Synthesis and Characterisation of Graphene Oxide (GO)

Submitted by

PREETISUDHA DASH

Adm. No.: 04-PHY/17

A Thesis submitted in partial fulfillment of the requirements

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CERTIFICATE – I

This is to certify that the thesis entitled, ***"Synthesis and characterisation of Graphene Oxide (GO) "*** *is submitted in partial fulfillment of the requirements for the award of the degree of* ***Master of Science*** *in* ***Physics*** *of the* ***Orissa University of Agriculture and Technology****, Bhubaneswar, is a faithful record of bona fide research work carried out by* ***PREETISUDHA DASH*** *under my guidance and supervision and that no part of this thesis has been submitted for any other degree or diploma or published in any form.*

It is further certified that the help and sources of information availed of during the course of study have been duly acknowledged.

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CERTIFICATE – II

*This is to certify that the thesis entitled, **" Synthesis and characterisation of Graphene Oxide "** submitted in partial fulfillment of the requirements for the award of the degree of **Master of Science** in **Physics** of the **Orissa University of Agriculture and Technology**, Bhubaneswar, is a faithful record of bona fide research work carried out by **PREETISUDHA DASH** under my guidance and supervision and that no part of this thesis has been submitted for any other degree or diploma or published in any form.*

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Abstract

In this study, graphene oxide(GO) was synthesized following Hummers method and further reduced by ascorbic acid to obtain reduced graphene oxide(RGO). Go and RGO are characterized by XRD, FTIR and UV spectroscopy.The characterization revealed presence of oxygen containing functional groups in GO and the removal of these functional groups after treatment with ascorbic acid.The dielectric study of GO pellets demonstrate its high dielectric permittivity in the frequency range of 1 Hz to 1 MHz . A high dielectric constant of GO ($\sim 10^5$) with low loss was observed at 1 Hz and at 35 °C, which is even very high compared to conventional dielectric materials such as $CaCu_3Ti_4O_{12}$. The ac conductivity of our GO was calculated and found to be 4×10^{-5} $ohm^{-1}cm^{-1}$at 1Hz and 75×10^{-5} $ohm^{-1}cm^{-1}$ at 1 MHz .The various mechanisms governing the variation of dielectric constant, dielectric loss, ac conductivity of GO with varying frequency are assessed using dielectric spectroscopy. The mechanistic approach and the role of functional groups, t and frequency are elucidated and discussed with regard to the high dielectric constant.The present findings suggest that the GO can be used for scaling advances high performance electronic devices and high dielectric-based electronic and energy storage devices.

Introduction

a. Overview

Electrical insulator materials which will prevent the flow of current in an electrical circuit are being used since from the beginning of the science and technology of electrical phenomena. Dielectrics are insulating materials that exhibit the property of electrical polarization; thereby they modify the dielectric function of the vacuum.

The first capacitor was constructed by Cunaeus and Mussachenbroek in 1745 which was known as Leyden jar [1]. The physical form and construction of practical capacitors vary widely and many capacitor types are in common use. Most capacitors contain at least two electrical conductors often in the form of metallic plates or surfaces separated by a dielectric medium. A conductor may be a foil, thin film, sintered bead of metal, or an electrolyte.

But there were no studies about the properties of insulating materials until 1837. Faraday published the first numerical measurements on these materials, which he called dielectrics[2]. He has found that the capacity of a condenser was dependent on the nature of the material separating the conducting surface. Materials commonly used as dielectrics include glass, Ceramic , plastic film , paper, mica and oxide layers. Unlike a resistor, an ideal capacitor does not dissipate energy.

This discovery encouraged further empirical studies of insulating materials aiming at maximizing the amount of charge that can be stored by a capacitor. Throughout most of the 19th century, scientists searching for insulating materials for specific applications have become increasingly concerned with the detailed physical mechanism governing the behavior of these

materials. In contrast to the insulation aspect, the dielectric phenomena have become more general and fundamental, as it has the origin with the dielectric polarization.

Mossotti [3, 4] and Clausius[5] have done a systematic investigation about the dielectric properties of materials. They attempted to correlate the specific inductive capacity, a macroscopic characteristic of the insulator introduced by Faraday[2] which is now popularly termed as dielectric constant with the microscopic structure of the material. Following Faraday in considering the dielectrics to be composed of conducting spheres in a non-conducting medium, Clausius and Mossotti succeeded in deriving a relation between the real part of the dielectric constant ε_r and the volume fraction occupied by the conducting particles in the dielectric.

In the beginning of 20th century, Debye[6] realized that some molecules had permanent electric dipole moments associated with them, and this molecular dipole moment is responsible for the macroscopic dielectric properties of such materials. Debye succeeded in extending the Clausius -Mossotti theory to take into account the permanent moments of the molecules, which allowed him and others to calculate the molecular dipole moment from the measurement of dielectric constant. His theory was later extended by Onsager[7] and Kirkwood[8, 9] and is in excellent agreement with experimental results for most of the polar liquids. Debye's other major contribution to the theory of dielectrics is his application of the concept of molecular permanent dipole moment to explain the anomalous dispersion of the dielectric constant observed by Drude.[10] For an alternating field, Debye deduced that the time lag between the average orientation of moments and the field becomes noticeable when the frequency of the field is within the same order of magnitude as the reciprocal relaxation time. This way the molecular relaxation process leads to the macroscopic phenomena of dielectric relaxation, i.e., the anomalous dispersion of the dielectric constant and the accompanying absorption of electromagnetic energy over certain range of frequencies

Debye's theory shows excellent agreement with the experiments for the polar liquids while the dielectric behavior for solids was found to be deviating considerably. Several modifications and extensions of Debye's theory have been proposed to correct this. There are two major approaches in the extension of Debye's theory. The first approach, pioneered by Cole

[11], Davidson[12] and William[13], interprets the non –Debye relaxation behavior of the material in terms of the superposition of an exponentially relaxing process, which then leads to a distribution of relaxation times. The second approach by Joncher [14] proposes that the relaxation behavior at the molecular level is intrinsically non-Debye-like due to the cooperative molecular motions.

After more than eighty years of development, the theory of dielectrics is still an active area for research. Understanding the behaviour of dielectric materials with the variations of field, temperature and frequency is of particular importance for present day electronics. Modern day electronics demand dielectric materials with narrowly defined properties tailored for particular applications.

Recent advances in wireless communication technologies have elevated the interest in materials with the unusual combination of properties like high dielectric constant, low dielectric loss and low values of temperature dependence of dielectric constant [15]. The constant need for miniaturization provides a continuing driving force for the discovery and the development of increasingly sophisticated materials to perform the same or improved function with decreased size and weight. The dielectric materials mentioned above are used as the basis for resonators and filterers for the microwaves carrying the desired information [16]. These materials are presently employed as bulk ceramics in microwave communication devices. They are not integrated into the microelectronics but are being used as discrete components. The need for better dielectrics with improved properties suitable for modern integrated manufacturing needs is the motivation behind the present study.

b.Motivation

“A pencil and dream can take you anywhere”. Literally, this is what Geim and his dedicated group did in 2004, by discovering GNsheets from Graphite using a simple Scotch tape technique. Graphene is a wonder super carbon with enough potential to revolutionize current scientific and technological world. Graphene and its derivatives stands as the centre of attraction of research

community and if bibliometrics are to be trusted, the quantity of research papers on graphene will continue to increase rapidly over the next few decades. With only few years of delay with respect to graphene [17], the interest on graphene oxide (GO) [18] has exponentially risen, as documented by the yearly number of peer-reviewed works published on this topic, which have passed from a few units in 2007 to some thousands in 2013 (data taken from Scopus). GO is a two dimensional material. It is the oxidized form of graphene, with O functional groups decorating the sp2 C basal plane [19]. All its physical properties can be tuned from those of fully oxidized GO to, approximately, those of graphene by simply removing the functional groups from its surface. This process allows it to pass from an insulating material to a semi-metal. Due to the presence of the O functional groups, GO is also hydrophilic and it can be dispersed in water solution [20], contrary to graphene which is hydrophobic. The size of the GO flakes can be also tuned and varied from a few nm to mm [21]. The tunability of both its chemical composition and flakes size makes GO an appealing material in many fields: electronics (sensors and transparent conductive films), composites materials, clean energy devices, biology and medicine. With focus on such different research fields, several reviews have been reported in the literature [22–32]. In the present study we give an account of the fundamental characterization of GO and few proposed applications, which we believe are among the most promising ones.

c. Research objectives

The main objective of our research is to synthesize graphene oxide(GO) and reduced graphene oxide (RGO) in cost effective method. This work subsequently demonstrated the effectiveness of GO as a gigantic dielectric material. The objective of the research includes:

1. Synthesis of GO from graphite using Hummers method.
2. Reduction of GO by ascorbic acid to form reduced graphene oxide(RGO)

3. Characterization of GO and RGO by XRD, FTIR and UV spectroscopy.

4. Investigate the dielectric behavior of GO

d. Thesis outline

The thesis is composed of five chapters.

The chapter 1 depicts about 3D graphite, how graphene is produced from graphite, history of graphene,different properties like chemical and electronic properties of graphene .Different forms of graphene like monolayer, bilayer etc are also discussed. Finally different applications of graphene are elaborated in this chapter.

The chapter 2 depicts about graphene oxide (GO)and how graphene oxide is derived from graphene.Various functional groups present in the GO are discussed.The detail chemical structure, properties and applications of graphene oxide are elaborated.Then reduction of GO to reduced graphne oxide(RGO) using different reducing agents are explained.Comparison of GO and RGO is also discussed with different applications of GO and RGO.A theoretical discourse of dielectric constant, its complex behavior, dielectric loss, different types of polarization in general is given.Finally the theoretical study of dielectric behavior of graphene oxide in particular is elaborated.

Chapter 3 discusses about detail experimental procedures in synthesis of GO and RGO.Differenr characterization techniques like XRD, FTIR , UV spectroscopy, dielectric measurements are discussed in details.

The chapter 4 is devoted for the characterization of prepared GO pellets by various analytical techniques such as UV-Visible spectroscopy, powder X-ray diffraction(XRD), fourier transform infrared spectroscopy(FT-IR) and the obtained results are discussed in details. This chapter also enumerates about dielectric studies of GO, variation of dielectric constant, dielectric losses, ac conductivity with variation in frequency are discussed with proper reasoning.

The final and the 5^{th} Chapter summarize the thesis and recommends for future work.

CHAPTER- 1

Literature Review

The chapter 1 depicts about 3D graphite, how graphene is produced from graphite, history of graphene, different properties like chemical and electronic properties of graphene .Different forms of graphene like monolayer, bilayer etc are also discussed. Finally different applications of graphene are elaborated in this chapter.

1.1 What is Graphite?

Graphite is a crystalline form of the element carbon with its atoms arranged in a hexagonal structure. It occurs naturally in this form and is the most state form of carbon under standard conditions. Its high conductivity makes it useful in electronic product such as electrodes, batteries, and solar panels.

Fig 1.1 Graphene specimen

1.2 What Graphene is?

Graphene is a single layer (monolayer) of carbon atoms, tightly bound in a hexagonal honeycomb lattice. It is an allotrope of carbon in the form of a plane of sp^2-bonded atoms with a molecular bond length of 0.142 nanometres. Layers of graphene stacked on top of each other form graphite, with an interplanar spacing of 0.335 nanometres. The separate layers of graphene in graphite are held together by Vander Waals forces, which can be overcome during exfoliation of graphene from graphite.

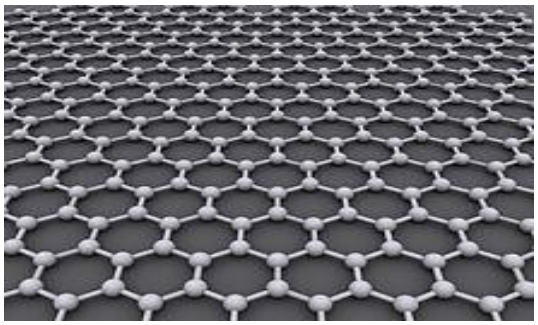


Fig: 1.2 Graphene as one layer of carbon atom

Graphene is the thinnest compound known to man at one atom thick, the lightest material known (with 1 square meter weighing around 0.77 milligrams), the strongest compound discovered (between 100-300 times stronger than steel with a tensile strength of 130 GPa and a Young's modulus of 1 TPa - 150,000,000 psi), the best conductor of heat at room temperature (at $(4.84\pm0.44) \times 10^3$ to $(5.30\pm0.48) \times 10^3$ W·m−1·K−1) and also the best conductor of electricity known (studies have shown electron mobility at values of more than 200,000 cm2·V−1·s−1). Other notable properties of graphene are its uniform absorption of light across the visible and near-infrared parts of the spectrum (πα ≈ 2.3%), and its potential suitability for use in spin transport.

Bearing this in mind, one might be surprised to know that carbon is the second most abundant mass within the human body and the fourth most abundant element in the universe (by mass), after hydrogen, helium and oxygen. This makes carbon the chemical basis for all known life on earth, making graphene potentially an eco-friendly, sustainable solution for an almost limitless number of applications.

Graphene has many properties. In proportion to its thickness, it is about 100 times stronger than the strongest steel. It conducts heat and electricity very efficiently and is nearly transparent. Graphene also shows a large and nonlinear diamagnetism. Researchers have identified the bipolar transistor effect, ballistic transport of charges and large quantum oscillations in the material.

