PROJECT REPORT

ON

STUDIES ON STRUCTURAL, LINEAR AND NON-LINEAR OPTICAL PROPERTIES OF GRAPHENE OXIDE AND REDUCED GRAPHENE OXIDE

SUBMITTED BY

SNEHA K J

REGISTER NO.: AM21PHY013

in partial fulfillment of

the requirements for award of the postgraduate degree in physics

DEPARTMENT OF PHYSICS AND CENTRE FOR RESEARCH

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M.Sc. PHYSICS PROJECT REPORT

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CERTIFICATE

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ABSTRACT

Nanoscience is a convergence of physics, material science and biology, which deals with the manipulation of materials at the atomic dimensions. The relevance of nanoparticles lies in their ability to change numerous fields, such as Electronics, energy and medicine by the provision of improved performance characteristics. In fact, nanomaterials are particles with structures and properties differ from those of bulk particles due to their small size. Graphene has emerged as one of the most important nanomaterials because of its unique properties like high optical transparency, high electrical conductivities, etc. Graphene oxide (GO) and reduced Graphene Oxide (rGO) are valuable derivatives of graphene. They show different chemical and structural characteristics due to the difference in their chemical compositions. In this work, we have synthesized graphene oxide by Modified Hummer's method and reduced graphene oxide by hydrothermal method. The synthesized products were characterized by X-ray Diffraction, Scanning Electron Microscopy, UV-Visible spectroscopy, Photoluminescence spectroscopy, Z-scan technique. The results confirmed the formation of graphene oxide and reduced graphene oxide.

CHAPTER 1

GRAPHENE AND IT'S DERIVATIVES- STRUCTURE, PROPERTIES AND APPLICATIONS

1.1 Introduction

In materials science, condensed matter physics, and solid-state physics, graphene research is expanding quickly. Due to their distinctive qualities of high mechanical flexibility, large surface area, chemical stability, and superior electric and thermal conductivities, graphene and graphene-based materials have garnered a lot of interest. These properties make them excellent choices for the fabrication of various devices and for use in various applications.

1.2 Graphene

Graphene is a new class of promising material which is one atom thick only, gives new scopes in low-dimensional physics. It is two dimensional which exhibits exceptionally high crystal and electronic quality. It has remarkable linear and nonlinear optical properties and has applications in photonics and optoelectronics.

Structure

Graphene is a wonderful material which has unique structure and excellent electronic, mechanical, optical and thermal properties. It is made up of pure carbon and it is one of the most important elements in nature. It is extracted from graphite, which is an allotrope of carbon. Graphene is a two-dimensional single layer of graphite with hexagonal honeycomb lattice structure composed of carbon atoms in sp^2 hybridized orbitals as shown in figure 2.1. Each carbon atom is covalently bonded to its nearest neighbours in a planar structure.

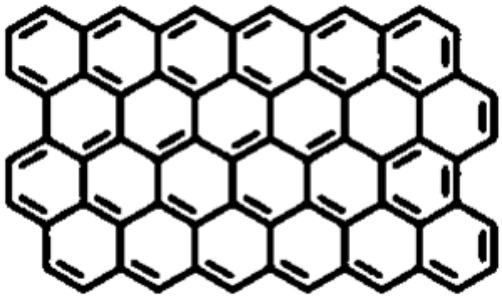


Figure 1.1: Graphene structure

Properties

Graphene is world's first 2D material and it is million times thinner than diameter of single human hair. Graphene is attractive, has a high heat conductivity, is elastic, has a large specific surface area, and is mechanically stable. It has young's modulus approximately 1100 GPa, fracture strength of 125 GPa, thermal conductivity approximately 5000 W$m^{-1}K^{-1}$, high charge mobility 200,000 $cm^2V^{-1}s^{-1}$, theoretical surface area value of 2630 m^2g^{-1}, magnetism and amazing fascinating transport phenomena. It is stronger than steel. Graphene is flexible and light material. Even though it is light it is tough enough. Graphene is a very resistant material as well as an excellent electric conductor. High optical and electrical transparency of graphene is a unique property of it. Graphene is a transparent material and absorbs only very little light (2%). It would prevent devices overheating.

Applications

Nowadays, graphene is a widely used substance with numerous applications. Nanotechnology, electronic gadgets, agriculture, food technology, and other fields can all benefit from the use of graphene. It is 200 times more resistant than steel and 5 times lighter than aluminium. Because of these properties, graphene has applications in energy, construction, health and electronics sectors. Battery's useful life can be increased by 10 and charging time can be decreased by the use of graphene. Because of its high optical and electron transparency and outstanding mechanical qualities, it can be used for biosensors, transparent electrodes, hydrogen storage, composites, and high energy supercapacitors. It is also used in batteries for drones as it is lighter and tougher. Because of this greatest limitation of drones can be minimized. Flexible screens can be manufactured using graphene because of its transparency and flexible nature. Chances of breakage is very small so that graphene can be folded like cling films. In cell phones, televisions and vehicles manufacture this property of graphene could be applied. Graphene light bulbs consume only less energy when compared to LED lights that we use now a days.

