we use Bragg's equation which is

$$2d \sin \theta = n\lambda,$$ where value of n is one.

The Scherrer's equation is applied with a constant 0.9 to (002) reflection to measure the average height of stacking layers of graphene oxide denoted as H. The Scherrer's equation with Warren constant of 1.84 is applied to two-dimensional (10) reflection to measure the average diameter of stacking layers denoted as D. We apply Pearson seven Fitting to the XRD data to get the FWHM(β) values. [4]

Scherrer's equation:

$$\tau = K \lambda / \beta \cos \theta$$

where:

τ is the crystalline size.

K is dimensionless means a constant having value equal to 0.9 for 3-D reflection and 1.84 for 2-D reflection.

β is the FWHM.

θ is the Bragg angle.

For the X-ray measurements, we used Panalytical's XPERT PRO. From SAIF PU. The step size was 0.013 and angle of measurements was from 5°-70°.

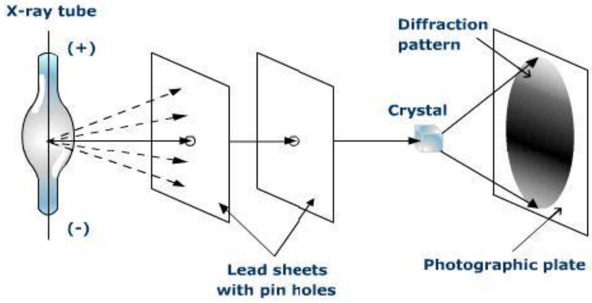


Fig.3.3.1 Systematic image of XRD

3.3.2 Fourier-transform infrared spectroscopy (FTIR)

FTIR is a spectrometer and an optical instrument which is basically used to determine properties of light over a specific range of electromagnetic spectrum. A Michelson interferometer is used in the FTIR spectrometer. In this technique the sample is pounding with the infrared radiation. The frequency of infrared radiation when coordinate the natural frequency of the bond at that time the amplitude of the vibrations increases and infrared is absorbed. In results we get a chart between the %Transmittance and wavenumber. [5]

We used FTIR Spectrophotometer Perkin Elmer MODEL RZX, from SAIF PU. The measurements were taken from 500cm^{-1} to 4000cm^{-1}.

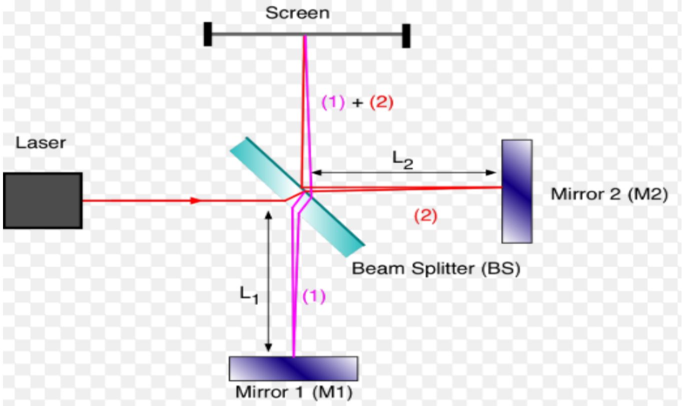


Fig. 3.3.2 Internal Diagram of FTIR

3.3.3 Raman Spectroscopy

Raman spectroscopy is a technique which generally used for the characterization of carbon products and depends on Raman effect. The Raman effect says that the frequency of scattered radiations by the sample is different from the frequency of incident monochromatic radiations. For Raman characterization, there is no sample preparation is required. It depends upon the polarizability of molecule's electron cloud. Raman spectroscopy works on the incident inelastic scattered radiations along its interaction with the vibrating molecules. In this technique the sample which has to be analysed is irradiate with monochromatic laser beam which falls on the sample and interact with the vibrating molecules of the sample and thus creates a scattered light. Then this scattered light containing different frequency than that of incident light which helps to creates a Raman Spectra.[6] This spectrum comes out between Raman shift(cm^{-1}) and intensity (a.u).

We done the Raman Spectroscopy from AIRF, JNU Delhi, with a solid-state laser (531nm).

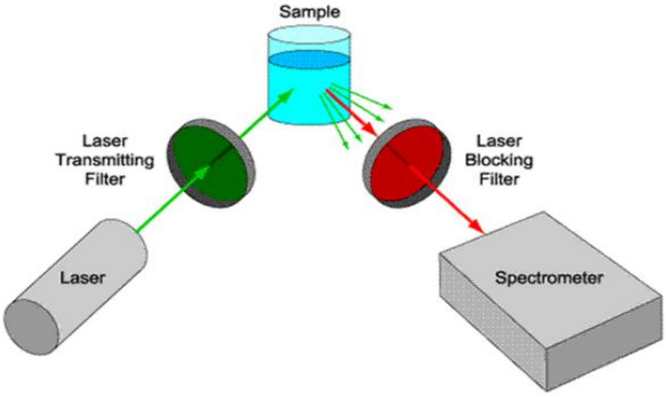


Fig.3.3.3 Systematic diagram of Raman Spectroscopy

3.3.4 Thermal Analysis

Thermal analysis is a bunch of techniques which are used to examine the change in the chemical or physical properties of the sample with respect to the temperature or time while the temperature for analysing a sample is already programmed. This temperature program involved the cooling as well as heating at a fixed rate. The sample is basically in solid form and the change we notice consist of sublimation, phase transitions, decomposition and melting.

TGA is thermogravimetric analysis gives the weight loss or change in mass of the sample while giving heat treatments. Also, DTA (Differential thermal analysis) gives difference of temperature between the given sample and inert substance which acts as a reference material. The DTG gives information about the reaction is endothermic or exothermic. The endothermic reaction which shows absorption of energy consist of sublimation, adsorption, vaporization and gives downward peek in the results. On the other side, exothermic reactions which shows releasing of energy consist of polymerization, catalytic reactions, oxidation and gives upward peek. [6]

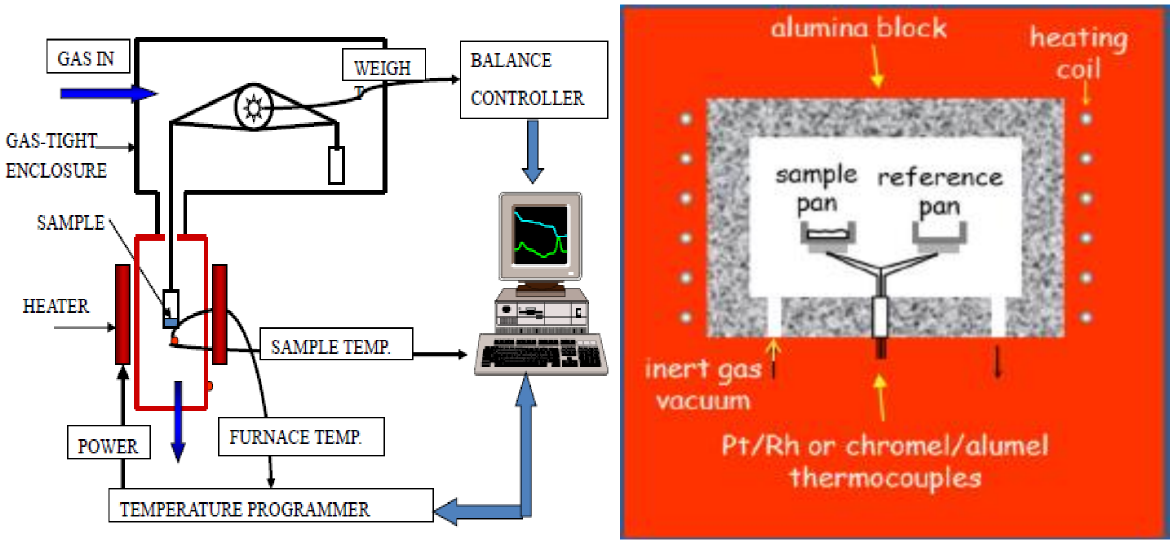


Fig.3.3.4 (a) Thermogravimetric Analysis & **(b)** Differential thermal analysis

3.3.5 Scanning Electron Microscopy & Energy Dispersive X-ray Spectrometer

The characterization scanning electron microscopy is commonly used to get high resolution image of the surface of the sample. This technique used electrons for getting high resolution image. The qualitative and quantitative information about chemical analysis will also be obtained by EDX or EDS spectrometer which is further a part of SEM. The SEM forms an incident beam of electrons in the sample chamber which maintained at vaccum conditions. These electrons are generated by using a tungsten filament and this is known as thermal emission source.