Scientists have theorized about graphene for decades. It has likely been unknowingly produced in small quantities for centuries, through the use of pencils and other similar applications of graphite. It was originally observed in electron microscopes in 1962, but only studied while supported on metal surfaces. The material was later rediscovered, isolated and characterized in 2004 by Andre Geim and Konstantin Novoselov at the University of Manchester.

1.3 Definition

Graphene" is a combination of "graphite" and the suffix -ene, named by Hans-Peter Boehm, who described single-layer carbon foils in 1962.

The term *graphene* first appeared in 1987 to describe single sheets of graphite as a constituent of graphite intercalation compounds (GICs); conceptually a GIC is a crystalline salt of the intercalant and graphene.

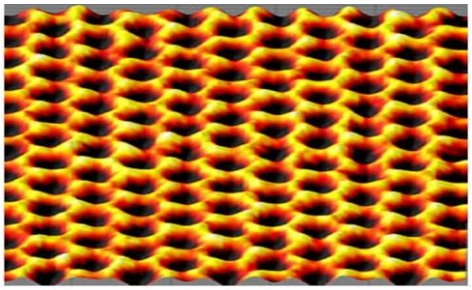


Fig 1.3honey comb structure of graphene

1.4 History

Single-layer graphene was explored theoretically by P. R. Wallace in 1947 as a starting point for understanding the electronic properties of 3D graphite. The earliest TEM images of few-layer graphite were published by G. Ruess and F. Vogt in 1948. Later, single graphene layers were observed directly by electron microscopy. Before 2004 intercalated graphite compounds were studied under a transmission electron microscope (TEM). Starting in the 1970s single layers of graphite were grown epitaxially on top of other materials. Initial attempts to make atomically thin graphitic films employed exfoliation techniques similar to the drawing method.

One of the first patents pertaining to the production of graphene was filed in October 2002 and granted in 2006. It detailed one of the first large scale graphene production processes. Two years later, Two University of Manchester scientists Andre Geim and his colleague, Konstantin Novoselov isolated Graphene in 2004 by repeatedly peeling away graphite strips with adhesive tape to obrain a single atomic plane. In 2010, both of them shared the Nobel Prize for Physics for groundbreaking experiments regarding the two-dimensional material Graphene."

In 2014, the National Graphene Institute was announced to support applied research and development in partnership with other research organizations and industry.

By 2017, 13 years after creation of the first laboratory graphene electronic device, an integrated graphene electronics chip was produced commercially and marketed to pharmaceutical researchers by Nanomedical Diagnostics in San Diego.

1.5 Properties of graphene

Graphene has a theoretical specific surface area (SSA) of 2630 m^2/g. This is much larger than that reported to date for carbon black (typically smaller than 900 m^2/g) or for carbon nanotubes (CNTs), from ≈100 to 1000 m^2/g and is similar to activated carbon.

Graphene is a crystalline allotrope of carbon with 2-dimensional properties. Its carbon atoms are densely packed in a regular atomic-scale chicken wire (hexagonal) pattern.

Each atom has four bonds, one σ bond with each of its three neighbours and one π-bond that is oriented out of plane. The atoms are about 1.42 Å apart.

Graphene's hexagonal lattice can be regarded as two interleaving triangular lattices. This perspective was successfully used to calculate the band structure for a single graphite layer using a tight-binding approximation.

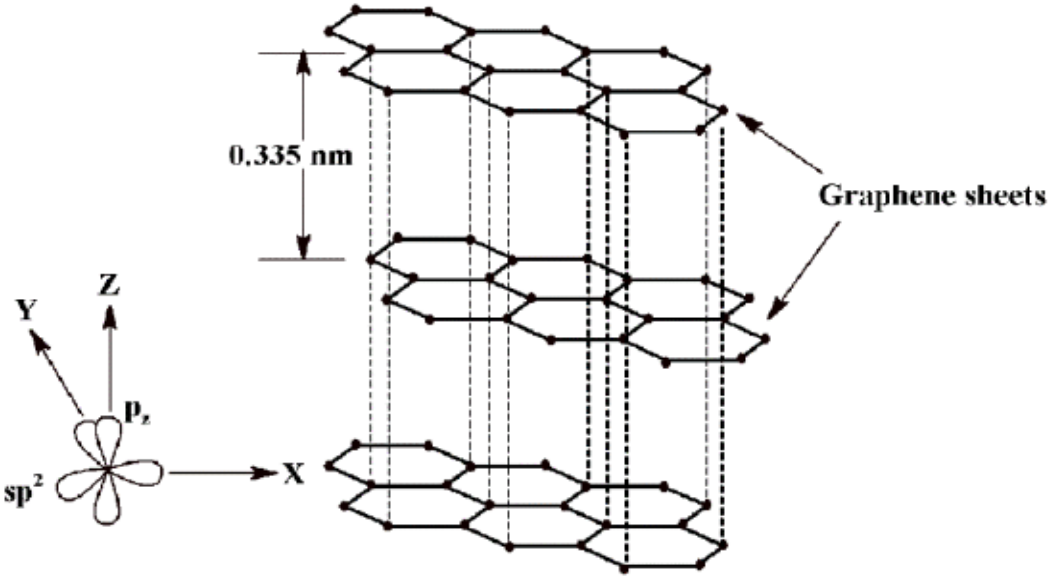


Fig: 1.4 Layered structure of graphene showing sp^2 hybridisation

Graphene's stability is due to its tightly packed carbon atoms and a sp^2 orbital hybridization– a combination of orbitals s, p_x and p_y that constitute the σ-bond. The final p_z electron makes up the π-bond. The π-bonds hybridize together to form the π-band and π-bands. These bands are responsible for most of graphene's notable electronic properties, via the half-filled band that permits free-moving electrons.

1.5.1 Chemical properties:-

Atoms at the edges of a graphene sheet have special chemical reactivity. Graphene has the highest ratio of edge atoms of any allotrope. Defects within a sheet increase its chemical reactivity. The onset temperature of reaction between the basal plane of single-layer graphene and oxygen gas is below 260 °C (530 K). Graphene burns at very low temperature (e.g., 350 °C (620 K)). Graphene is commonly modified with oxygen- and nitrogen-containing functional groups and analyzed by infrared spectroscopy and X-ray photoelectron spectroscopy.

1.5.2 Electronic properties:-

Graphene is a zero-gap semiconductor, because its conduction and valence bands meet at the Dirac points. The Dirac points are six locations in momentum space, on the edge of the Brillouin zone, divided into two non-equivalent sets of three points. The two sets are

labelled K and K'. The sets give graphene a valley degeneracy of $g_v = 2$. By contrast, for traditional semiconductors the primary point of interest is generally Γ, where momentum is zero. Four electronic properties separate it from other condensed matter systems.

However, if the in-plane direction is no longer infinite, but confined, its electronic structure would change. They are referred to as graphene nanoribbons. If it is "zig-zag", the band gap would still be zero. If it is "armchair", the band gap would be non-zero.

1.6 Different Forms of Graphene

Monolayer Sheets

In 2013 a group of Polish scientists presented a production unit that allows the manufacture of continuous monolayer sheets. The process is based on graphene growth on a liquid metal matrix. The product of this process was called HSMG.

Bilayer Graphene

Bilayer graphene displays the anomalous quantum Hall effect, a tunable band gap and potential for excitonic condensation making it a promising candidate for optoelectronic and nanoelectronic applications. Bilayer graphene typically can be found either in twisted configurations where the two layers are rotated relative to each other one way to synthesize bilayer graphene is via chemical vapour deposition, which can produce large bilayer regions that almost exclusively conform to Bernal stack geometry.

Graphene super lattices

Periodically stacked graphene and its insulating isomorphs provide a fascinating structural element in implementing highly functional super lattices at the atomic scale, which offers possibilities in designing nanoelectronic and photonic devices. Various types of super lattices can be obtained by stacking graphene and its related forms.

Graphene nano ribbons

Graphene nano ribbons ("nanostripes" in the "zig-zag" orientation), at low temperatures, show spin-polarized metallic edge currents, which also suggests applications in the new field of spintronics. (In the "armchair" orientation, the edges behave like semiconductors.)

Graphene quantum dots

Graphene quantum dots (GQDs) have mainly been fabricated by the microwave assisted hydrothermal method (MAH) ,the Soft-Template method the hydrothermal method, the ultrasonic exfoliation method, the lithography method, the chemical synthesis method, the electrochemical preparation method, the graphene oxide (GO) reduction method, and the C60 catalytic transformation method, etc.

1.7 Production of graphene

Graphene can be prepared with a “top-down” approach that involves obtaining a single-layer graphene isolated from multilayer graphite crystals, or with a “bottom-up” method causing the graphene crystals to self-assemble from small molecules used to create graphene, respectively.

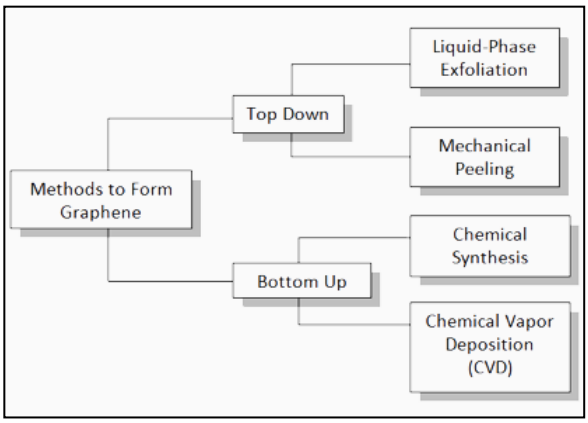


Fig1.5 diagrammatic representation for production of graphene

One top-down method incorporates mechanical peeling using the “Scotch tape method” to mechanically peel pyrolytic graphite crystals, creating a single-layer graphene material. Another top-down method involves the liquid-phase exfoliation, a different mechanical process used to get a single-layer graphene and is more advantageous as large quantities can be produced.

The bottom-up approach provides a more stru creating graphene that can be acquired with the possibility of chemical synthesis. Through this method, small-sized nano graphene or graphene nanoribbons (GNRs) are formed with the smallest nano graphene size ranging from 1 to 5 nanometers and the largest synthesized monodispursed nano graphene molecule containing more than 200 carbon atoms . However, the most current and trending method to create graphene from the bottom-up is through chemical vapor deposition (CVD) Treating the substrate before beginning the CVD process is commonly done to improve graphene formation and obtain a smoother surface. Wet chemical treatments are considered for copper films to prevent oxide reduction and if this step is taken, the copper film must be soaked in acetic acid then, through CVD, a metal substrate, typically copper, is heated in a reaction chamber under low vacuum. Then, Decomposed methane is supplied to the carbon needed to form Graphene.

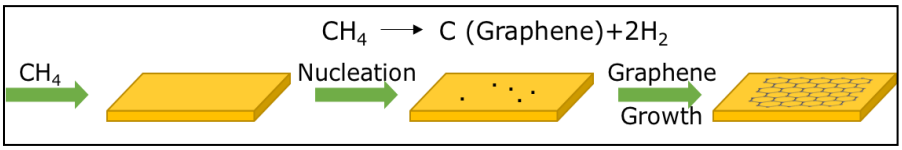


Fig 1.6 :CVD technique

Nevertheless, the greatest advantage of CVD is that it allows Graphene to be transferred onto a substrate. Polymethylmethacrylate (PMMA) is often used as a stiffening polymer surface to make this Graphene transfer possible and the process of etching out the original substrate can begin.

1.8 Application

Being able to create super capacitors out of graphene will possibly be the largest step in electronic engineering in a long time. While the development of electronic components has been progressing at a very high rate over the last 20 years, power storage solutions such as batteries and capacitors have been the primary limiting factor due to size, power capacity and efficiency .In initial tests carried out, laser-scribed graphene (LSG) supercapacitors demonstrated power density comparable to that of high-power lithium-ion batteries that are in use today. Not only that, but also LSG supercapacitors are highly flexible, light, quick to charge, thin, and as previously mentioned comparably very inexpensive to produce.

Graphene is also being used to boost not only the capacity and charge rate of batteries but also the longevity. Currently, while such materials as lithium are able to store large amounts of energy, that potential amount diminishes on every charge or recharge due to electrode wear

Fig 1.7 Powder form of graphene

Graphene has long been regarded as an ideal candidate channel material for radio frequency (RF) flexible electronics. The flexible nature of graphene allows for various electronic devices on flexible substrates, such as for example flexible, all-solid-state graphene-based super capacitors, wearable touch panels, strain sensors, and self-powered turboelectric sensors, all recently demonstrated, with applications such as flexible, robust touch screen devices such as mobile devices and wrist watches closely on the horizon.

Graphene is a promising material for telecomm photo detectors, because it absorbs light over a large bandwidth, including standard telecomm wavelengths. It is also compatible with CMOS technology, which means it can be technologically integrated with silicon photonics. Furthermore, graphene is an excellent heat conductor, promising a reduction in heat consumption of graphene-based photonic devices. For these reasons, graphene for optical communications has been an intense field of research, which is now gaining fruition in full working prototypes.

Graphene produced with chemical vapour deposition (CVD) will form the cornerstone of future graphene-based chemical, biological, and other types of sensors. Furthermore, graphene provides excellent mechanical strength, thermal and electrical conductivity, compactness, and potentially low cost, which is necessary for competing on the crowded sensor market.

Graphene-based gas/vapor sensors have attracted much attention in recent years due to their variety of structures, unique sensing performance, room-temperature working conditions, and tremendous application prospects.