Graphene has many applications in energy sector. Rechargeable batteries with graphene are good in energy efficiency. Using paints with graphene and graphene with different materials in homes gives a better thermal regulation of home and saving in air conditioning of spaces. It will be a turning point in renewable energy sector. Graphene in construction improves insulation in buildings and it could be more resistant to corrosion, dampness and fire.

Graphene has important application in health and medical sector. Making of artificial bones and muscles can be done using graphene because of its stronger and flexible property. Lighter hearing aids can be made using it. Graphene changes the electronic sector completely. Electronic circuits use graphene makes devices immune to dampness. Graphene is 1000 times better than copper, because of its excellent thermal and electrical conductivity.

Graphene has ground-breaking biomedical applications. In drug transport (delivery) systems, ultrasensitive biosensors, tissue engineering and biological agents, graphene are used.

1.3 Graphene Oxide (GO)

Graphene oxide is a unique material which is an oxidised form of graphene which is an allotrope of carbon. It is a monolayer material formed by oxidation of graphite, which is cheap and readily available. It contains many oxygen-containing functionalities such as epoxide, carboxyl, carbonyl and hydroxyl groups.

Structure

GO has a hexagonal carbon structure similar to graphene, but also contains a hydroxyl (–OH), an alkoxy group (C–O–C), a carbonyl (C=O), carboxylic acid (–COOH) and other oxygen-based functional groups. Structure of graphene oxide is shown in the figure 1.2. Graphene oxide layers are 0.9 to 1.3 nm thick. Strong paper-like materials, membranes, thin films, and composite materials have all been created using graphene oxide sheets. Graphene oxide is a possible intermediate for the manufacture of graphene. Largest monolayer GO with carbon framework and minimal impurity concentrations can be synthesized in inert containers using highly pure reactants and solvents.

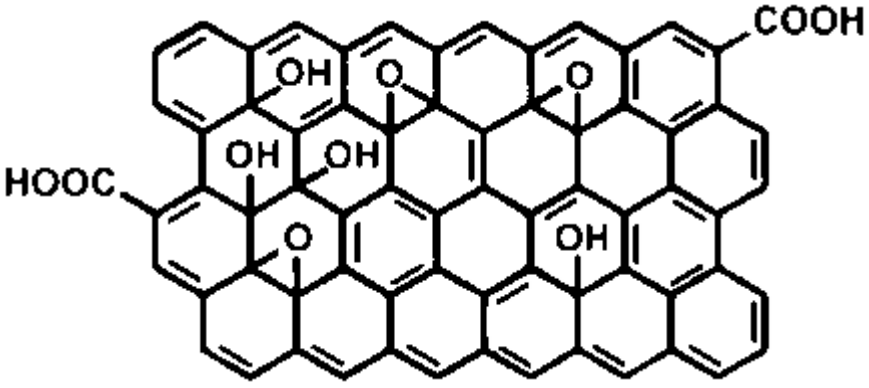


Figure 1.2: Graphene oxide structure

Properties

Graphene oxide is a good surfactant material with unique surface properties. In proportion to humidity, graphite oxides absorb moisture and expand when exposed to liquid water. Water absorbed by graphene oxide shows strong temperature dependence. Graphene oxide is vacuum tight and impermeable to nitrogen and oxygen, but are permeable to water vapours. GO sheets are chemically reactive in liquid water and thereby they acquire a small negative charge. Graphene oxide is hydrophilic and it can be easily hydrated when exposed to water vapour or immersed in liquid water. This results in increased inter planar distance. It also can incorporate other polar solvents like alcohols. Different synthesis methods produce different type of graphene oxide. Graphene oxide have very limited electrical and thermal transport due to the presence of oxygen functional groups.

Applications

Graphene oxide is one nonlinear optical material which have great importance for ultrafast photonics and optoelectronics. Optical limiting of GO is helpful in protection of sensitive instruments from laser-induced damage. Saturable absorption and nonlinear refraction of GO have applications in pulse compression, mode locking, Q-switching and all-optical switching, signal regeneration, fast optical communications respectively. Electrical and optical properties can be tuned dynamically by changing the content of oxygen-containing groups through chemical or physical reduction methods. Optical nonlinearities can be demonstrated during laser-induced reduction process by continuous increases of laser irradiance. Metal nanoparticles enhances optical nonlinearity and fluorescence of graphene oxide.