The EDX is conjugate with the SEM. The basic work of EDX is that it recognizes the X-ray which emitted by the sample at the time of irradiation with the incident beam just to characterize the chemical or elemental composition. EDX can detects the material which was even present in very small size. [5]

We done the SEM analysis using JEOL JSM-6510LV model from SAI Labs TIET Patiala.

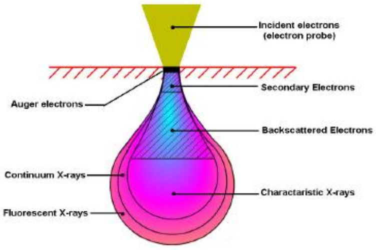


Fig. 3.3.5 Diagram of Electron beam interaction

3.3.6 DC resistivity and Impedance measurements

For the impedance analysis and DC resistivity measurements the 10 mm diameter pellets of MH1, NGO-Open & NGO-AC were formed (without any binder) using 0.25 g powder. Silver paste was applied for contact formation. The DC resistivity measurements were taken on KEITHLEY 2410 1100V Source Meter. The voltage range is fixed from 0V to 20V.

Fig.3.3.7 Instruments of DC resistivity

3.3.7 Electrochemical capacitance measurements

Standard three electrode setup in a Bio-Logic EC Lab SP300 with has been used to check the electrocatalytic capacitance performance of the synthesized GO and doped-GO samples in acidic medium. Reversible hydrogen electrode (RHE) is used as reference electrode with the graphite rod as counter electrode. The working electrode consists of glassy carbon electrode loaded with sample. These were immersed in 1M H_2SO_4 solution for the electrochemical studies. Prior to the actual measurement, the pre-treatment of the working electrode/sample was carried out by cycling the potential between -0.245 V and +1.24 V (sweep rate of 20 mV/s for 30 cycles) for the removal of surface contamination, catalyst activation and electrochemical current stabilization. This is followed by recording of the cyclic-voltammetry (CV) in the range of +0.245 - 1.24 V at different scan rates (2-200 mV/s) for determination of the electrochemical capacitance. [7]

Electrode fabrication: For the preparation of the working electrode, considered sample (~1.0 mg) was dispersed in ethanol (250 μL) and Nafion®117 (Sigma Aldrich; 40.0 μL) through ultrasonication (30 min). Thereafter, 20 μL dispersed solution was drop-casted on the cross-section of GCE ($A = 0.07065\ cm^2$; $\phi = 3$ mm) and dried overnight at room-temperature providing the catalyst loading ~ 0.976 mg/cm^2.

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Chapter 4

Results and Discussions

Overview

This section contains the experimental outcomes of different characterization techniques. The techniques such as XRD, FTIR, Raman Spectroscopy, TGA/DTA/DTG, SEM, EDX, impedance is used.

This chapter is divided in two sections: a) the synthesis and characterization of Graphene oxide (GO) and b) the Nitrogen doping of GO using microwave.

Section A

Table 4.1 gives details of the various samples synthesized using the fast and facile method as well as the modified Hummer method. The details of the synthesis conditions are given in chapter 3.

Table 4.1: Details of the samples synthesized.

Sample ID	Synthesis Method	Synthesis Temperature	Time	Product(s)
FF1	Fast & facile route	110°C	5 min.	Graphite
FF2	Fast & facile route	110°C	5 min.	Graphite
MH1	Modified Hummer	Room Temperature	6 hrs	Pure graphene oxide with 5.3 layers
MH2	Modified Hummer	40°C	6 hrs	Pure graphene oxide with 1 layer
MH3	Modified Hummer	40°C	4 hrs	Pure graphene oxide with 7 layers
MH4	Modified Hummer	40°C	2 hrs	Pure graphene oxide with 7 layers

4.1 XRD

Fast and facile method uses a strong oxidising agent which is Benzoyl Peroxide (BPO). In FF1 we use 5gm of BPO and 0.25g of raw graphite powder and in case of FF2, we just double the quantity that is 10gm of BPO and 0.5g of raw graphite powder. XRD analysis shown in fig. 4.1, that the product is still graphite ((ICDD card number 00-001-0640) and no GO has been formed [1].

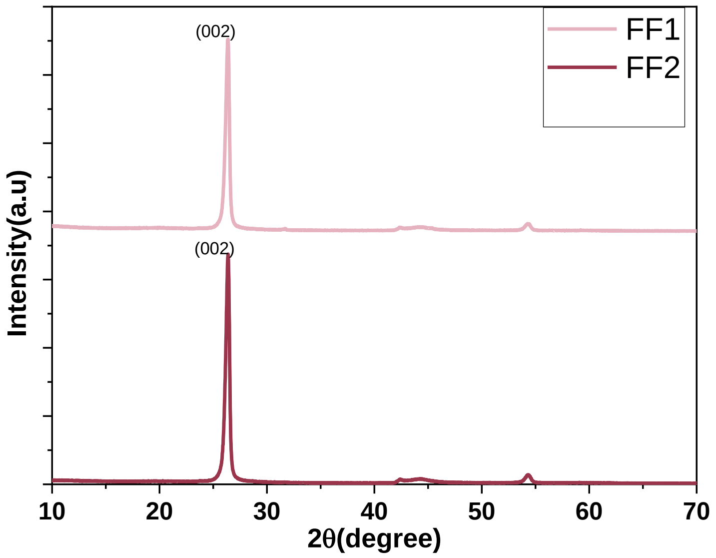


Fig.4.1 XRD data of FF1 and FF2

The XRD line profiles for the as prepared samples using the modified Hummer's method are given in fig. 4.2. The data clearly shows that the GO has been synthesized with two characteristic peaks at 2θ=10.06 (002) and 2θ=42.19 (10). The characteristic peaks have been fitted with the Pearson VII peak function using Origin Pro™ (Figure 4.3). The results of the HRD line analysis are given in Table 4.2.

The maximum yield was obtained for sample MH1. XRD analysis shows that it is a 5-layer sample consisting of graphene oxide flakes of ~ 13 nm. The XRD analysis shows that as the synthesis time increases from 2 hr to 6 hr (Samples MH4 to MH2) the number of layers change from 10 to 1.