The market will soon see clothing containing graphene-enhanced photovoltaic cells and super capacitors, meaning that we will be able to charge our mobile telephones and tablet computers in a matter of minutes (potentially even seconds) whilst walking to school or work. We may possibly even see security-orientated clothing offering protection against unwanted contact with the use of electrical discharge.

CHAPTER 2

The chapter 2 depicts about graphene oxide (GO) and how graphene oxide is derived from graphene. Various functional groups present in the GO are discussed. The detail chemical structure, properties and applications of graphene oxide are elaborated. Then reduction of GO to reduced graphne oxide(RGO) using different reducing agents are explained. Comparison of GO and RGO is also discussed with different applications of GO and RGO.A theoretical discourse of dielectric constant, its complex behavior, dielectric loss, different types of polarization in general is given. Finally the theoretical study of dielectric behavior of graphene oxide in particular is elaborated.

2.1 Graphene Oxide (GO)

Graphene oxide (GO) is a chemically modified graphene containing oxygen functional groups such as epoxies, alcohols, and carboxylic acids, and chemical analysis shows the carbon to oxygen ratio to be approximately three to one.

Graphene oxide is a single-layer sheet of graphite oxide, which was proposed one and a half century ago. In recent years, graphene oxide has attracted great concern mainly because it is a potential starting material for the mass production of graphene. Chemistry of graphene oxide has been reviewed.

Graphene oxide can be a semiconductor or insulator, depending on the degree of oxidation, and their electronic and optical properties can be tuned in large scope. The controllable optical and electronic properties enable graphene oxide to be used in many fields. The major concern about graphene oxide is mainly focused on its chemical structure, electronic properties, reduction reaction [360,361] and chemical functionalisation.

The structure of graphene oxide is still unclear due to its complicated non-stoichiometric nature. There are different kinds of oxygen species and bondings to carbon in graphene layer, such as epoxy, hydroxyl, carbonyl, carboxylic groups.

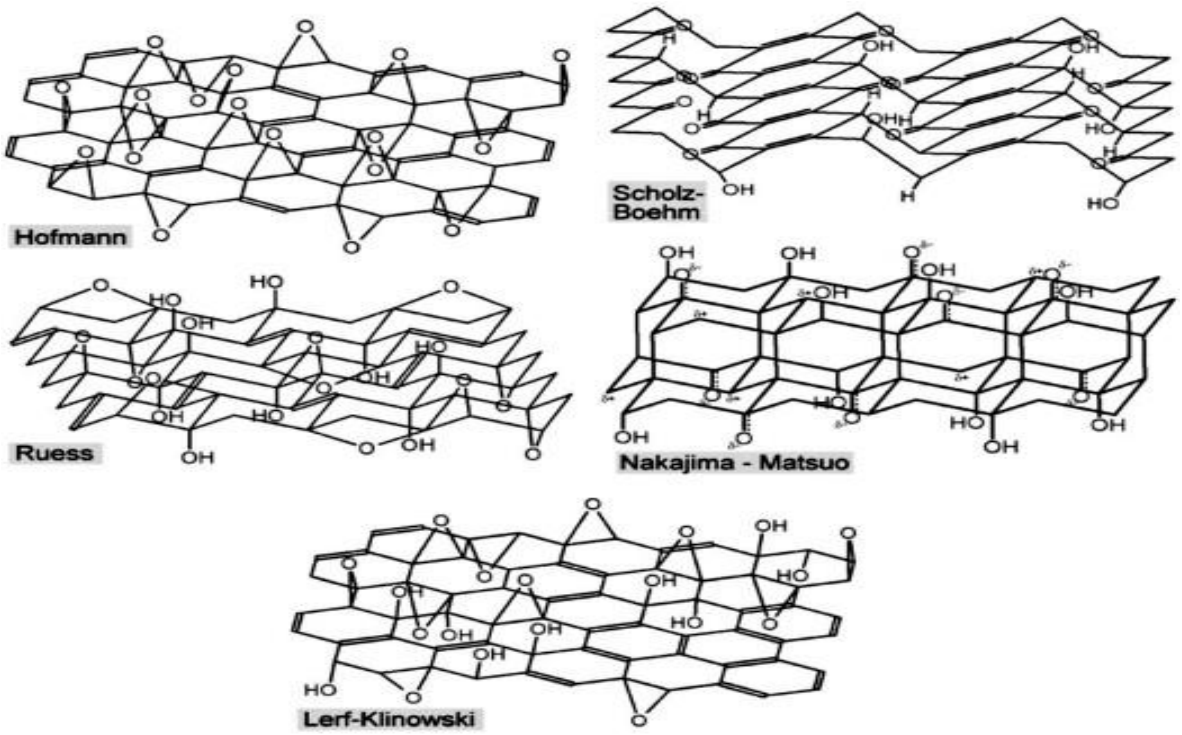


Fig: 2.1 Proposed structure of graphene oxide (GO)

The electronic properties of graphene oxide mainly depend on the oxidation level and chemical composition; it can be tailored by removal or addition of certain oxygen groups to adjust the proportion of sp^2 and sp^3 carbon. Graphene oxide is easily converted into graphene, as explained above. The application fields of graphene oxide are mainly focused on sensor and drug delivery. With a large amount of functional groups, graphene oxide can react with many chemical groups and can be easily modified to improve its functionalities and create new functionalities.

Graphene Oxide is a two-dimensional crystal structure formed by a flat monolayer of carbon atoms arranged in a hexagonal lattice . Graphene oxide and derivatives thereof have been widely explored for their antimicrobial properties due to their unique chemical and physical properties; and the apparently low toxicity enabled graphene oxide materials to be promising candidates for the next generation of antimicrobial agents.

Graphene oxide and carbon nanotubes oxide composite has been synthesized and applied in the treatment for trichomoniasis disease. The nanocomposite formed a stable

colloidal aqueous solution and had a strong interaction with the cell membrane of trichomonas foetus protozoa. Therefore, the hybrid nanocomposite might be an excellent candidate for a drug carrier, which could be used to deliver therapeutic agents to treat trichomoniasis disease.

2.2 Properties and Applications of Graphene Oxide

Due to the presence of oxygen functionalities, graphene oxide can easily disperse in organic solvents, water, and different matrixes. This is a major benefit when combining the material with polymer or ceramic matrixes to enhance their mechanical and electrical properties.

With respect to electrical conductivity, graphene oxide functions as an electrical insulator, because of the disturbance of its sp^2 bonding networks. It is important to reduce the graphene oxide so as to recover the honeycomb hexagonal lattice of graphene, in order to restore electrical conductivity.

After a large number of oxygen groups have been removed, it is not easy to disperse the reduced graphene oxide (rGO), because this material tends to produce aggregates.

The properties of graphene can be changed by the functionalization of graphene oxide. The chemically-altered graphenes obtained by this method could possibly be used in several applications. Depending on the intended application, the graphene oxide can be functionalized in a number of ways.

One way to ensure that the chemically-altered graphenes disperse easily in organic solvents is to use amines through organic covalent functionalization, for instance. This makes the material better suited to production of biodevices and optoelectronics, and for use in drug delivery.Also, it has been shown that it is possible to attach fullerene-functionalized secondary amines and porphyrin-functionalized primary amines to graphene oxide platelets, to enhance the nonlinear optical performance of the material.

Graphene oxide could potentially be used as an intermediary in the production of single layer or few-layer graphene sheets. To achieve this, an oxidization and reduction process should be developed that can isolate carbon layers and separate then without changing their structure.In terms of mass production of graphene, the chemical reduction of graphene oxide is considered to be one of the most viable methods. However, scientists have found it challenging

to create graphene sheets that have the same quality as those made by mechanical exfoliation on a large scale

-
- 

Fig: 2.2 Thin film of graphene oxide(GO)

2.3 Applications

Graphene oxide films are used in the following applications:

- Graphene research
- Biomedical
- Solar cells
- Graphene/polymer composite materials
- Batteries
- Super capacitors
- Support for metallic catalysts
- Low permeability materials
- Biosensors
- Multifunctional materials

2.4 Reduced Graphene Oxide (RGO)

(Graphene Oxide to Reduced Graphene Oxide)

Reducing graphene oxide to produce reduced graphene oxide (rGO), is an extremely vital process as it has a large impact on the quality of the rGO produced, and therefore will determine how close rGO will come, in terms of structure, to pristine graphene. In large scale operations where scientific engineers need to utilize large quantities of graphene for industrial applications such as energy storage, rGO is the most obvious solution, due to the relative ease in creating sufficient quantities of graphene to desired quality levels.

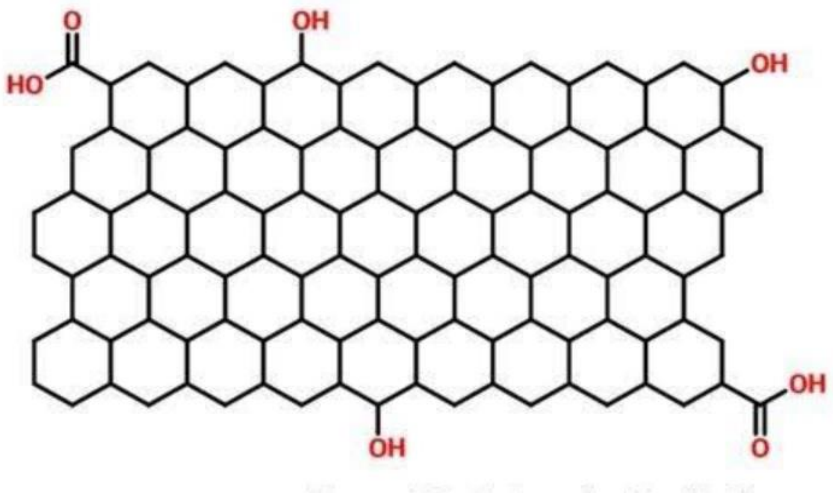


Fig 2.3: Reduced Graphene Oxide

As expected , there are a number of ways reduction can be achieved, though they are all methods based on chemical, thermal or electrochemical means. Some of these techniques are able to produce very high quality rGO, similar to pristine graphene, but can be complex or time consuming to carry out.

In the past, scientists have created rGO from GO by:

- Treating GO with hydrazine hydrate and maintaining the solution at 100 for 24 hours
- Exposing GO to hydrogen plasma for a few seconds
- Exposing GO to another form of strong pulse light, such as those produced by xenon flashtubes
- Heating GO in distilled water at varying degrees for different lengths of time

Reducing GO by using chemical reduction is a very scalable method, but unfortunately the rGO produced has often resulted in relatively poor yields in terms of surface area and electronic conductibility. Thermally reducing GO at temperatures of 1000 or more creates rGO that has been shown to have a very high surface area, close to that of pristine graphene even.

Unfortunately, the heating process damages the structure of the graphene platelets as pressure between builds up and carbon dioxide is released. This also causes a substantial reduction in the mass of the GO (figures around 30% have been mentioned), creating imperfections and vacancies, and potentially also having an effect on the mechanical strength of the rGO produced.

The final example given above could eventually be the future of large scale production of rGO. Electrochemical reduction of graphene oxide is a method that has been shown to produce very high quality reduced graphene oxide, almost identical in terms of structure to pristine graphene, in fact.

This process involves coating various substrates such as Indium Tin Oxide or glass with a very thin layer of graphene oxide. Then, electrodes are placed at each end of the substrate, creating a circuit through the GO. Finally, linear sweep voltammetry is carried out on the GO in a sodium phosphate buffer at various voltages; at 0.6 volts reduction began, and maximum reduction was observed at 0.87 volts.

In recent experiments the resulting electrochemically reduced graphene oxide showed a very high carbon to oxygen ratio and also electronic conductivity readings higher than that of silver (8500 S/m, compared to roughly 6300 S/m for silver). Other primary benefits of this techniques are that there are no hazardous chemicals used, meaning no toxic waste to dispose of. Unfortunately, the scalability of this technique has come into question due to the difficulty in depositing graphene oxide onto the electrodes in bulk form.

Ultimately, once reduced graphene oxide has been produced, there are ways that we can functionalise rGO for use in different applications. By treating rGO with other chemicals or by creating new compounds by combining rGO with other two dimensional materials, we can enhance the properties of the compound to suit commercial applications.

2.5 Properties of Reduced Graphene Oxide

Properties of rGO are as follows:

- Reduction method: Chemically reduced
- Color: Black
- Form: Powder
- Odor: Odorless
- Sheet dimension: Variable
- Solubility: Insoluble
- Density: 1.91g/cm^3
- Dispersability: It can be dispersed at low concentrations of less than 0.1mg/mL in DMSO, NMP, DMF
- Electrical conductivity: 666,7 S/m
- Humidity (Karl Fisher, TGA): 3.7 - 4.2%
- BET surface area: 422.69 – 499.85m^2/g

2.6 Applications

rGO is used in the following applications:

- Graphene research
- Batteries
- Biomedical
- Super capacitors
- Printable graphene electronics

2.7 Dielectric Constant

2.7.1 What Is Dielectric Constant?

Dielectric constant is the ratio of the capacitance formed by two plates with a material between them to capacitance of the same plates with air as a dielectric.

2.7.2 How It Arises?

When an insulating material is placed in an electric field, it allows the electric lines of flux to enter inside it. As a result positively charged nucleus of an atom pushed in the direction of the field while negatively charged electrons pushed in the opposite direction of field. Thus polarization occurs, which is the main cause of development of dielectric constant.