Graphene oxide is a possible route for large-scale production and manipulation of graphene. Desalination of water by reverse osmosis using graphene oxide is studied. Graphene based films that powered by sun is used to filter dirty or salty water. Material consists of 2 nanocellulose layers, lower layer having pristine cellulose and top layer having cellulose and graphene oxide, absorb sunlight and heat is produced. Water below the material draws up by the system through layers, water gets evaporated leaving contaminants within the layer. Water purification can be done by this. Multilayer films made from graphene oxide which are optically transparent are impermeable under certain conditions. Containers for corrosive acids and medical packaging to improve shelf life are made by these films.

In DNA analysis applications, graphene oxide has been used now. Inexpensive rapid DNA analysis can be done using graphene-based DNA sensors. For room temperature lithium ion

and sodium ion batteries, graphene oxide is used as a flexible free standing battery anode material. And also, as a high surface area conducting agent in lithium-sulphur battery cathodes. Functional groups on the surface of graphene oxide serve as a site for chemical modification and immobilization of active species. These properties of lithium-ion batteries help in rechargeable at cost of low-capacity limits. Enhanced battery performance is obtained by graphene oxide-based composites functionalized with metal oxides and sulphides. Giant refractive index modification that means GO has one order magnitude larger than the current materials. Overall lens thickness can be reduced by more than ten times because of this. Phase modulation and amplitude modulation can be simultaneously achieved using GO flat lens.

Photocatalytic water splitting, which is an artificial photosynthesis process in which dissociated into hydrogen and oxygen, are currently being investigated to produce hydrogen as a source of energy. Graphene oxide's compositional functional groups allow flexible control in water splitting process. In photocatalytic water splitting, targeted band gap and band positions are tailored because of this flexibility. Graphene oxide used in composite material with CdS exhibit increased hydrogen production and quantum efficiency.

Graphene oxide has hydrogen storage capability. Oxygen-based functional groups throughout the sheet stores the hydrogen molecule. By modulating interlayer distance between sheets hydrogen storage capability can be improved. Graphene oxide are used now a days in tissue engineering, cancer diagnosis and treatment, medical imaging and drug delivery. Graphene oxide are used in vaccines and immunotherapy, as an adjuvant and carrier of biomedical materials.

1.4 Reduced Graphene Oxide (rGO)

Reduced graphene oxide is an interesting member in the family of graphene as it is the reduced form of graphene oxide. It resembles graphene but having residual oxygen and other heteroatoms, as well as structural defects. GO and rGO used in nanocomposite materials, polymer composite materials, biomedical applications, energy storage and catalysis and as a surfactant with some overlaps between these fields. rGO can be produced by different reduction mechanisms of GO.

Structure

Reduced graphene oxide has structure similar to graphene, but have some oxygen functional groups. But not have that much functional groups in GO. It has almost same interplanar spacing

similar to graphene less than graphene oxide. Reduced graphene oxide can be made as a thin film from aqueous dispersion of GO in water which has moderate conductivity and it is used in electronic devices.

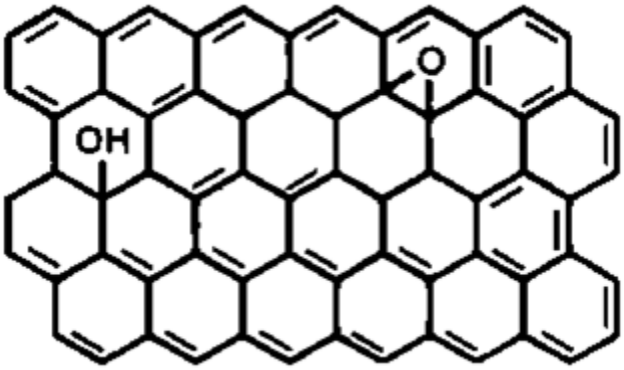


Figure 1.3: Reduced graphene oxide structure

Properties

Functional groups of reduced graphene oxide joint with DNA, proteins, peptides and enzymes consequently, they can chemically fabricate easily. It has greater surface area and low toxicity. It has high chemical stability and carrier mobility. Due to the low content of oxygen functional groups, reduced graphene oxide is only less sensitive to RH.

Applications

GO and rGO can be used in nanocomposite materials, polymer composite materials, energy storage, biomedical applications, as a surfactant and catalysis. Reduced graphene oxide has applications in batteries, in super capacitors and in printable graphene electronics. Low toxicity of reduced graphene oxide enables therapeutic applications, because of greater surface area of it. Due to reduced graphene oxide's high conductivity, it can transfer electrons between it and other sensing materials.