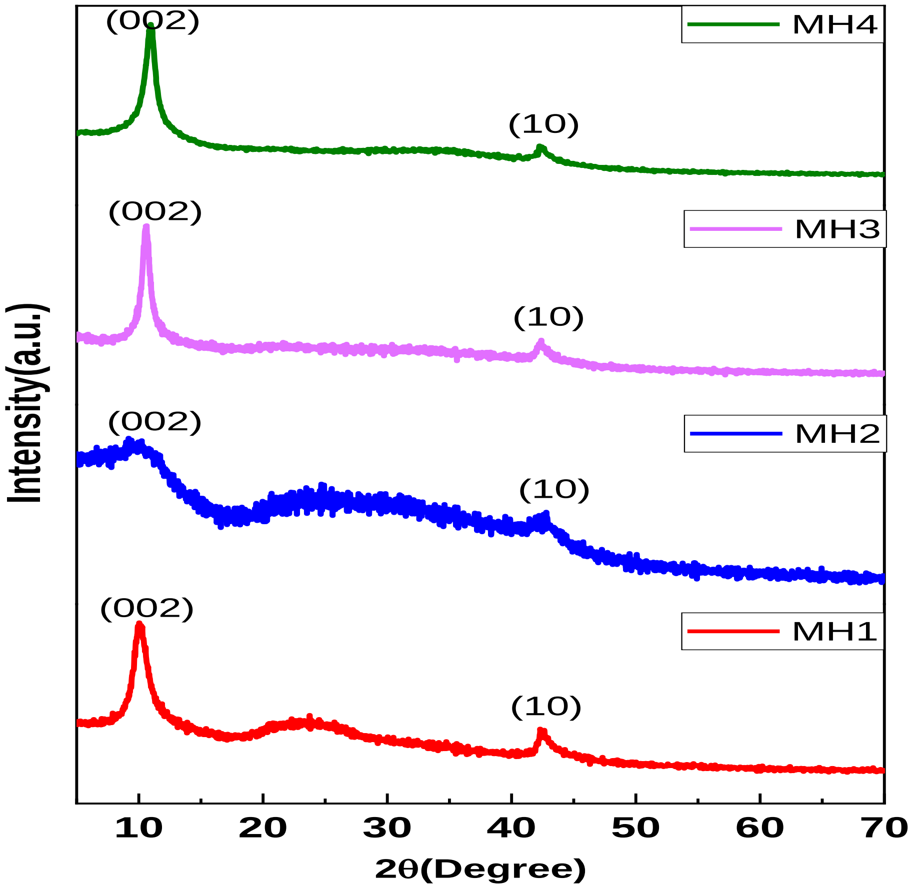


Fig.4.2: XRD line profiles for the samples synthesized using modified Hummer's method

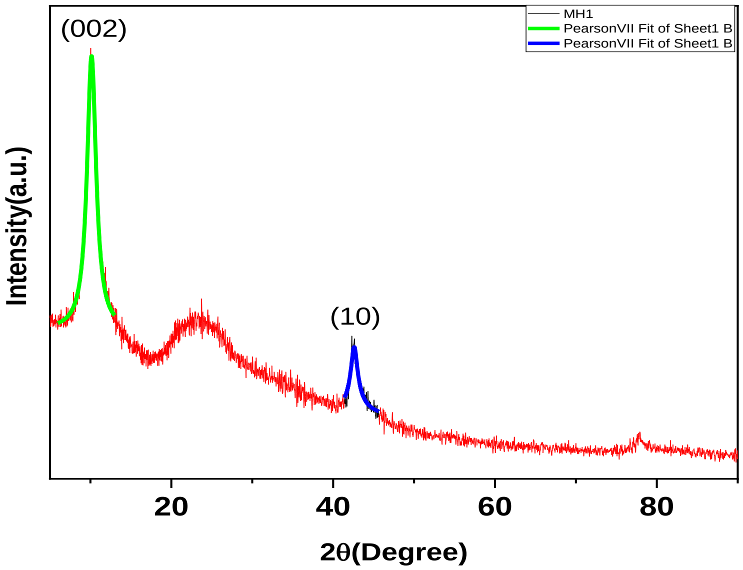


Fig.4.3: Pearson VII fitting of XRD line profile for MH1 sample.

Table 4.2: Table for the calculations of average height (H) and diameter (D) of stacking layer of graphene oxide using the XRD line profile analysis

Samples	**2θ (Deg.)**	**FWHM (Deg.)**	**H(nm)** $\tau = K \lambda/\beta \cos\theta$	**d(nm)** $2d \sin\theta = n\lambda$	**No. of layers(n)**	**2θ (Deg.)**	**FWHM (Deg.)**	**D(nm)** $\tau = K \lambda/\beta \cos\theta$
MH1	10.06	1.36	5.85	0.87	5	42.31	1.35	12.9
MH2	9.01	6.22	1.28	0.02	1	42.19	4.77	3.6
MH3	10.59	1.09	7.74	0.83	7	42.57	1.09	15.9
MH4	10.58	1.21	10.9	0.83	10	42.40	1.21	14.3

4.2 Fourier-transform infrared spectroscopy (FTIR)

FTIR is a molecular spectroscopy which characterizes organic or inorganic bonds present in the system. The results come out between the wavenumber (cm^{-1}) on X-axis and %Transmittance on Y-axis. The confirmation of oxidation of graphene for samples MH1and MH2 is done with the presence of bands in the FTIR spectra (Table 4.3). In case of MH1, a widest peak occurs at 3413 cm^{-1} which attributes the presence of C-OH stretching vibration of hydroxyl groups. A low intense peak obtained at 1721cm^{-1} because the presence of C=O stretching vibration of carbonyl group. Which present at edges of the plane of graphite layer. The peak at 1571cm^{-1} shows information about C=C skeletal vibration of graphene plane. The peak 1224cm^{-1} & 1051cm^{-1} are corresponds to stretching vibration of epoxy group C-O-C and C-O stretching vibration. Similarly, in case of MH2, the peaks around 3403cm^{-1}, 1717cm^{-1}, 1587cm^{-1}, 1218cm^{-1}, 1051cm^{-1} are corresponding to hydroxyl group C-OH stretching vibrations, C=O stretching vibration of carbonyl group present, C=C skeletal vibration and stretching vibration of epoxy group C-O-C and C-O stretching vibrations[3].

Table 4.3: Table for the FTIR data analysis

MH1 peaks (cm^{-1})	**MH2 peaks (cm^{-1})**	**Identified bonds**
3413	3403	C-OH stretching vibration of hydroxyl group
1721	1717	C=O stretching of carbonyl group
1571	1587	C=C skeletal vibration of graphene plane
1224	1218	C-O-C Stretching vibration of epoxy group
1051	1052	C-O stretching vibration of epoxy group(C-O-C)

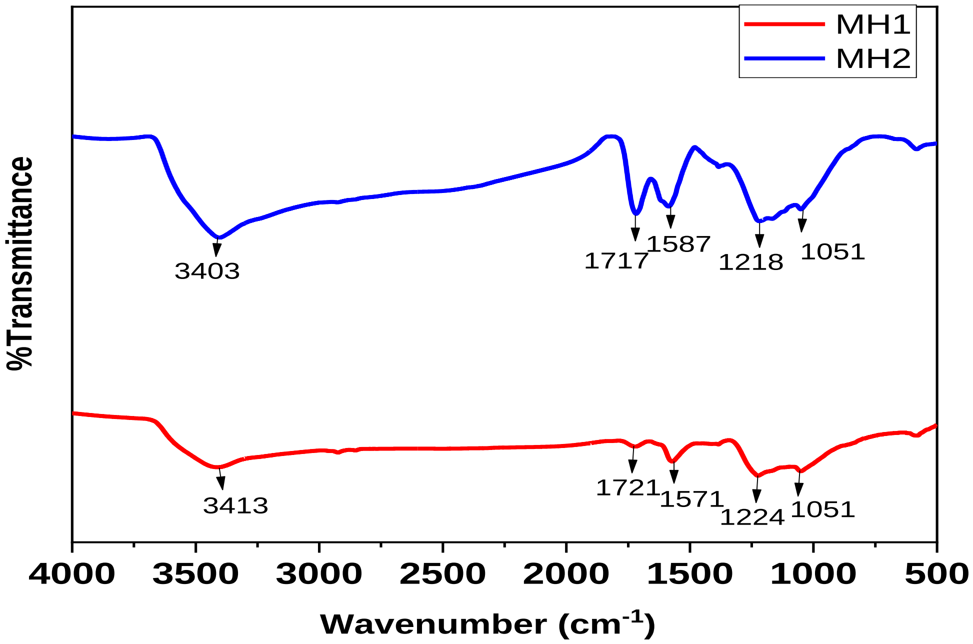


Fig. 4.4: FTIR spectrum of MH1 & MH2

4.3 Raman Spectroscopy

Raman Spectroscopy is a very strong technique which is used for the characterization of carbon products or compounds. Mainly the conjugated and C=C bonds gives high intensities peaks in Raman peaks. A comparison of Raman data for MH1 and MH2 samples shows that the G band broadened and shift little bit towards to 1582 cm^{-1} and 1593 cm^{-1} respectively. The explanation for this kind of behaviour is due to the presence of isolated double bonds which only resonates at high frequency. The intensity of D band is also increasing considerably at 1347 cm^{-1} and 1348 cm^{-1} respectively. The large intensity and line width of D band as compare to the G band shows that there is more disorder present due to defects arising from strong treatment with the chemicals. The number of layers of MH1 and MH2 is 5.3 and 1.1 respectively.