2.7.3 Types of Dielectric Constant.

Dielectric constant arises due to polarization is of two type i.e. real dielectric constant (ε'_r) and imaginary part of dielectric constant (ε_r''). Imaginary part of dielectric constant also known as imaginary part of dielectric loss.

2.7.4 Dielectric Loss

Dielectric loss quantifies a dielectric material's inherent dissipation of electromagnetic energy .It can be parameterized in terms of either the loss angle б or the corresponding loss tangent tan delta . Both refer to the phasor in the complex plane whose real

and imaginary parts are the resistive (lossy) component of an electromagnetic field and its reactive (lossless) counterpart.

2.7.5 Ac Conductivity

It is a fundamental property of a material that quantifies how strongly it resists or conducts the flow of current . Generally it is the reciprocal of electrical resistivity . It represents a material's ability to conduct electric current. It is commonly signified by Greek letter 'σ'.

2.8 Polarisation

2.8.1 What Is Polarization?

An insulator has low electrical conductivity because all the charges in insulator are in bound state. When electric field is applied to an insulator, as it has no free charge like that of conductor, with the applied electric field +ve ly and –ve ly bound charges are separated. We can say that a dipole is created by atom of the insulator. This is known as polarization. Polarization in dielectrics is of four types.

2.8.2 Types of Polarization

2.8.2.1 Dipolar polarization

Dipolar polarization arises in those substances in which molecules have a permanent dipole moment. But in absence of electric field the net polarization vanishes due to random orientation of molecules. When electric field is applied the molecular dipole tends to align with the field and this result in a net non-vanishing polarization. This is called dipolar polarization.

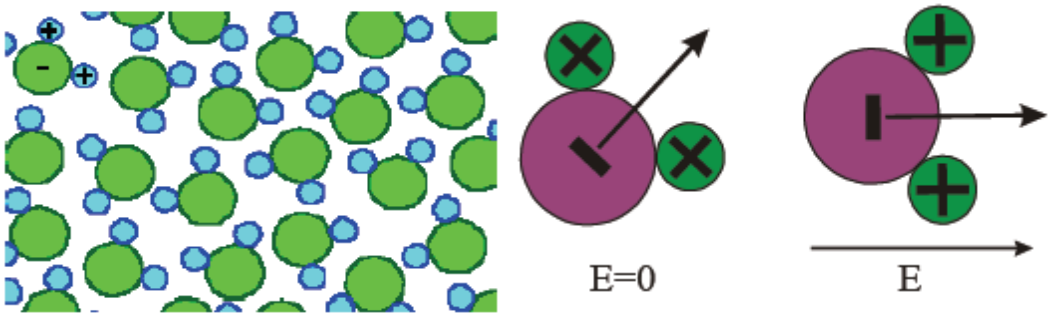


Fig2.4 : Orientation of dipoles in presence of electric field

2.8.2.2 Ionic polarization

If the molecule contains ionic bonds, then the field tends to stretch the lengths of these bonds. The effect of this change in length is to produce a net dipole moment in the unit cell where previously there was none. Since the polarization here is due to the relative displacements of oppositely charged ions, we speak of ionic polarisability.

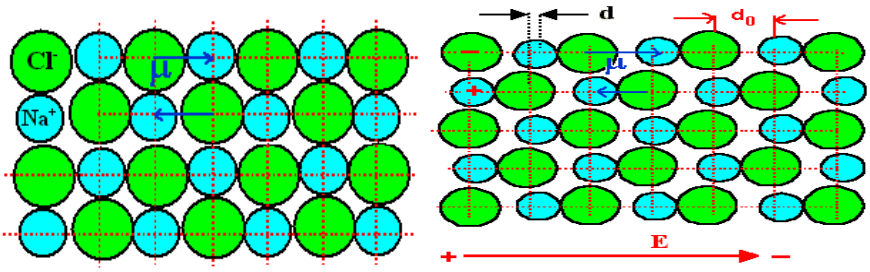


Fig2.5: Inter atomic distance changes due to ionic polarization

2.8.2.3 Electronic polarisability

This type of polarisability arises because of the individual atoms or ions in a molecule are themselves polarized by the field i.e. the electrons in its various shells are displaced with respect to the nucleus.

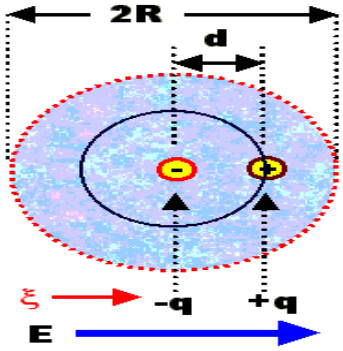


Fig2.6: Inter atomic distance changes due to electronic polarization

2.8.2.4 Interfacial **Polarisability**

This type of polarisability arises because of presence of some free charges in an insulator, but these are not responsible for conduction of current as their amount is very less. During polarization these free electrons appear at the interface of the dipoles. So this is called interfacial polarization.

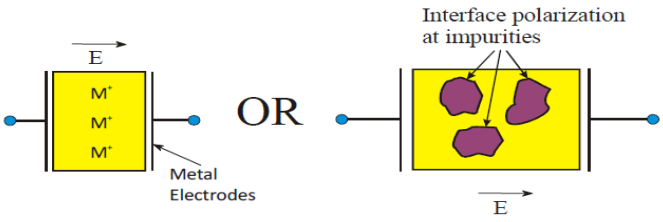


Fig2.7-Interfacial polarization

2.8.3 Frequency dependence of dielectric constant

In absence of electric field only force acting is restoring force.

F_{rest}=ma

=>-mω_0^2x=ma

=>$\omega_0^2 x+\frac{d^2x}{dt^2}=0$ (ω_0=Natural frequency of oscillation)

Now in presence of electric field we can write

$F= F_{rest} + F_{ext}$

$=> a = \frac{F_{rest}}{m} + \frac{F_{ext}}{m}$

$=> \frac{d^2x}{dt^2} = -\omega_0^2 x + \frac{F_{ext}}{m}$

$=> \frac{d^2x}{dt^2} +\omega_0^2 x= \frac{F_{ext}}{m} = \frac{qE_0 e^{-i\omega t}}{m}$ ----------(2.1)

We have from the definition of dipole moment

p=qx

Where q =charge and x=distance between charges

If N be the number of dipoles per unit volume, then total number of dipoles will be, Np=Nqx=P

Multiplying equation 2.1 by Nq

$$Nq\frac{d^2x}{dt^2}+Nq\omega_0^2x=Nq.\frac{qE_0e^{-i\omega t}}{m}$$

$$\Rightarrow \frac{d^2P}{dt^2}+\omega_0^2P=\frac{Nq^2E_0e^{-i\omega t}}{m}$$

$$\Rightarrow \frac{d^2P}{dt^2}+\omega_0^2P=\frac{Nq^2\varepsilon_0\omega_0^2E}{m\varepsilon_0\omega_0^2}$$

$$\Rightarrow \frac{d^2P}{dt^2}+\omega_0^2P=\chi_0\varepsilon_0\omega_0^2 \quad \text{----------(2.2)}$$

Solution of equation 2.2 can be written as

$$P=P_0e^{-i\omega t}$$

Putting this solution in equation 2.2

$$\Rightarrow P_0(-i\omega)^2e^{-i\omega t}+\omega_0^2P_0e^{-i\omega t}=\chi_0\varepsilon_0\omega_0^2E$$

$$\Rightarrow -\omega^2P+\omega_0^2P=\chi_0\varepsilon_0\omega_0^2E$$

$$\Rightarrow P=\frac{\chi_0\varepsilon_0\omega_0^2E}{\omega_0^2-\omega^2}$$

$$\Rightarrow P=\left(\frac{\chi_0\varepsilon_0\omega_0^2}{\omega_0^2-\omega^2}\right)E \quad \text{----------(2.3)}$$

From equation(2.3) it is clear that P α E

$$P=\varepsilon_0\chi(\omega)E$$ Where

$$\chi(\omega)=\frac{\chi_0\omega_0^2}{\omega_0^2-\omega^2}$$

When $\omega \rightarrow \omega_0$

Then $\chi(\omega)=\infty$

But this is impossible.So there must be some resistive force i.e. damping force, F_{damp} α $\frac{dx}{dt}$

$$\alpha\ Nq\frac{dx}{dt}$$

$$\alpha\ \frac{d(Nqx)}{dt}$$

$$\alpha\ \frac{dP}{dt} = \sigma\frac{dP}{dt}$$

So total force

$F=F_{rest}+F_{ext}+F_{damp}$

$\frac{d^2P}{dt^2} + \omega_0^2P+\sigma\frac{dP}{dt}=\chi_0\varepsilon_0\omega_0^2E$ ----------(2.4)

Now putting the solution in above equation

$=>(-i\omega^2)P+\sigma(-i\omega)P+\omega_0^2P=\chi_0\varepsilon_0\omega_0^2E$

$=>P=\frac{\chi_0\varepsilon_0\omega_0^2E}{\omega_0^2-\omega^2-i\sigma\omega}$

$=>P=(\frac{\chi_0\omega_0^2}{\omega_0^2-\omega^2-i\sigma\omega})\varepsilon_0E$ ----------(2.5)

Where $\chi(\omega)=\frac{\chi_0\omega_0^2}{\omega_0^2-\omega^2-i\sigma\omega}$

$$\frac{\chi(\omega)}{\omega_0^2-\omega^2+i\sigma\omega} = \frac{\chi_0\omega_0^2}{\omega_0^2-\omega^2-i\sigma\omega} \times \frac{1}{\omega_0^2-\omega^2+i\sigma\omega}$$

$$=>\frac{\chi(\omega)}{\omega_0^2-\omega^2+i\sigma\omega} = \frac{\omega_0^2\chi_0}{(\omega_0^2-\omega^2)^2+(\sigma\omega)^2}$$

$$=>\chi(\omega)= \frac{\omega_0^2\chi_0(\omega_0^2-\omega^2)}{(\omega_0^2-\omega^2)^2+(\sigma\omega)^2} + \frac{i\omega_0^2\chi_0\sigma\omega}{(\omega_0^2-\omega^2)^2+(\sigma\omega)^2}$$

$=> \chi(\omega)= \chi'(\omega) + \chi''(\omega)$ ----------(2.6)

We have

$$\varepsilon = \varepsilon_0(1+\chi)$$

$$=\varepsilon_0(1+\chi'(\omega) + i\chi''(\omega))$$

$$= \varepsilon_0(1+\chi'(\omega)) + i\varepsilon_0\chi''(\omega)$$

$$=\varepsilon'(\omega) + i\varepsilon'' \quad \text{----------(2.7)}$$

Where, $\varepsilon'(\omega) = \varepsilon_0[1+\frac{\omega_0^2\chi_0(\omega_0^2-\omega^2)}{(\omega_0^2-\omega^2)^2+(\sigma\omega)^2}]$

$$\varepsilon'' = \frac{\varepsilon_0\omega_0^2\chi_0\sigma\omega}{(\omega_0^2-\omega^2)^2+(\sigma\omega)^2}$$

2.8.4 Dielectric loss

Dielectric relaxation is the lag in dipole orientation behind an alternating applied electric field. Under the influence of such a field the polar molecules of a system rotate towards an equilibrium distribution. When the polar molecules are large or the frequency of alternating field is high, the rotational motion of molecules is not sufficiently rapid for attainment of equilibrium with the field. The polarization then acquires a component out of phase with the field and the displacement current acquires a conductance component in phase with the field. This conductance component obeys ohms law and it results in thermal dissipation of energy.

In an ideal electrical circuit having condenser, the charging current is 90^o out of phase with applied voltage. In vector notation the total current is the sum of charging current and loss current. The angle δ between the vector for the amplitude of total current and that for the amplitude of charging current is known as the loss angle. The tangent of the loss angle can be expressed as

$$tan\delta = \frac{loss\,current}{charging\,current} = \frac{\varepsilon''}{\varepsilon'} \quad \textbf{.....(2.8)}$$

where ε′ is the measured dielectric constant of the sample and ε″ is the dielectric loss factor.

A complex dielectric constant therefore can be expressed as

$$\varepsilon^{*} = \varepsilon' - j\varepsilon'' \qquad \text{.....(2.9)}$$

2.9: Theoretical Background of Dielectric Behaviour of Graphene

Graphene as discussed is a monolayer of carbon atoms and possesses some unique properties for which the grapheme is also called as silicon of the 21st century. The objective of this dissertation is to find out the dielectric constant or relative permittivity of graphene and how this property can be used for next generation electromagnetic devices. The dispersion relation of dielectric constant of graphene is supported by various theories. Let's start with the Maxwell's equation and how the Maxwell's equation will lead to dispersion relation of Graphene. The Maxwell's equation is

$$\vec{\nabla} \times \vec{H} = \mu_0 \vec{J} + \mu_0 \frac{\partial \vec{D}}{\partial t}$$

$$= \mu_0 \sigma \vec{E} + \mu_0 \epsilon \frac{\partial \vec{E}}{\partial t} \qquad (\because \vec{J} = \sigma \vec{E} \ \ and \ \vec{D} = \epsilon \vec{E})$$

Let $\vec{E} = E_0 e^{-i\omega t}$

$$\Longrightarrow \frac{\partial \vec{E}}{\partial t} = -i\omega \vec{E}$$

Then, $\vec{\nabla} \times \vec{H} = \mu_0 \sigma \vec{E} - i\omega\mu_0 \epsilon \vec{E}$

$$\vec{\nabla} \times \vec{H} = -i\omega\mu_0 \left[\epsilon - \frac{\sigma}{i\omega}\right] \vec{E}$$

$$= -i\omega\mu_0 \left[\epsilon + \frac{i\sigma}{\omega}\right] \vec{E}$$

$$= -i\omega\mu_0 \tilde{\epsilon} \vec{E} \qquad \text{.....(2.10)} \qquad \text{Where } \tilde{\epsilon} = \left[\epsilon + \frac{i\sigma}{\omega}\right]$$

Graphene oxide is a monolayer of graphite oxide which consists of different functional groups like carbonyl, carboxyl, hydroxyl, and epoxy. All functional groups are polar groups. The high dielectric constant of GO at low frequency has contribution from three different reasons

A. PRESENCE OF VARIOUS POLAR GROUPS

As shown in figure GO structure shows a presence of 4 polar groups like carbonyl, carboxyl, hydroxyl, epoxy. When the GO is exposed to external electric field all polar

groups experience torque and orient in the direction of external electric field. This is known as orientation polarization which increases the dielectric constant.

B.PRESENCE OF DIRAC FERMIONS

A single layered graphene consists of a mono layer of carbon atom packed in 2D honeycomb lattice, with lattice constant 0.142nm. There is SP^2 hybridization involving 2S, $2P_X$, $2P_Y$ in XY plane. The SP^2 hybridized orbitals make 120^0 with each other. The honeycomb lattice consists of six σ bonds. The remaining $2P_Z$ orbital is perpendicular to the XY plane and make bond. Each two P_Z orbitals have one electron and hence the bond is half filled. The half-filled bands play an important role in the physics of strongly co-related bond because of their strong tight binding character and large Coulomb energy.

The energy band of a single layered graphene from the electron is expressed as

t=nearest n $E_{\pm}(K) = \pm t\sqrt{3 + f(k)} - t^{'} f(k)$

$t^{'}$ =next nearest neighbor hopping energy

f(k) is a function given by

$$2\cos\left(\sqrt{3}k_y a\right) + 4\cos\left(\frac{\sqrt{3}}{2}\,k_y a\right)\cos\left(\frac{3}{2}k_x a\right)$$

Solving the equations we get two bands E_+ And E_-. E_+ is known as upper band or □⁺ band. E_- band is known as lower band or □⁻ band. The lower band is completely filled and the upper band is completely empty. The two band touch each other at certain points known as Dirac points.

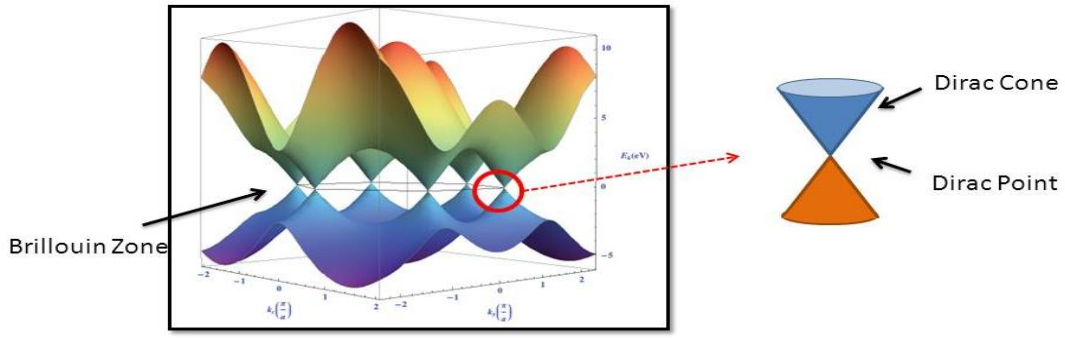


Fig 2.8 Dirac Points and dirac fermions

C.SURFACE PLASMON RESONANCE

Oscillation simply represents back and forth swing of an object induced by a driving factor either outside or inside. This behavior is observed in nearly all materials starting from vast universe to tiny molecules. Among various oscillations electromagnetic oscillations has been paid greatest attention in the recent years. Electrons in graphene behave like Dirac fermions which are assumed mass less. Due to the presence of Dirac fermions, the GO possesses extraordinary properties such as ultra high conductivity and long mean free path. The frequency at which Dirac fermions oscillate is called plasma frequency and plasma frequency is expressed as

$$\omega_p{}^2 = \frac{e^2 n_e}{\epsilon_0 m}$$

$n_e =$ number density of Dirac fermions

The Maxwell's equation can be expressed as

$$\vec{\nabla} \times \vec{H} = -i\omega\epsilon_0 \left(1 - \frac{\omega_p{}^2}{\omega^2}\right)\vec{E}$$

ω= Frequency of the incoming electromagnetic wave

In the low frequency range $\omega < \omega_p$

$$\frac{\omega_p{}^2}{\omega^2} > 1$$

The conduction current dominates the displacement current. In the high frequency range ω is much greater than ω_p , the current is dominated by displacement current.

Relation between dielectric constant and frequency is

$$\epsilon(\omega) = \epsilon_0 \left(1 - \frac{\omega_p{}^2}{\omega^2}\right) \text{.....(2.11)}$$

2.10: Recent advances in graphene oxides

In the recent years GO has been synthesized by variety of methods and GO is highly conducting in nature. It can be used as dielectric material in various applications. Reduced graphene oxide (r-GO) films were used to grow cells and showed enormous

biocompatibility.[34] 60 Films formed of r-GO have shown potential even in solar cells.[20] Few reports on the dielectric study of GO/graphene based materials composites exist in the literature to increase the dielectric properties of host materials,[35]and graphene based materials.[36] Recently, MnO2 65 decorated graphene nanoribbons showed superior permittivity and excellent microwave shielding properties.[37]S. Ruoffetetal. showed that chlorinated r-GO can enhance the dielectric constant of r-GO/Polymer composites.[38] The low dielectric constant and ultrahigh strength graphene oxide/polyimide composite films were also reported.[39] Verdejoet al. showed that the homogeneous dispersion of GO through out the polymer matrix can effectively increase the dielectric permittivity.[40]Graphene-poly(vinylidene fluoride)composites with multi-layered structure prepared by a solution-cast and hot-pressing showed a large dielectric constant as high as 7940 after percolation threshold.[41]

2.11: Gap in the literature survey

Though there are a large number of papers are found in scopus about use of GO as dopant in composite materials, the dielectric study of pure GO pellets are scarce.In this view the present study will fulfill the gap.

CHAPTER 3

Chapter 3 discusses about detail experimental procedures in synthesis of GO and RGO. Different characterization techniques like XRD, FTIR , UV spectroscopy, dielectric measurements are discussed in details.

3.1 Materials :

- Graphite flakes
- Potassium permanganate ($KMnO_4$)
- Conc. Sulphuric acid (H_2SO_4)
- Hydrogen peroxide(H_2O_2)
- Sodium nitrate ($NaNO_3$)[for modified hummer's method]
- Beaker – 250 ml.
- One magnetic stirrer
- Magnetic bead
- Measuring flask
- Thermometer
- Spatula
- Funnel
- Ultrasonicator
- Ice bath set up (below 20 degree Celsius)
- Centrifuge machine
- Vacuum oven

3.2 Synthesis of Graphene Oxide (GO) By Hummer's Method

Graphene oxide was synthesized by Hummer's method through oxidation of graphite in stepwise preparation.

1. First of all a steel bowl was taken and some cold water was poured into it. The temperature was maintained below 20^0C.

Fig 3.1 Magnetic Stirrer heating

2. Then a volumetric flask was taken and 25 ml. of concentrated sulphuric acid (H_2SO_4) was taken in it. Then 1 gm. of graphite powder with 99% of purity was added into the solution . Then 3 gm. of potassium permanganate ($KMnO_4$) was added slowly into the solution.

3. Now the above solution was put on magnetic stirrer with rpm 200 and is continuously stirred inside the ice bath set-up (maintained below 20 ^{0}C for 4 h .

4. The mixture was continuously stirred still the solution became pasty brownish colour .

5. Then it was diluted with slow addition of 100ml. distilled water. The reaction temperature was rapidly increased with effervescence and colour was changed to brown colour .

6. The solution was finally treated with 5ml. of hydrogen peroxide (H_2O_2) to terminate the reaction by appearance of greenish yellow

Fig 3.2 Greenish yellow colour precipitation of GO

7.Now the solution was put in the ultrasonicator for one h for purification of mixture.

8.After purification the solution was centrifuged and its pH was maintained neutral. Now the pasty GO was put in the vacuum oven for drying and then it was powdered to get the powder form of GO.

Fig 3.3 Semi liquid form of GO

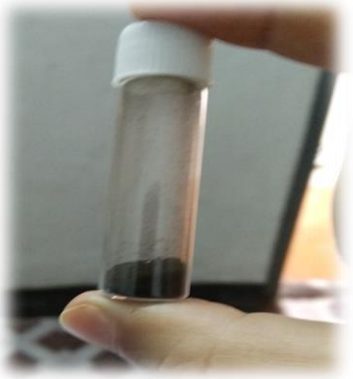


Fig 3.4 Powdered GO

3.3 Reduction of GO to RGO

GO was treated with ascorbic acid and maintaining the solution at 100^0C for 24 h .

3.4 Preparation of GO pellet

GO powder was mixed with 3%polyvinyl alcohol and thoroughly grounded.Then the groundd powder was pressed with 3.5 ton load to get the desired specimen.

3.5 Characterisation

The characterization of the sample aimed to obtain information of surface morphology, crystalline structure, mechanical properties and dielectric properties of Graphene Oxide . Hence, the techniques viz X-Ray diffractometer (XRD), Fourier Transform Infrared Spectroscopy (FTIR), ultraviolet Spectroscopy (UV), and dielectric properties analysis using LCR meter were employed.

3.5.1 Fourier Transform Infrared spectroscopy (FTIR)

A mixture of 5.0 mg of dried sample and 200 mg of KBr was pressed into a disk for FTIR measurement. The amount of mixture was kept constant to obtain repeatable transmission from the sample. KBr pellet is used because KBr does not absorb in the IR wavelengths between 4000- 400 wavenumbers (cm^{-1}). This way we can disperse the material usually in KBr to make a pellet. All the samples were examined by FTIR spectroscopy (FTIR Nicolet 6700/Thermofisher Scientific) using KBr pellet technique in the region 500 cm^{-1} - 4000 cm^{-1} to identify the functional groups in the samples.

Figure 3.5 Photograph of Nicolet 6700 used for obtaining FTIR spectra

3.5.2 Ultraviolet Spectroscopy (UV)

UV-visible spectral analysis of the GO powder were carried out by SHIMADZU UN 2550/JAPAN UV spectrophotometer at room temperature in the wavelength range of 240 nm to 800 nm. The sample was kept in the sample holder. The UV light source was switched on so

that the light falls on the sample. The detector detected the remaining UV light that passes through the sample. The processor compared the intensity of original UV light from light source from the detected UV light. The variation of absorbance and transmittance with wavelength were recorded.

Figure 3.6 Photograph of UV 2550/SHIMADZU/JAPAN used for obtaining UV

3.5.3 Wide angle X-ray diffraction (WAXD)

Ni filtered Cu Kα radiation having wavelength 0.1542 nm was generated at 40KV and 35 mA using WXRD/SHIMADZU/JAPAN. This monochromatised X-rays were suitably collimated by passing them through slits and fall on the specimen sample which is present in the goniometer. With the help of goniometer the angle at which the sample is positioned was measured. The detector is of high sensitivity and could detect X-rays diffracted by the sample. In this way it analyzes the orientation distribution of the crystallites present in the sample.

The X-ray diffractograms were recorded from Bragg angle 10^{o} to 80^{o} at room temperature of 28^{o}C by goniometer. The goniometer was equipped with scintillation counter at a scanning speed of 10^{o}/minute. The X-ray diffractograms show the variation of intensity with braggs angle

Figure 3.7 Photograph of XRD/SHIMADZU/JAPAN used for obtaining X-ray diffractogram

3.5.4 Dielectric Properties

Rectangular shaped specimens of 1cmx 1cmx 1mm were used. The rectangular surfaces of the test samples were coated with conductive silver paint. The test samples were fixed between two electrodes and kept inside the sample holder.

The capacitance and dielectric loss measurements in this study were performed by using a computer interfaced LCR HIOK/ 3532-50, JAPAN. Two sets of measurements were carried out: One is from room temperature around 26^{o}C to 100^{o}C at various frequencies with a heating rate of 2^{o}C/min and another is from 1Hz to 1MHz frequency at various temperatures for the evaluation of dielectric properties of GO.

CHAPTER 4

Results and Discussion

This chapter 4 is devoted for the characterization of prepared GO pellets by various analytical techniques such as UV-Visible spectroscopy, powder X-ray diffraction(XRD), fourier transform infrared spectroscopy(FT-IR) and the obtained results are discussed in details. This chapter also enumerates about dielectric studies of GO, variation of dielectric constant, dielectric losses, ac conductivity with variation in frequency are discussed with proper reasoning.

4.1 XRD of GO

XRD is an important characterization technique for characterization of GO. XRD pattern of GO is presented in fig4.1. As shown in fig 4.1, XRD pattern of GO exhibits a unique peak at 2Θ value of 9.178^0 . It corresponds to (001) reflection plane of material. The interplanar spacing (d) is 9.62784Å.The full width half maximum(FWHM) is found to be 0.284 A^0.