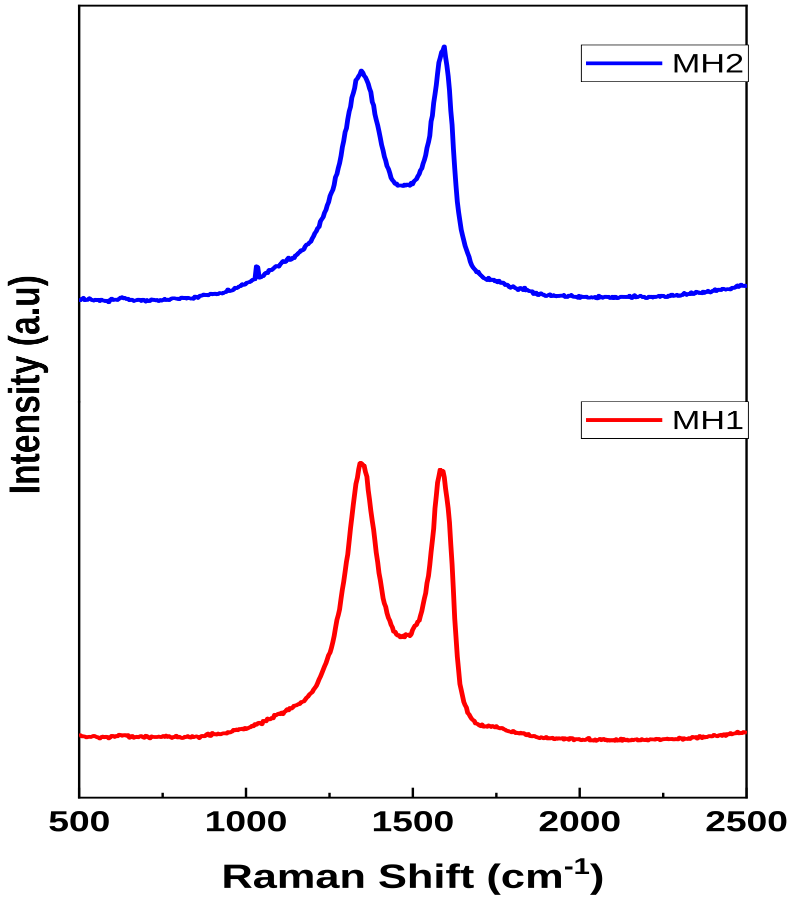


Fig. 4.5 Raman Spectra of MH1, MH2

4.4 Thermal Analysis

The TGA was taken for MH1 sample in the air atmosphere at the rate of 5 °C/min. Graphene Oxide shows low thermal stability which may be due the presence of interlayer spacing arising due to the reduction of van der wall interactions between the layers at the time of oxidation reaction. Graphene Oxide initial weight loss is due to the evaporation of absorbed water molecules during the reaction because we use the DI water. Significant weight loss (20%) of GO occurs around 200 °C with a corresponding exothermic peak in DTA. This is due to chemicals decomposition of oxygen containing functional groups such as carboxyl, hydroxyl etc. Also, above 600 °C, there was steady weight loss due to removing of more stable oxygen groups like epoxy groups. The DTA cure showing that the reaction is exothermic up to 200°C. After that the reaction becomes exothermic in nature [1]. Above 700 °C the weight becomes zero indicating the complete decomposition and also purity of the sample

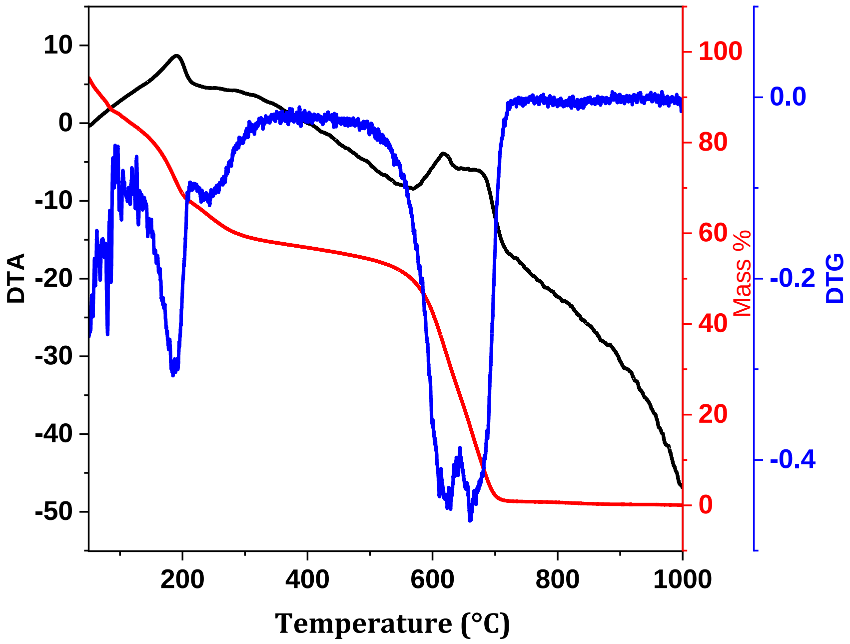


Fig. 4.6 TGA/DTA/DTG analysis of MH1

4.5 Scanning Electron Microscopy

For SEM analysis, the samples (MH1, MH2) are dispersed in the ethanol by ultrasonication method for 1 hour and then deposited on carbon tape. The morphology of both samples shows clustered flakes (Fig 4.5). The SEM images for the MH1 sample show layered structure and are larger in size compared to sample MH2 (fig 4.5 (b)). In both the cases, the surface reveals wrinkles and the thin edges are shown clearly.

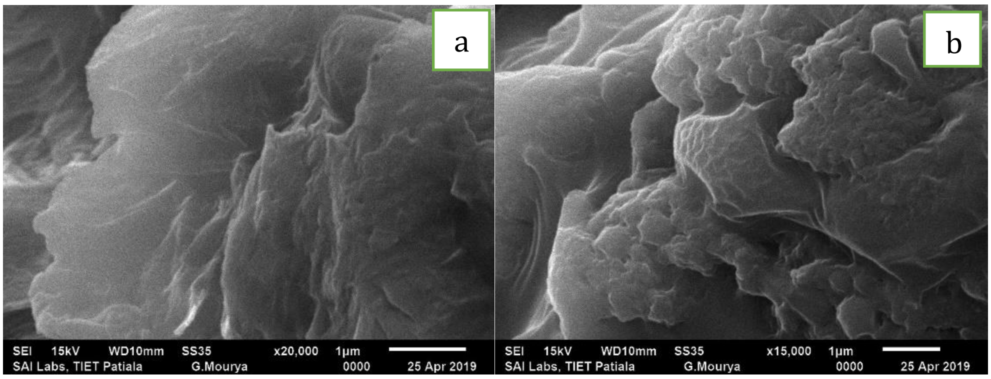


Fig. 4.7 SEM micrographs of (a) MH1 & (b) MH2

4.6 Energy-Dispersive X-ray Spectroscopy

To approve the existence of carbon and oxygen in case of sample MH1, we done the EDX analysis. This again supports the TG data showing that the sample consists of only C and O with no impurities.