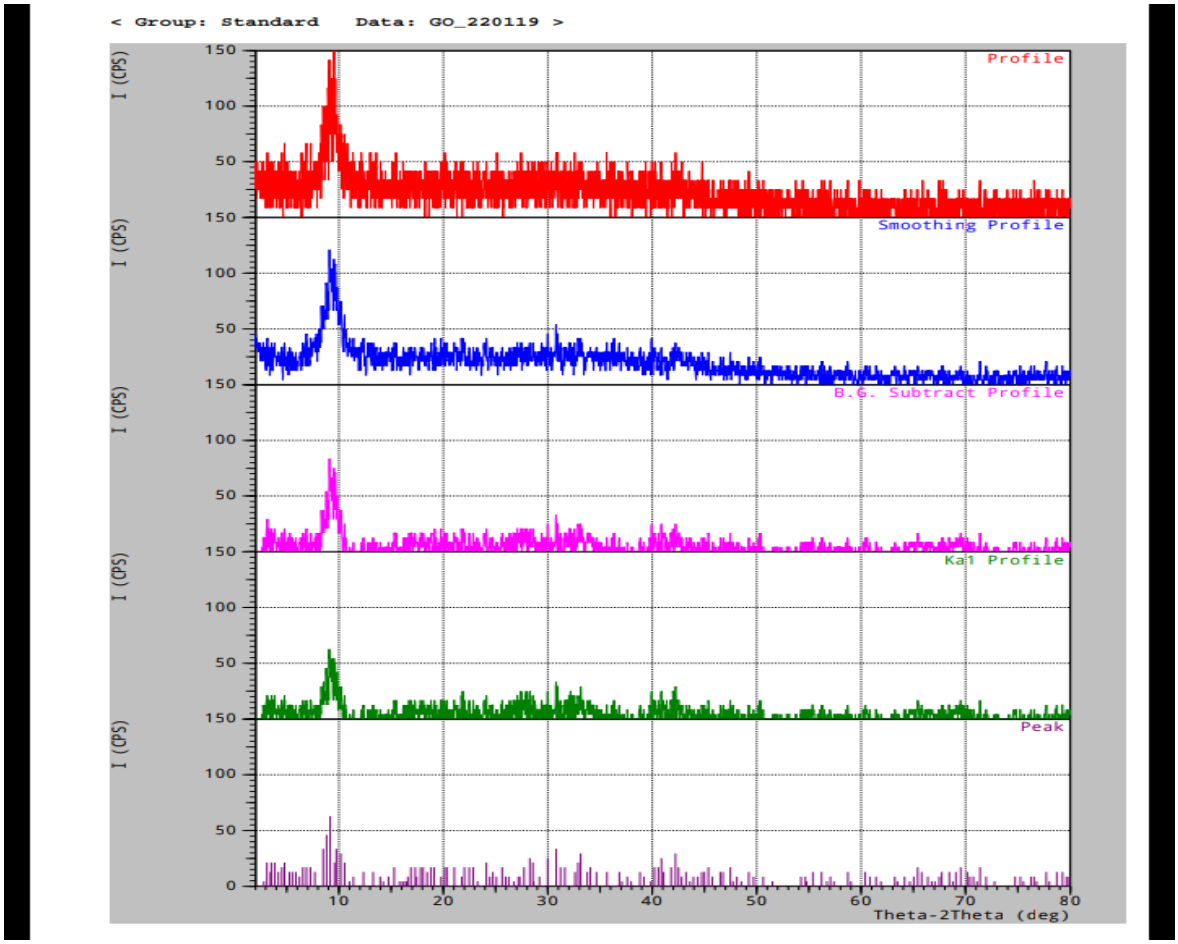


Fig 4.1: XRD of GO

4.1.1 Calculation of Crystallite Size

Particles in a material are present as a single crystal or an agglomeration of several crystals present in a particle. Thus the particle size is usually bigger than crystalline size.
The GO was prepared in powder form during synthesis process. For powdered sample the size of crystallite form is given by Debye Schererr formula. The sharp peak observed in fig4.1 indicates the crystalline shape of GO. The broad peak indicates amorphous nature. The observed interplanar spacing in GO (9.62784 A^0) is more than standard interplanar spacing of graphite (3.54 A^0). The increased interplanar spacing in GO is due to presence of diferent functional groups.

Debye schererr formula is given as

$$D=\frac{K\lambda}{\beta cos\theta} \quad \text{.....(4.1)}$$

Where K-Shape factor

λ- wavelength of incident beam

β- Full width half maximum

θ- angle of refraction

For spherical particle, shape factor is chosen as 0.9, wavelength of incident beam as 1.5 A^0.

The crystal size obtained using Debye schererr formula is 27.34 nm at 9.178^0 but crystallite size is however different from particle ,the particle size is larger than crystallite size.

The particle size is measured by TEM, SAXS.

4.1.2 XRD of Reduced graphene oxide (RGO)

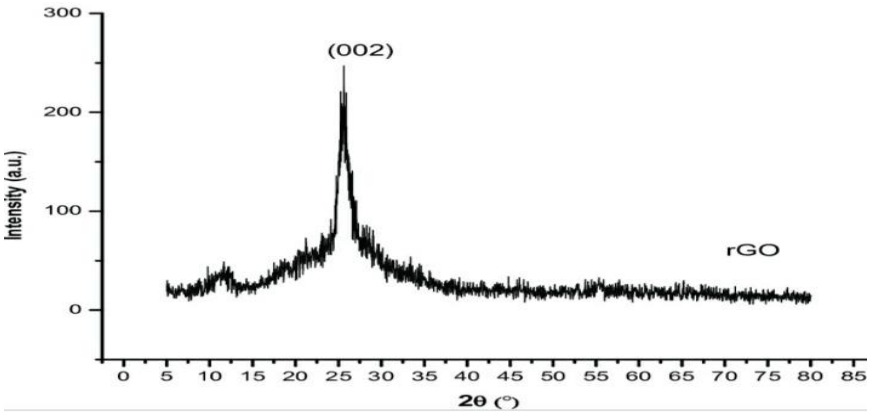


Fig:4.2: XRD pattern of RGO

The XRD of RGO is shown in fig 4.2, as observed in the XRD pattern the peak of GO at 9.178^0 disappears for RGO.The removal of this peak from XRD pattern confirms the removal of the functional groups present in GO.The peak at around 9.178^0 in GO is replaced by a less intense and broad peak at 26^0. It corresponds to 002 reflection plane for RGO. The interplanar spacing obtained for RGO is 3.84Å.The interplanar spacing in RGO is reduced due to the removal of the oxygen functional group. Further due to absorption of moisture from the surrounding in GO the interplanar spacing is more.

The peak position 'd', FWHM and crystallite size are presented in tabular form in table1.

Table 1: Crystallography comparison of GO and RGO

Sample	Peak position	d Spacing	FWHM	Crystalite size
GO	9.1780^0	$9.627A^0$	0.284^0	27.34nm
RGO	26^0	$3.84A^0$	0.546^0	9.82nm

The increase in FWHM of RGO leads to decrease of crystallite size .The small crystallite size of RGO compared to that of GO underlines the increase in amorphous nature of RGO.

4.2 FTIR Spectra of GO

FTIR spectra of GO is shown in fig 4.3 .The specimen of GO contains numerous functional groups. The strong band at $3275.97cm^{-1}$ is assigned due to –O-H stretching vibrations in the absorbed water molecules . The bands at $1638.96cm^{-1}$ and $1089.94cm^{-1}$ present –C-O stretching vibrations of carboxylic acid and carbonyl group respectively. All FTIR peaks and corresponding assignments are presented in table-2

Table -2:FTIR assignments

Sl No.	Wave numer	Assignment
1	3275.97	O-H Stretching vibration
2	1638.96	C-O stretching vibration from carboxylic
3	1089.94	C-O stretching vibration

Fig 4.3 FT-IR spectrum of GO

The functional groups are at 1638.96 cm^{-1} and 1089.94 cm^{-1} testify the presence of oxygen containing functional groups.

However when the FTIR spectrum of RGO is obtained the percentage of transmittance is reduced and the absence of peaks at 1638.96 cm^{-1} and 1089.94cm^{-1} testifies the removal of these peaks, fig 4.4 represents the FTIR spectrum of RGO.

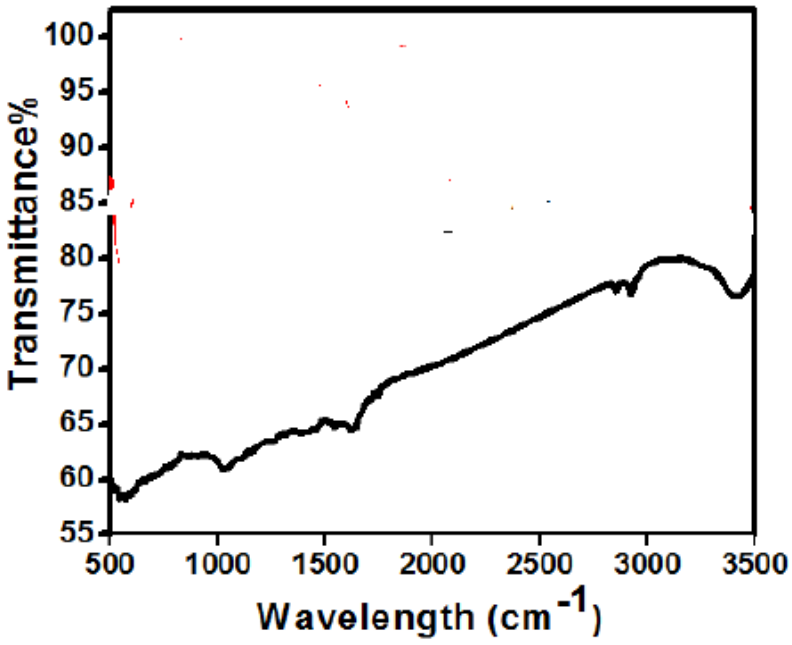


Fig 4.4 FT-IR spectrum of RGO

A low intensity band observed at 955cm^{-1} in RGO can be ascribed to C-O stretching vibrations of carbonyl group after reduction

4.3 Ultra Violet Spectra Of GO

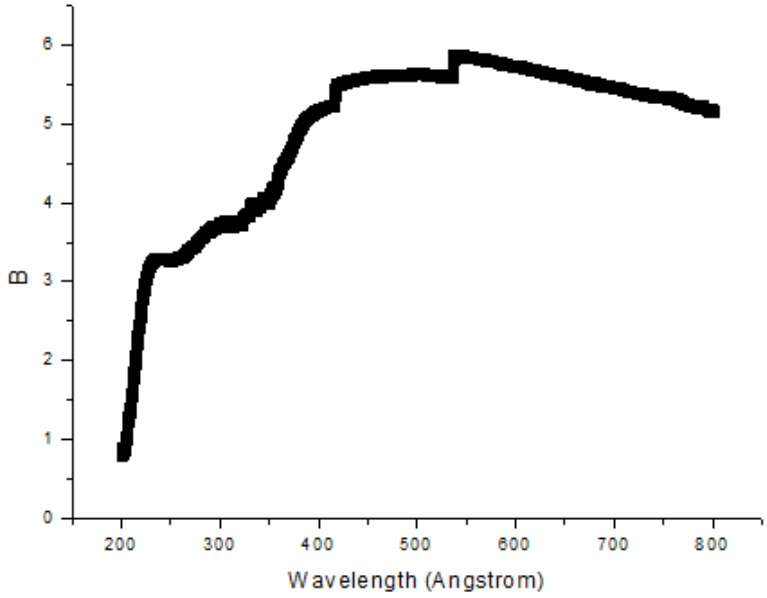


Fig 4.5 : U-V visible spectra of GO

The U-V visible light scanning wave length ranges from 200nm to 1000nm.The UV visible spectra of GO exhibits a prominent peak at 230nm. The peak at 230 nm arises due to π-π* transition of aromatic C-C bond. The visible peak at 277nm arises (π-π) transition of aromatic C-C bonds and C=O bonds.

Therefore the GO powder is a UV absorber for wave length 230nm.

4.4 Study of Dielectric Behaviour

Dielectric measurements were conducted for GO pellets to study its relaxation behaviors. Measurements were conducted with varying frequency from low frequency of 1 Hz to high frequency 1 MHz at room temperature of 35 ^{0}C.

Dielectric dispersion is the dependence of permittivity of a material on the frequency of an applied electric field. There is a lag between changes in polarization and changes in electric field. Thus permittivity is a complicated function of frequency of electric field. Dielectric relaxation is the lag in dielectric constant of a material . It is analogous to hysteresis in changing magnetic field .

4.4.1 Variation of Dielectric Constant Of GO At Low Frequency

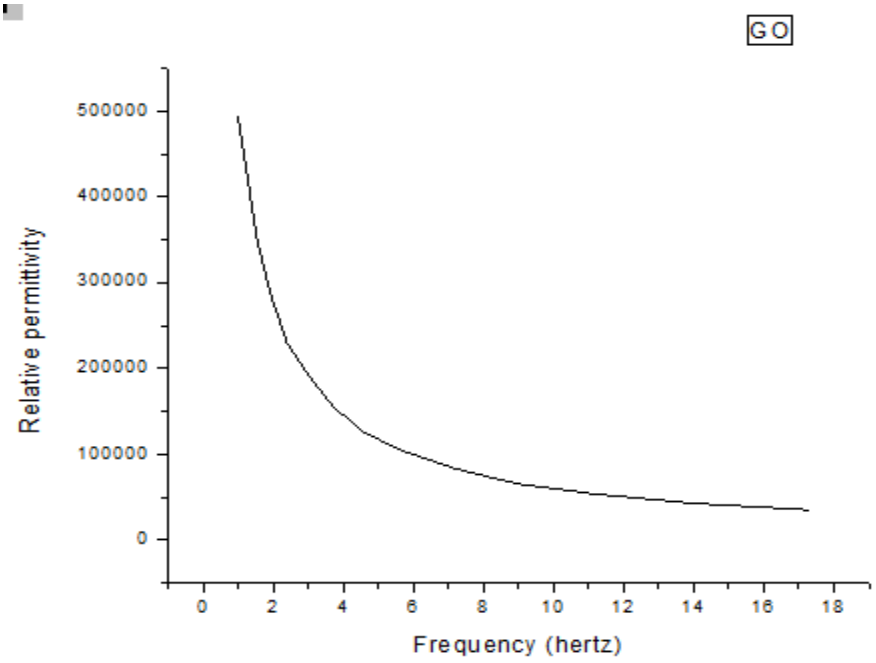


Fig 4.6: Variation of dielectric constant in low frequency domain

The frequency dependence of the relative permittivity known as dielectric constant is depicted in fig 4.6 .The fig 4.6 shows the variation of ε_r in low frequency range spanning from 1 Hz to 20 Hz . At low frequency of 1 Hz the dielectric constant is very high i.e. $5x10^5$. As the frequency increases dielectric constant decrease to 5000 at 20 Hz .This is an important result obtained from the experiment, because of evolution of gigantic dielectric constant material. It is comparable to materials like $CaCu_3Ti_4O_{12}(10^5)$ and higher than various ferro electrics and perovskite titanates (1000-50000). This high dielectric constant of GO is due to various facts such as

a) Presence of mass less Dirac fermions which are equivalent to electrons in metals
b) Presence of surface Plasmon resonance
c) Presence of various functional group contributing for high orientation polarization due to their polar nature
d) Presence of high interfacial polarization (IP). The IP is due to accumulation of unbounded charges at the interface leading to formation of large dipole.

In the low frequency region , a sudden fall of dielectric constant is obsereved . ε_r falls from $5x10^5$ at 1 Hz to $1x10^5$ at 20Hz. As frequency increases , some of the contributions to polarisation , such as ionic polarization , orientation polarization

decreases. With increase of frequency the time interval decreases and not much time is left for polar groups to realign with external field . Thus lag increases with increase of frequency and contribute for decrease of dielectric constant.

4.4.2 Variation of dielectric constant of GO at high frequency

Fig 4.7 depicts variation of dielectric constant from 0.2 MHz to 1MHz where dielectric constant decreases from 95 to 75 . If we compare fig 4.6 and fig 4.7 , it is observed that there is no sudden fall of dielectric constant as observed in fig 4.6 . Here the decrease of ε_r is slow . The dielectric constant of GO is 75 even at frequency of 1MHz and it opens up many applications of GO.

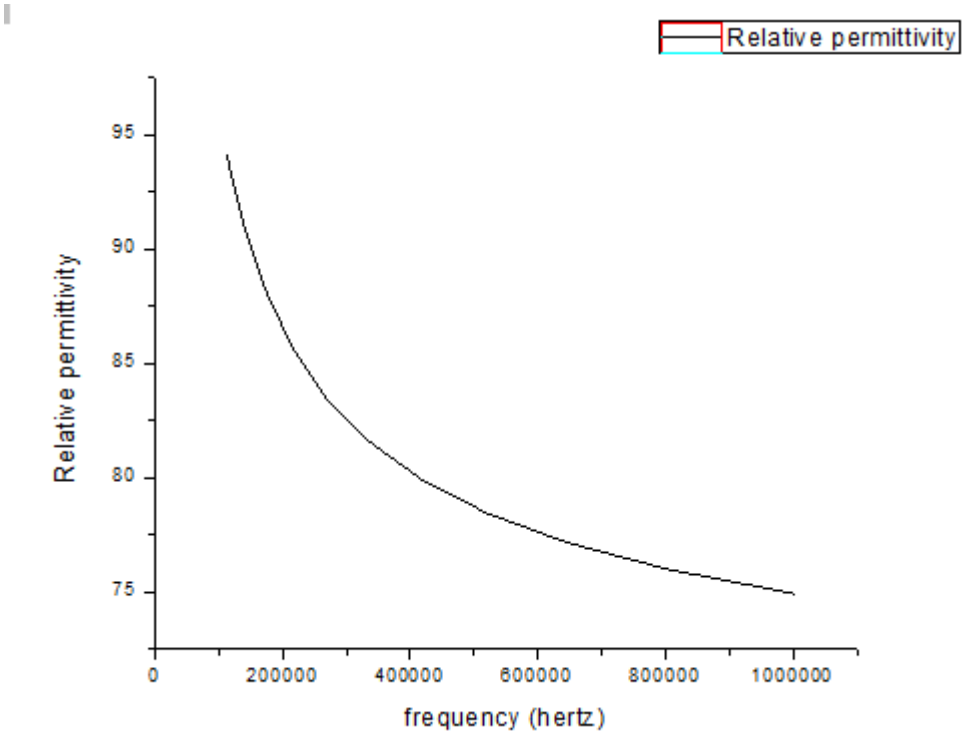
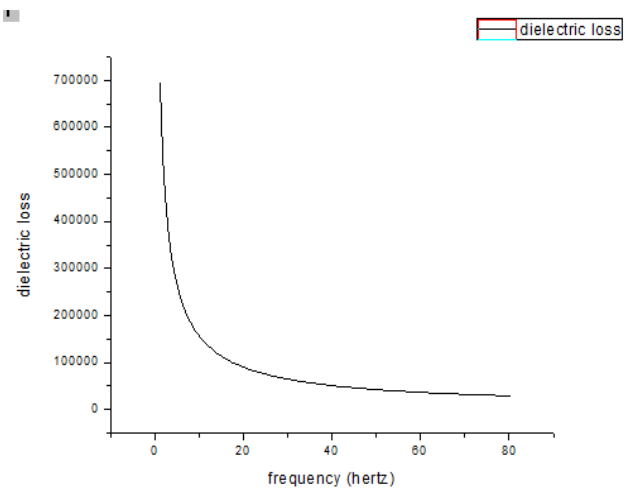
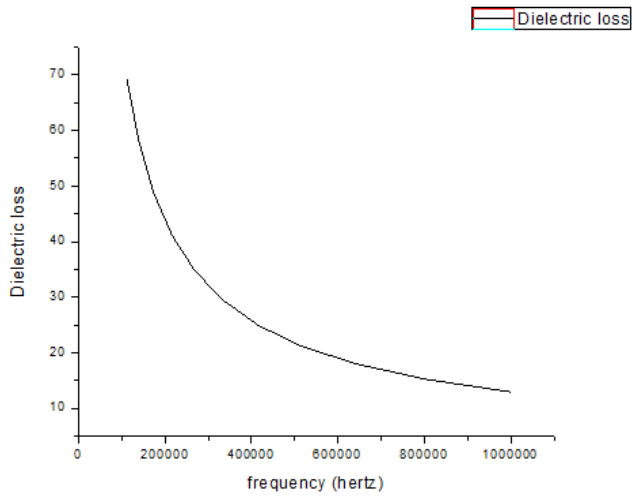


Fig 4.7: Variation of dielectric constant in high frequency domain

4.4.3 Variation of dielctric loss with Frequency





4.8(a) Low frequency vs. dielectric loss **4.8(b) High frequency vs. Dielectric loss**

Fig 4.8(a) and fig 4.8(b) depicts the variation of dielectric loss with frequency in low frequency and high frequency domain respectively. It is observed from Fig 4.8(a) and fig 4.8(b), that dielectric loss (ε") shows similar behaviour with ε'. ε" decreases with frequency with increase of frequency in low frequency domain and high frequency domain.

The oscillating electric field polarize the GO. This creates a dipole that also oscillates. The dipole absorbs and then reoriented or scattered in the electric field. The dipoles' responses to external field is always lagging by a certain phase.The polarizable molecules spend energy in changing the dipole orientation. When frequency of oscillating electric field resonates with frequency of oscillation of dipoles, the dipole absorbs energy and a peak is observed.

It is observed that dielectric loss is high in the low frequency domain and also the fall of dielectric loss is sudden in the low frequency domain. In the high frequency domain the dielectric loss falls but slowly as compared to low frequency region. The current in dielectric is initially displacement current at low frequency but later this is conduction current in high frequency region. When conduction current flows, it generates heat energy. We know

$$\frac{J_D}{J_C}=\frac{\varepsilon\omega}{\sigma} \quad \text{.....(4.2)}$$

With increase of frequency, J_D (displacement current) increases, J_C (conduction current) decreases and hence loss decreases.

$J_c=\sigma E$,

$J_d=\varepsilon(\partial E/\partial t)=\varepsilon\omega E$

4.4.4 Tan delta variation with frequency

Tan delta function is defined as ratio of dielectric loss to dielectric constant. $\tan\sigma = \frac{\epsilon''}{\epsilon}$

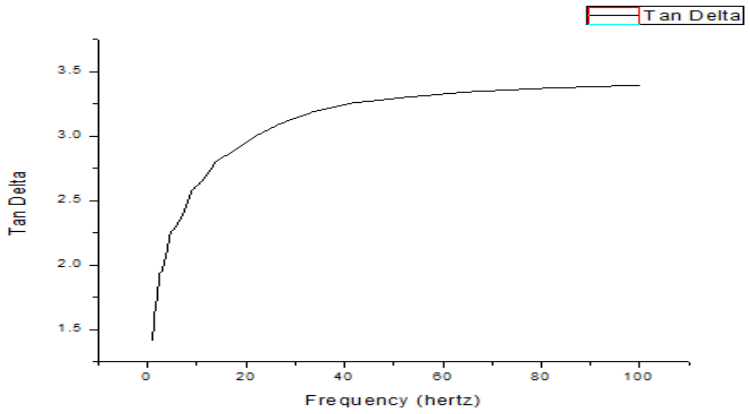


Fig4.9(a)Variation of tanϭ in low frequency domain

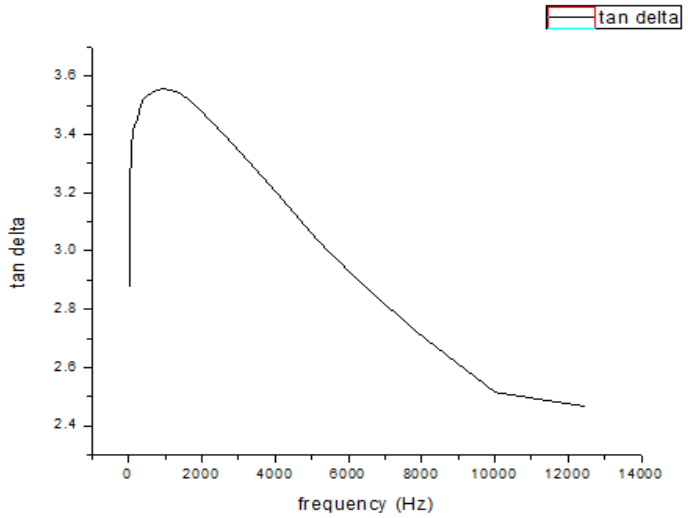


Fig 4.9(b)Variation of tanϭ in mid frequency domain

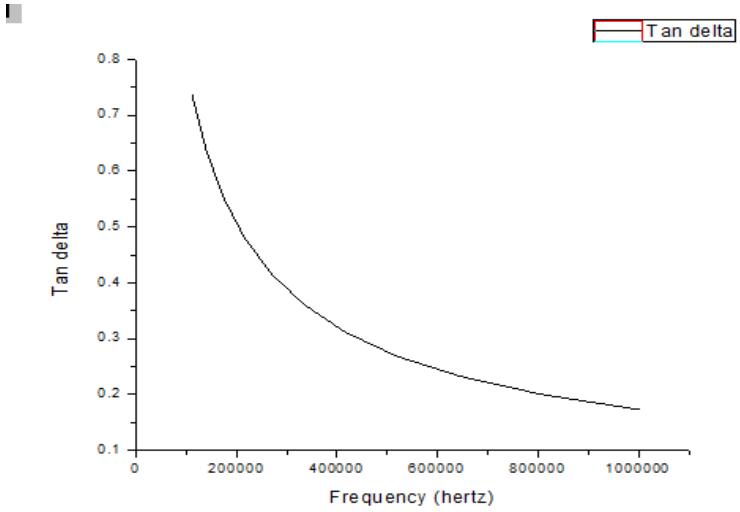


Fig 4.9(c) Variation of tanϭ in high frequency domain

Fig 4.8 (a),(b),(c) depicts the variation of tanσ in the low frequency range , mid frequency range , and high frequency range respectively .In the low frequency region as shown in fig 4.8(a) , the tanσ increases with increase of frequency . In the low frequency region both dielectric constant and dielectric loss are high. However the change in dielectric loss is more compared to the change in dielectric constant. Therefore tanσ increases with increase of frequency and suffers a transition at $1.39x10^{3}$Hz. Beyond this frequency tanσ decreases with increase of frequency. Then at high frequency both dielectric constant and dielectric loss are minimum leading to decrease of tanσ.