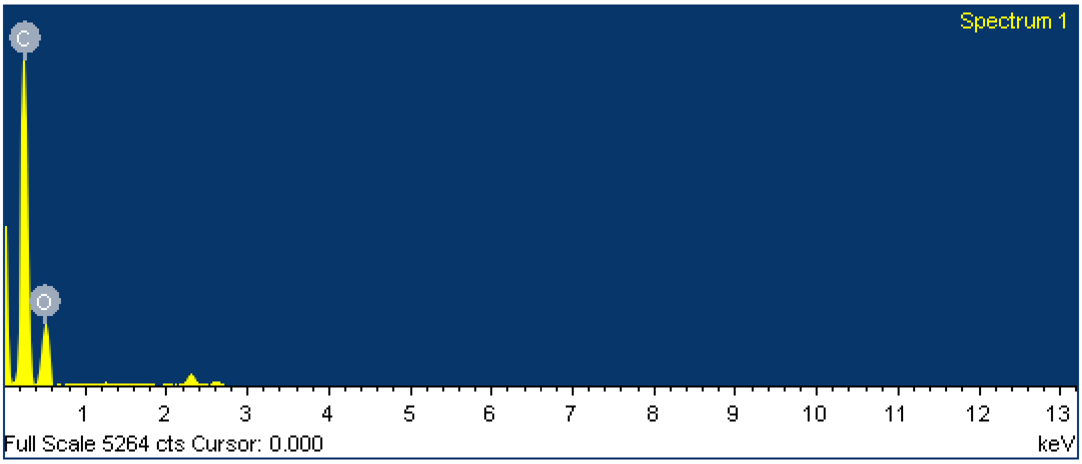


Fig.4.6 EDX data of MH1

Section B

This section tells about the results and discussion of nitrogen doped graphene oxide.

Table 4.4 gives details of the various nitrogen doped samples synthesized using the microwave technology method. The detalis of synthesis conditions are given in chapter 3.

Table 4.4: Details of the nitrogen doped samples synthesized.

Sample ID	Equipment	Time (s)
NGO-80OP400	Microwave Safe Container	400
NGO-80AC100	Teflon Autoclave	100
NGO-80AC300	Teflon Autoclave	300
NGO-80AC400	Teflon Autoclave	400

4.7 XRD

In this we have done the XRD of NGO-80OP400 and NGO-80AC400. In case of NGO-80OP400 (2θ=11.2°, 2θ=23.5° and 2θ=42.7°) there is a partial formation of nitrogen doped graphene oxide because a peek of graphene oxide is appears at 2θ=11.2°. Also in case of NGO-80AC400, a complete nitrogen doped graphene oxide is formed. A intense peek is obtained at 2θ=24.2° which shows the presence of nitrogen in our samples and 2θ=42.7°[4].

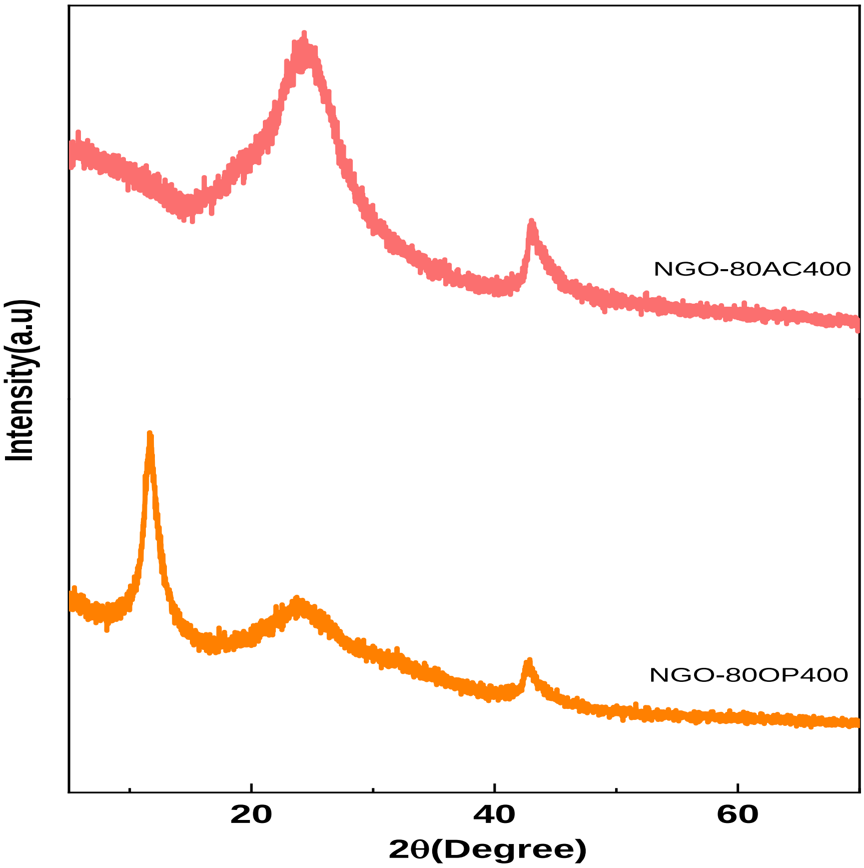


Fig.4.7 XRD data of NGO-80OP400 & NGO-80AC400

4.8 FTIR

In case of nitrogen doping of graphene oxide (NGO-80OP400 and NGO-80AC400) which represents that NGO-80OP400 is formed when we place the beaker open in to the microwave. Also, NGO-80AC400 is prepared when we use autoclave for the nitrogen doping of GO. The nitrogen doping of graphene oxide is confirmed by FTIR spectra which contained several bands (Fig 4.8, Table 4.5). The broad band that occurs around 3382cm^{-1} and 3380cm^{-1} reveals N-H & hydroxyl -OH stretching. The peaks at 1725cm^{-1} & 1716cm^{-1} are obtained due to the presence of C=O stretching vibrations of carbonyl groups. Also, the peaks around 1574cm^{-1} & 1567cm^{-1} shows the nitrogen doping and gives the evidence of presence of amide group(-NH_2). The peaks in FTIR spectra shows at 1215cm^{-1} and 1203cm^{-1} attributes to the presence of C-N bonds. The stretching vibrations of C-O obtained at 1060cm^{-1} & 1054cm^{-1} in case of both open and autoclave mode of preparation [3]. The samples named NGO-80OP400 and NGO-80AC400 basically describes that we vary the amount of urea for the nitrogen doping. As we add 80mg of urea for nitrogen doping in case of NGO-80OP400 & NGO-80AC400 but here we add 60mg and 120 mg of urea. Their FTIR spectrum also shows peeks of nitrogen doping around 1500cm^{-1} which represents the amide group(-NH_2).

Table 4.5: Table for the FTIR data analysed of NGO's

NGO-80AC400 (cm^{-1})	**NGO-120OP400 (cm^{-1})**	**NGO-60OP400 (cm^{-1})**	**NGO-80OP400 (cm^{-1})**	**Bond Identification**
3380	3404	3422	3382	C-OH stretching of hydroxyl group
1716	1720	1713	1725	C=O stretching vibration of carboxyl group
1571	1578	1574	1574	C=N bonds and prove the nitrogen doping
1203	1226	1202	1215	This peeks attributes due to the presence of C-N bonds.
1054	1052	1074	1060	C-O stretching vibration of epoxy group(C-O-C)