4.4.5 AC conductivity variation with frequency

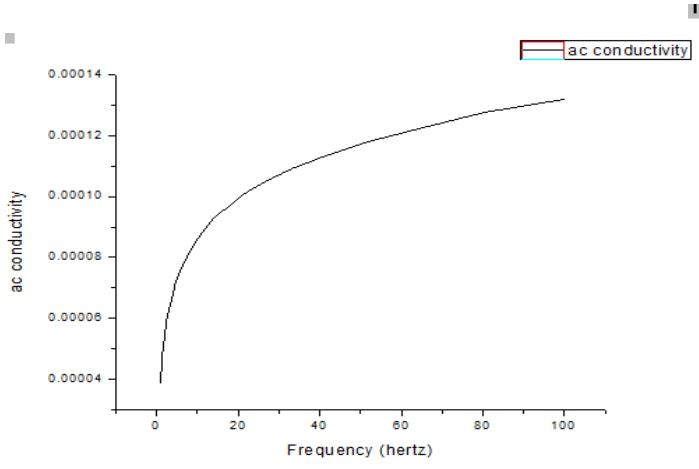
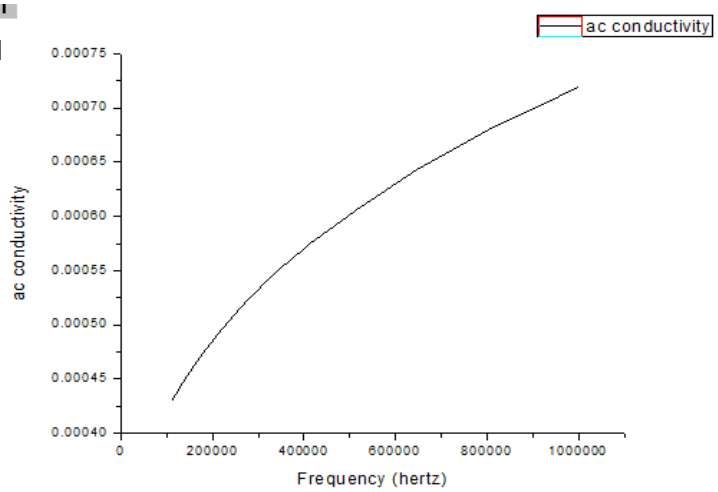


Fig4.10(a)low frequency variation vs conductivity



[Fig4.10(b)high frequency vs conductivity]

DC conductivity is determined only by resistance.

$$\sigma_{dc} = \frac{l}{RA}$$

but ac conductivity depends on skin depth i.e. the thickness in conducting material upto which the amplitude of electromagnetic wave decreases to 1/e . The ac current flows only at the skin of the conductor.

$$J = j_S \exp(-\frac{d}{\lambda})$$

J_s is the current density at surface and J is the current density at depth 'd'.

λ = skin depth

$\lambda = \sqrt{2\rho/\omega\mu}$

With increase of ω , λ decreases , $\frac{d}{\lambda}$ increases , J_c decreases .

Now σ_{ac} is given by

$$\sigma_{ac} = \varepsilon_r (\tan\delta)\omega\varepsilon_0$$

$$\sigma_{ac} = \varepsilon'' \omega \varepsilon_0$$

$$\sigma_{ac} = \sigma_0 \exp(-E_a/KT) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.3)$$

As frequency increases more and more of bound charges start to oscillate out of phase with applied voltage. This contribute to increase the ac conductivity with increase of frequency.ac conductivity increases from 0.00004ohm $^{-1}$ cm^{-1}at 1 Hz to 0.00075 at 1MHz.

4.4.6 Cole cole plot

Cole cole plots are indicator of relaxation present in a material. These are plotted by taking imaginary part of relative permittivity i.e dielectric loss on y axis and real part i.e dielectric constant on y axis.The variation of dielectric loss and dielectric constant with frequency are governed by Debye equation.

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2}$$

$$\varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^2 \tau^2}$$

……(4.4)

Equation 4.1 are known as Debye expression and gives frequency dependence of both dielectric constant and dielectric loss.The material that obeys debyes relation will have cole cole plot like a perfect semicircle. And for materials not obeying debyes laws or whose dielectric loss does not show any relaxation , cole cole plots are not semicircles.Fig 4.10 gives the cole cole plot for GO keeping frequency as the varying parameter.

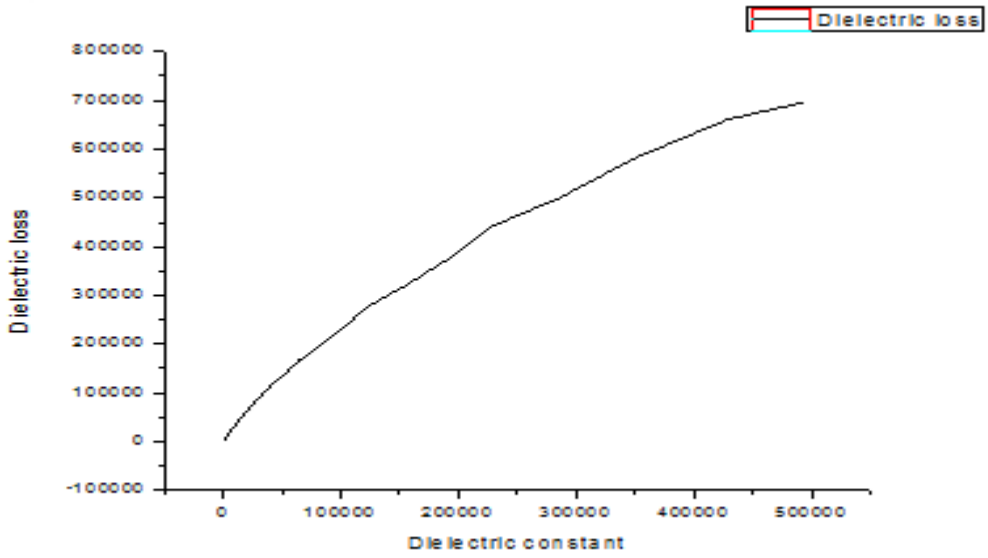


Fig 4.11 Cole cole plot for GO

As there is no relaxation observed in the imaginary part of dielectric constant as shown in fig 4.8 in both low and high frequency domain, Cole Cole plots are not semicircles having no relaxations. GO does not obey Debye's relaxation.

Chapter 5

Conclusion

Graphene oxide pellets prepared by Hummers Method were well characterised by well known physiochemical techniques and confirmed the reduction of Graphene Oxide to Graphene.The XRD analysis hinted the conversion of Graphene oxide to Graphene as indicated by the disappearance of characteristic peak of Graphene Oxide. The FTIR spectral analysis indicated the removal of several oxygen functional groups namely epoxide groups and hydroxyl groups after reducing Graphene oxide to Graphene. .A systematic investigation has been performed to study the dielectric behaviour of GO. Novel GO contains mainly –OH and –COOH functional groups which are responsible for the change in polarization of GO sheet under the applied electric fields at the various frequency range. Present study strongly concluded that the novel GO exhibits very high dielectric constant and is in the order of 10^5 in magnitude. This value is very high, which is even very high compared to the conventional giant dielectric material such as $CaCu_3Ti_4O_{12}$. The reorientation/rearrangement of the attached functional groups (- OH and - COOH) in the GO resulted change in the dipole moment and the polarization which lead to the high dielectric constant at low frequency range. All the defects are very prone to chemical oxidation of single layered graphite/graphene. These defects cause to the restriction of л→л transition of electrons and give rise to the strong dipole at the defect sides and results an extraordinarily high value of dielectric constant with relatively low dielectric losses. This newly synthesized GO with colossal dielectric constant is likely to enable us further scaling advances in performances of the electronic and energy storage devices.These GO can be used as reinforcements like dopants to synthesize composite materials of high dielectric constant.

References

1. P.Van Musschen Broek, Introduction Philosophion Naturalem, Luchtman,Leiden (1762)

2. M.Faraday, Phil.Trans 128:1 79 265 (1837)

3. O.F.Mossoti, Bibl.univ.modena 6, 193(1847)

4. O.F.Mossoti, Mem. di Mathem e.di.fisica in modena, 24(2) 49 (1850)

5. R.Clausius Volume 2 Vieweg. Braunschweigh (1879)

6. P.Debye, Phys.Z, 13,97(1912)

7. L.Onsager, J.Amer.Chem.Soc, 58,1486(1936)

8. J.G.Kirkwood J.Chem.Phys, 7, 911(1939)

9. J.G.Kirkwood and R.M.Fuoss, J.Chem.Phys, 9,329(1941)

10. P.Drude, Z.phys.Chem, 23,267 (1897)

11. K.S.Cole and R.H.Cole, Journal of Chemical phys, 9, 341 (1941)

12. D.W.Davidson and R.H.Cole. J.Chem.Phys, 19,1484(1951)

13. G.Williams and D.C.Watt Trans Faraday Soc, 66, 80 (1970)

14. A.K.Jonsher, Dielectric relaxation in solids, Chelsea dielectric press, London (1983)

15. R.Chau, J.Brask, S.Datta,G.Dewey,A.Majumdar Microelectronic Engineering 80, 1(2005)

16. P.P.Jenkins, A.N.Maclnnes, M.Tabib Azar and A.R.Barron, Science 263, 1751(1994)

17. B. J. Li, H. Q. Cao, J. Shao, M. Z. Qu and J. H. Warner,, *J.Mater. Chem*., , 21, 5069(2011)

18. S. Dubin, S. Gilje, K. Wang, V. C. Tung, K. Cha, A. S. Hall, J.Farrar, R. Varshneya, Y. Yang and R. B. Kaner, *ACSNano*, 4, 3845(2010)

19. S. Xu , L .Yong, and P. Wu, *ACS Appl. Mater. Interfaces*, 5, 654(2013)

20. K. P Loh, Q. L. Bao, G. Eda and M. Chhowalla, *Nat. Chem.* 2, 1015(2015)

21. Y. Hernandez, V. Nicolosi, M. Lotya, F.M Blighe and Z.Y. SunDe, *Nat Nanotechnol.*, , 35, 63.(2008)

22. V. G. Kozlov, V. Bulovic, P. E. Burrows, S. R. Forrest,*Nature*, , 389 362.(1997)

23.T. Förster , *Discuss Farady Soc.* ,27, 7(1959)

24. D. M. Willard, L. L. Carillo, J. Jung and A. V. Orden, *NanoLett*., 1, 469.(2001)

25. Jares- Erijman, E. A., and T. M. Jovin, *Nat. Biotechnol*.21,1387(2003)

26. S .Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y.Y Jia, Y .Wu, S. B. T Nguyen and R.S Ruoff *Carbon*, 45,1558(2007)

27. M. Qian , T. Feng, H. Ding, L. F. Lin, H. B.Li, Y.W. Chen andZ. Sun *Nanotechnology* , 20, 425702(2009).

28. J. Nishijo, Ch. Okabe, O. Oishi and N. Nishi, *Carbon*, 2943–2949.(2006)

29.R. Sergiienko, E. Shibata, Z. Akase, H. Suwa, T. Nakamura and D. Shindo, *Mater.Chem. Phys*. 98, 34.(2006)

30. K. Morishige and T. Hamada, *Langmuir* , , 21, 6277(2005)

31. M. Bystrzejewski, S. Cudziło, A. Huczko, H. Lange, G. Soucy, G. Cota-Sanchez, W. Kaszuwara, *Biomol. Eng* 24, 555.(2007)

32.K Santosh kumar, Suresh Pittala,RSC Advances, 23,65(2018)

33. H. Chen, M. B. Müller, K. J. Gilmore, G. G. Wallace, and D. Li, Adv. Mater., 20, 3557–3561. (2008)

34. Y. Bai, Y. Cao, J. Zhang, M. Wang, R. Li, P. Wang, S. M. Zakeeruddin, and M. Gratzel, Nat Mater, 7, 626–630. 95 (2008)

35. RamanathanT., A. A., StankovichS., D. A., Herrera-AlonsoM., P. D., A. H., S. C., ChenX., R. S., N. T., A. A., P. K., and B. C., Nat Nano, 3, 327–331(2008)

36. S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, and R. S. Ruoff, 100 Nature, 442, 282–286(2006)

37. T. K. Gupta, B. P. Singh, V. N. Singh, S. Teotia, A. P. Singh, I. Elizabeth, S. R. Dhakate, S. K. Dhawan, and R. B. Mathur, J. Mater. Chem. A 2, 4256–4263(2014).

38. J.-Y. Kim, W. H. Lee, J. W. Suk, J. R. Potts, H. Chou, I. N. 105 Kholmanov, R. D. Piner, J. Lee, D. Akinwande, and R. S. Ruoff, Adv. Mater., 25, 2308–2313(2013).

39. J.-Y. Wang, S.-Y. Yang, Y.-L. Huang, H.-W. Tien, W.-K. Chin, and C.-C. M. Ma, J. Mater. Chem., , 21, 13569–13575.(2011)

40. L. J. Romasanta, M. Hernández, M. a López-Manchado, and R. 110 Verdejo, Nanoscale Res. Lett 6, 508. (2011)

41. P. Fan, L. Wang, J. Yang, F. Chen, and M. Zhong, Nanotechnology, , 23, 365702(2012)