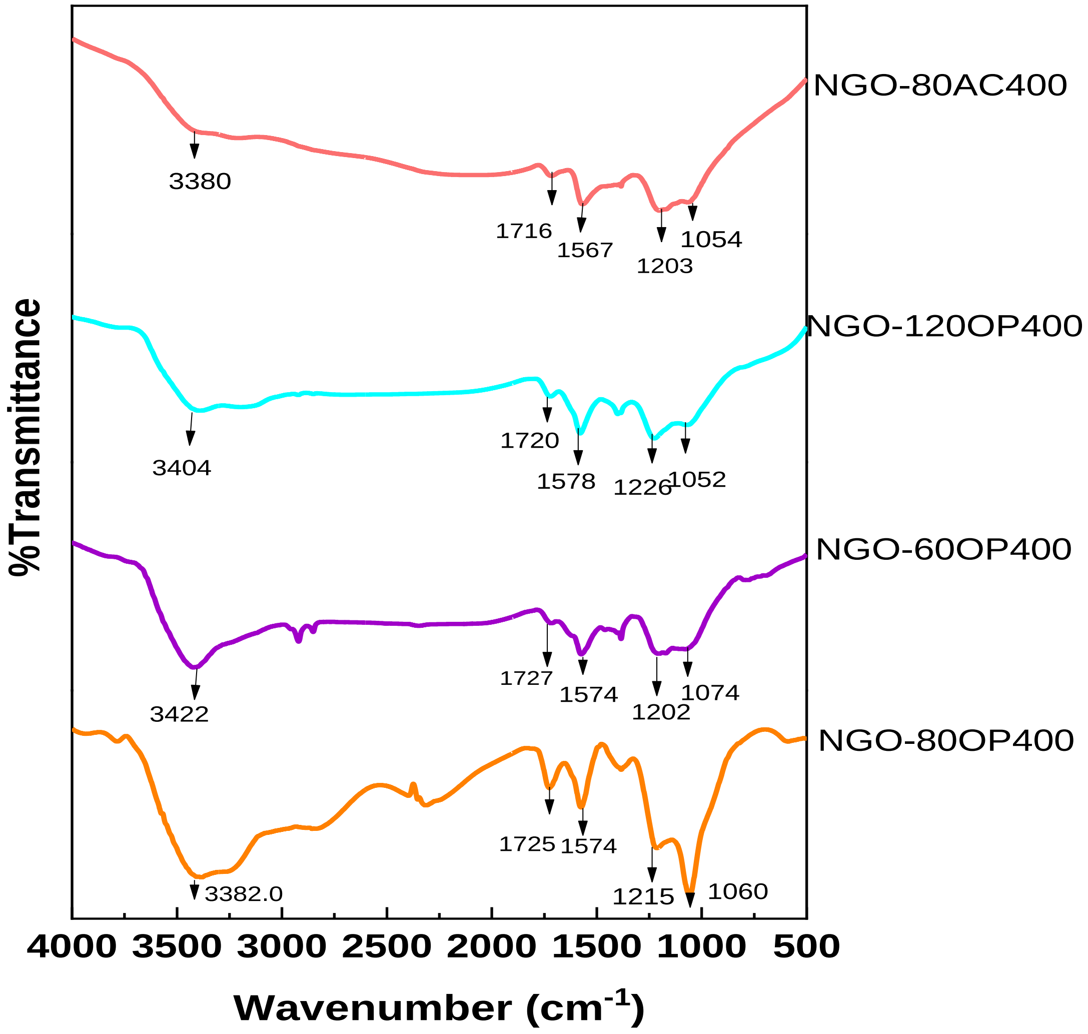


Fig.4.8 FTIR spectrum of NGO-80AC400, NGO-120OP400, NGO-60OP400, NGO-80OP400

4.9 Raman Spectroscopy

Here we have done the Raman spectroscopy data of sample MH1 and NGO-80OP400. On Lorentz fitting of both the samples, we get the value of FWHM and determined the I_D/I_G value and ΔG for the samples (Table 4.6). where ΔG indicates the increase in defect density. The ΔG is shifted to negative for nitrogen doped sample. The negative value of ΔG implies that there is increased in defects in nitrogen doped sample [12].

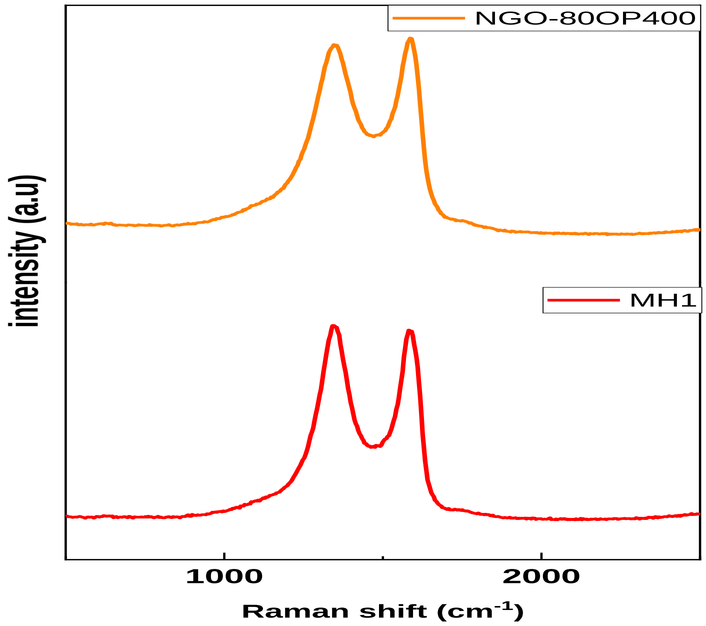


Fig. 4.9 Raman Data of NGO-80OP400 and MH1

Table 4.6: Table for the calculations of Raman Data

Sample ID	**D (cm^{-1})**	**I_D/I_G**	**FWHM(cm^{-1})**	**G (cm^{-1})**	**ΔG**
MH1	1347	1.0	142.9	1582.4	0
NGO-80OP400	1348	0.98	198.4	1580.9	-1.5

4.10 SEM

For the SEM analysis of NGO-80OP400 and NGO-80AC400, we again disperse both the sample in ethanol with the help of sonication. The morphology of both the samples is showing flakes and layered structure with thin edges.

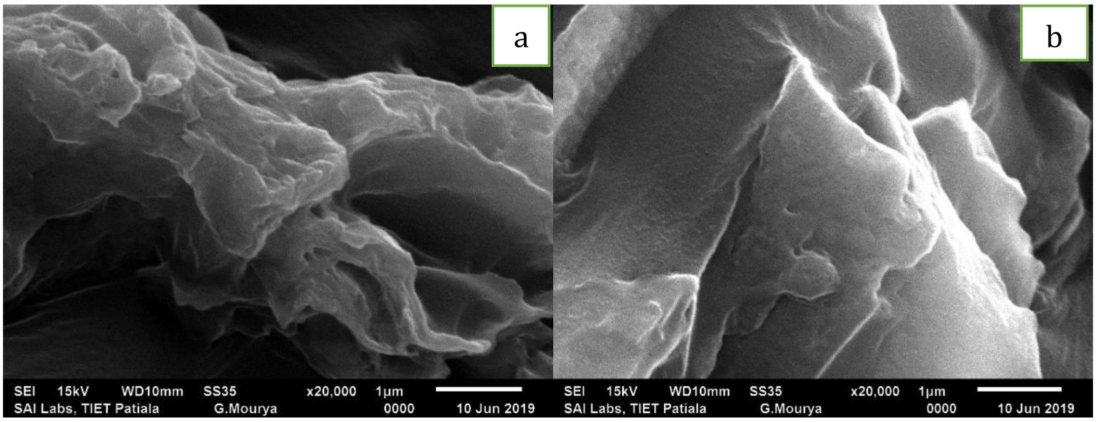


Fig.4.10 SEM micrographs of (a)NGO-80OP400 & (b)NGO-80AC400

4.11 EDX

In sample, NGO-80OP400 and NGO-80AC400 we confirm the presence of carbon, oxygen and nitrogen. Where the presence of nitrogen shows the successful doping of nitrogen using urea in graphene oxide.

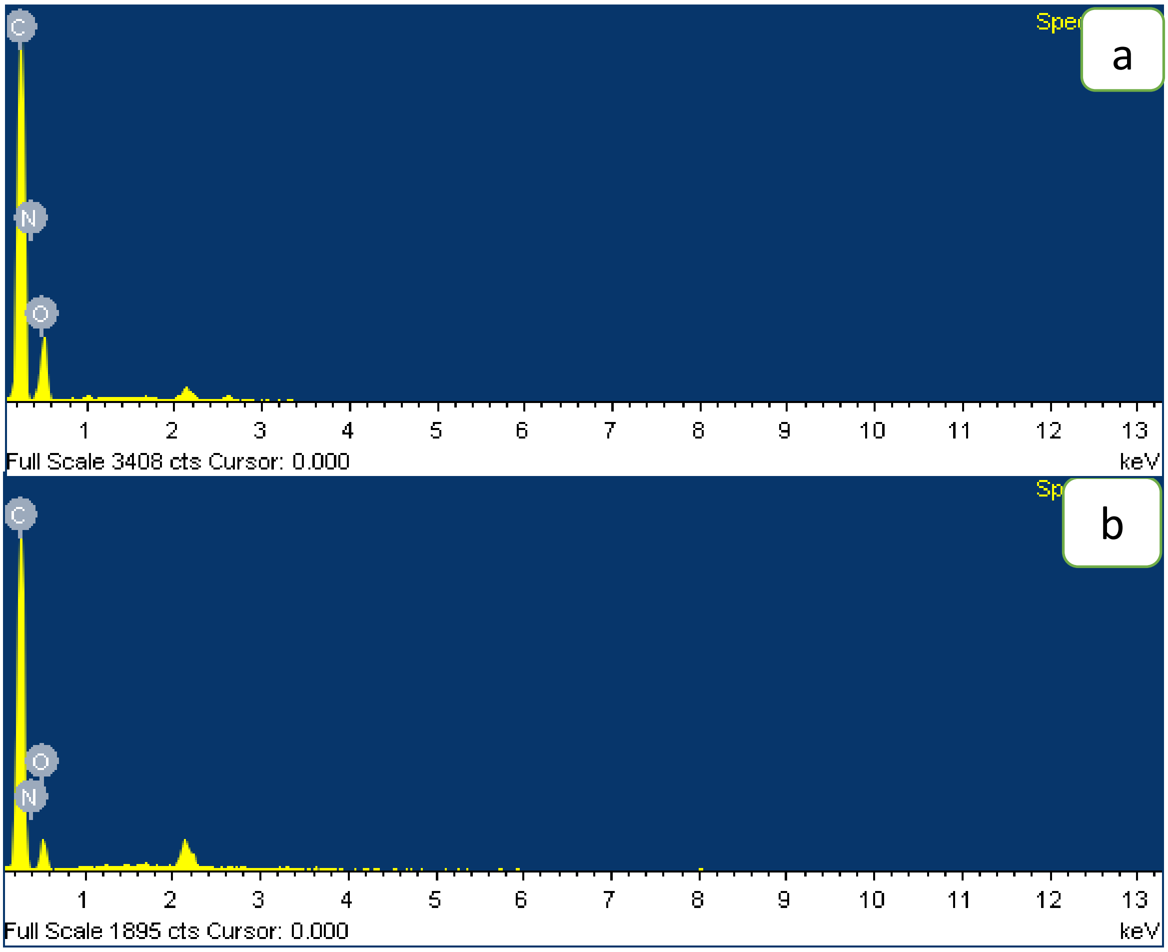


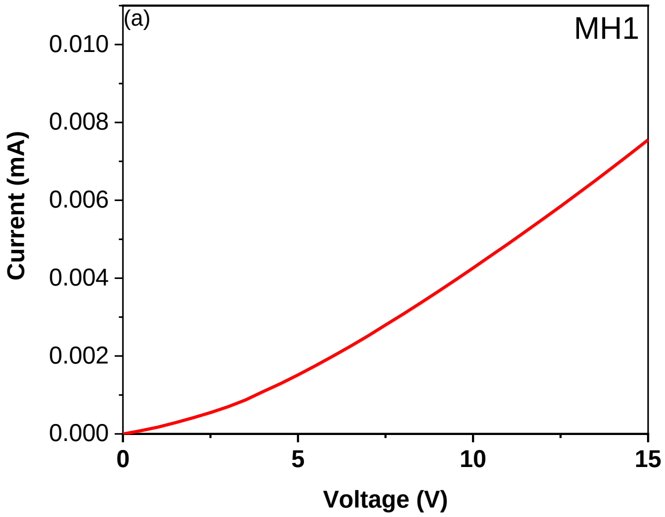
Fig.4.11 EDX data of (a) NGO-80OP400 and (b) NGO-80AC400

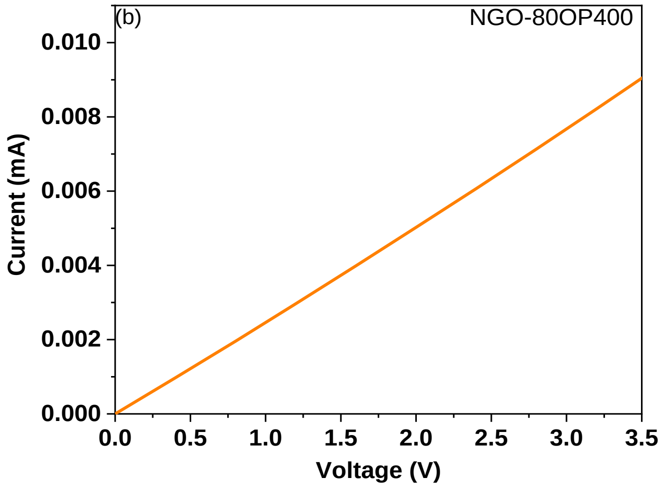
4.12 DC resistivity measurements (ρ)

To understand the effects of N-doping on the conductivity of the graphene oxide samples the resistivity measurements of pellets for MH1, NGO-80OP400 and NGO-80AC400 samples is done using 2-probe method (Fig 4.2, Table 4.7). The above data shows that the value of conductivity increases for the nitrogen doped samples as resistivity decreases.

Table 4.7: Table for the calculations of Resistivity and conductivity

Sample ID	Resistivity (ρ)[ohm-m]	Conductivity (σ) [S/m]
MH1	1.92	0.52
NGO-80OP400	5.87	0.17
NGO-80AC400	0.601	1.66





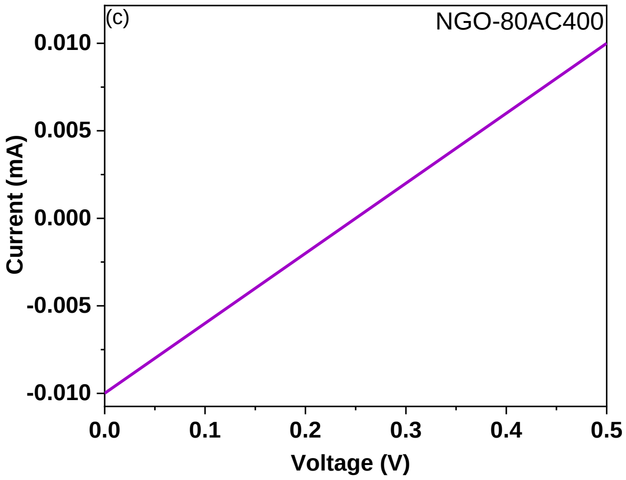


Fig. 4.12 I-V plots with linear fit for (a) MH1, (b) NGO-80OP400 and (c) NGO-80AC400

4.13 Electrochemical Capacitance

For supercapacitors energy storage is mostly taken by two methods one is ion absorption and other is fast surface redox reactions. The ion absorption is known as electric double-layer capacitance (EDLC) and fast surface redox reactions is known as pseudocapacitance (PC). The EDLC function by electrostatic gathering of charge as of reversible desorption or adsorption of ions. Also, due to the procedure of solvent molecules present between the electrolyte and the surface of using electrode. By which quantity of charge kept is relational to the capacitance and give high surface area material. The pseudocapacitor functions profligate and reversibly at the surface of given electrode. By which they may attain high energy density in comparison with the EDLC devices [7].

Fig 4.13 gives the representative CV plots for the variation observed as we change the scan rate from 2 mV/s to 200 mV/s. Fig 4.14 (a) shows the variations in the CV curve for the doped and undoped GO samples. The graph clearly shows that the N-doped samples synthesized with autoclave have larger charge storage capacity which increases with synthesis time (Fig 4.14(b)). The CV curve area has been used to determine the EDLC and PC components for the samples [8] table 4.8, Fig 14.15).

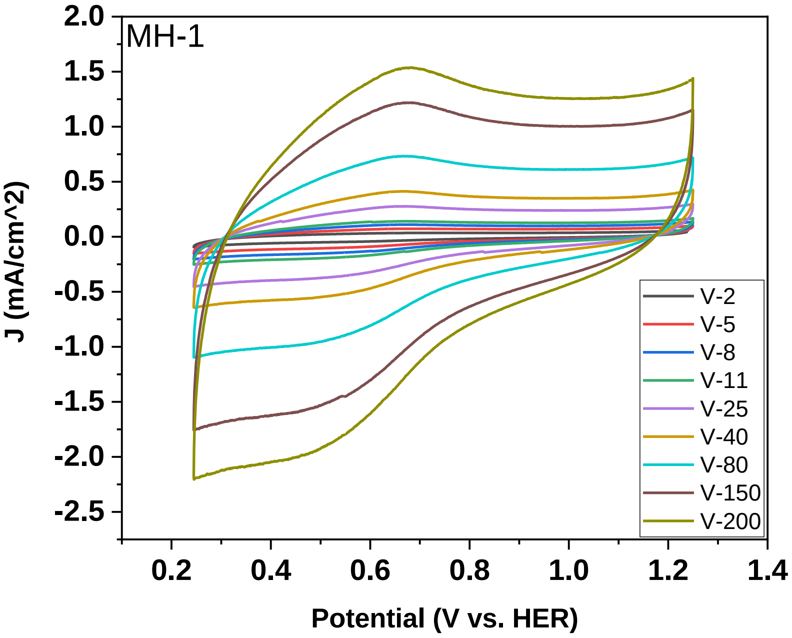
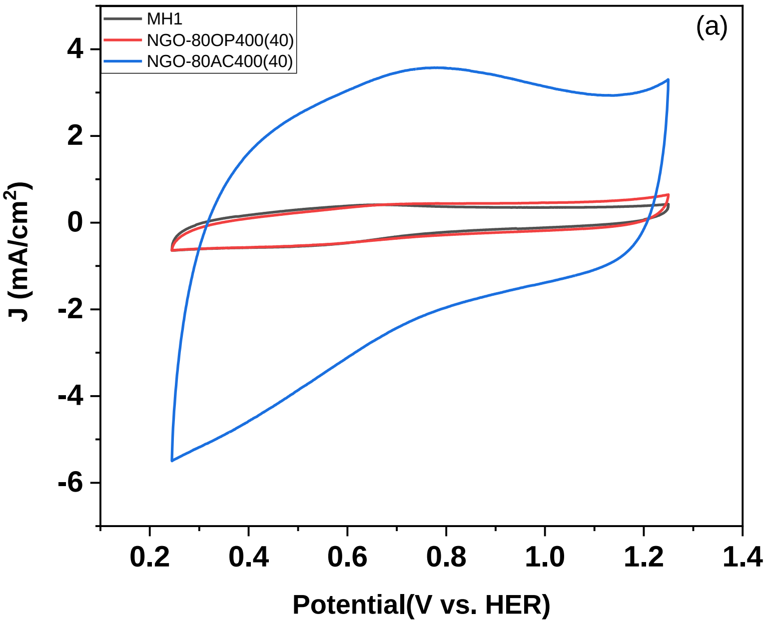


Fig.4.13 CV curves of sample MH1 with scan rate



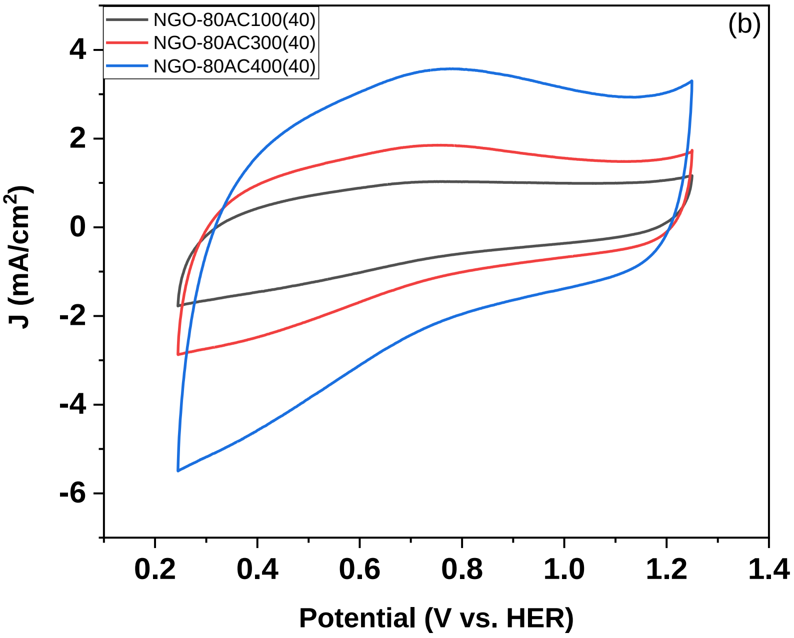


Fig.4.14 Comparison of the CV curves at scan rate 40 mV/sec (a) for N-doped and undoped GO samples(b) with synthesis time using autoclave

Table 4.8: Table for the calculations of supercapacitance

Sample ID	**C_SP (F/cm^2)**	**C_DL (F/cm^2)**	**C_P (F/cm^2)**
MH1	13.82	4.44	9.37
NGO-80OP400	19.67	2.62	17.05
NGO-80AC400	147.79	12.16	135.63
NGO-80AC300	67.82	9.38	58.43
NGO-80AC100	49.51	7.04	42.47

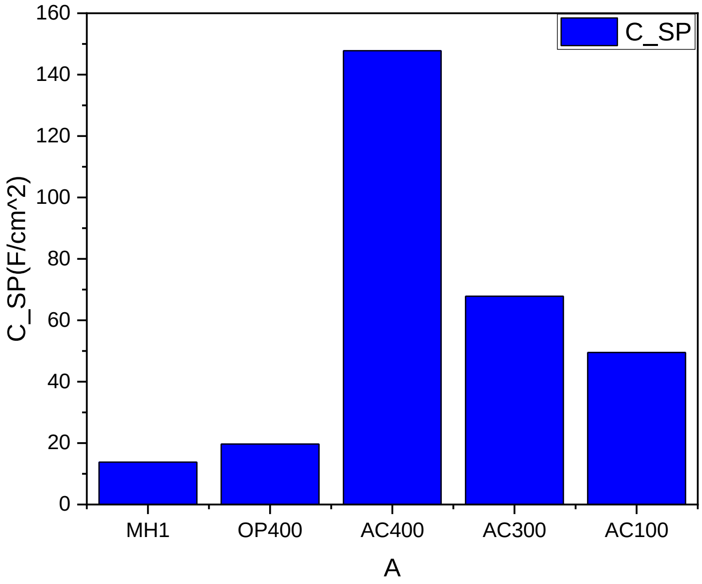


Fig.4.15 Specific capacitance of MH1, OP400, AC400, AC300 & AC100 samples

The samples synthesized using autoclave show multifold increase in the specific capacitance of the samples and it increases as we increase the synthesis time.

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Chapter 5

Conclusions and Future Scope

5.1 Conclusions

In this study the GO is synthesized with modified Hummer's method at room temperature. The formed GO was further doped with nitrogen using Urea by microwave technique using open container and Teflon Autoclave. XRD, TGA and Raman Spectroscopy indicated the successful preparation of graphene oxide and nitrogen doped-GO samples. FTIR reveals the presence of N-containing functional groups for the doped samples. DC resistivity measurements show that the conductivity is enhanced for the nitrogen doped samples with maximum conductivity for the sample synthesized in Teflon autoclave (1.66 S/m). SEM and EDX measurements were done to know the morphology and presence of elements. All the samples show flake like morphology with sharp edges with EDX confirming the presence of N in the doped-GO samples. The samples were characterized for their use for supercapacitor applications. The samples synthesized in Teflon autoclave showed multi fold enhancement in specific capacitance (147.79 F/cm^2) as compared to undoped (13.82 F/cm^2) and doped sample synthesized in open container (19.67 F/cm^2).

5.2 Future Scope

By doing the XPS, we can determine that which type of nitrogen (Pyrrolic, Pyridinic and Graphitic) is present in nitrogen doped graphene oxide. Further, the role of various nitrogen species present in graphene oxide can be studied for applications in electrocatalysis and supercapacitance.