CHAPTER 2

NON-LINEAR OPTICS

2.1 Linear Optics

Linear optics and Non-linear optics are the sub-fields of optics. Optics is a branch of physics which includes behaviour and properties of light, including its interactions with matter and construction of instruments. Linear optics is a field of optics which consists of linear systems which have applications in lenses, mirrors, diffraction gratings, waveplates and have applications of optical components. Linear optical systems have many properties like monochromaticity and superposition.

When monochromatic light enters linear optical system, it doesn't undergo any change. The output wave will be at same frequency that of incident wave. For example, if red light enters a linear optical system like lens, it will be red light itself after coming outside of it. This is shown in the figure 2.1. Figure 2.2 shows the energy level diagram showing the transmissions in a linear material. In linear system, superposition principle is also valid. That is, when a mirror transforms light input X into output X1 and input Y into output Y1, then input consists of X and Y simultaneously give an output X1 and Y1 simultaneously.

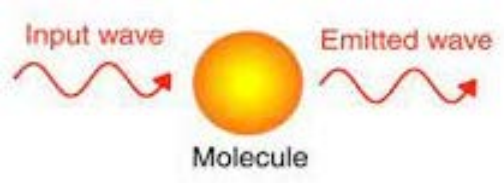


Figure 2.1: Linear interactions of light with matter

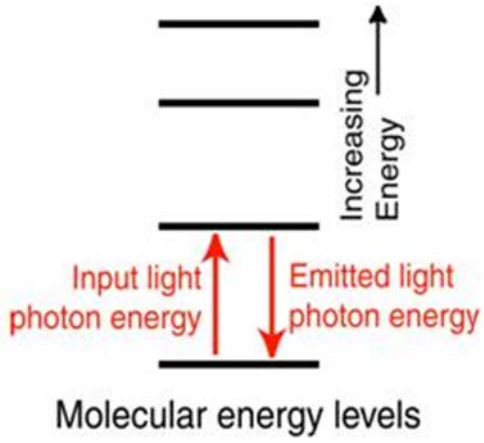


Figure 2.2: Energy transmission in linear material

Linear optics is also known as optics of weak light. Light gets deflected or may be delayed but its frequency is not changed. Optical properties like absorption coefficient and refractive index are independent of light intensity in linear optics. In linear optical system, two beams of light present in a same region have no effect on each other. That is, Light cannot interact with light in linear optical system.

Non-linear optics is another branch in optics that includes the behaviour of light in non-linear media. It is also known as optics of intense light. In this chapter we discuss about non-linear optics theory and applications.

2.2 Non-linear optics

Theory

Non-linear optics is a branch of optics which describes light's behaviour in non-linear media. Non-linear media is the media in which polarization density P which responds non-linearly to light's electric field. This effect is observed only at very high light intensities. That is why it is also called optics of intense light. Light itself gets induced when it propagates through non-linear medium. Superposition principle doesn't hold in the case of non-linear optics. When an input wave propagates through non-linear medium, output wave obtained don't have same frequency. This is shown in the figure 2.3. Figure 2.4 shows the energy level diagram in a non-linear material.

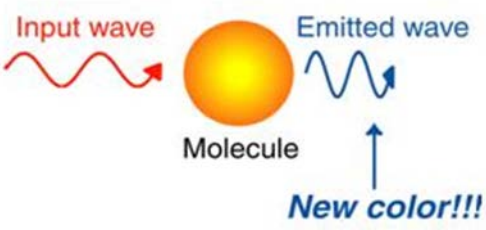


Figure 2.3: Non-linear interaction of light with matter

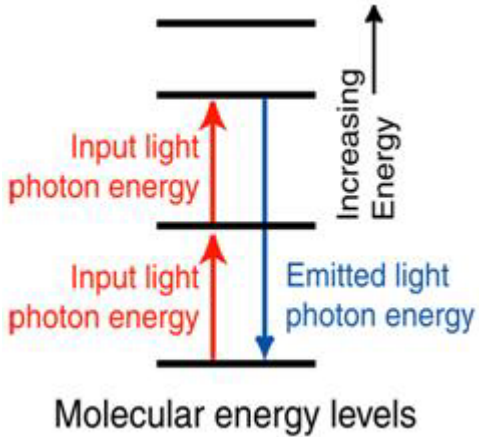


Figure 2.4: Energy transmissions in non-linear material

In non-linear optical systems, refractive index and speed of light changes with change in intensity of light. Frequency of light gets altered when it passes through non-linear medium. For example, red light changes to blue light after passing through non-linear medium. Two beams of light can interact with each other in this medium. That is, light can control light. Non-linear optical materials have many applications in photonic devices, photonics, etc.

First predicted non-linear optical phenomena was two-photon absorption. It is predicted by Maria Goeppert Mayer. Discovery of second-harmonic generation explains the unexplored theoretical curiosity of two photon absorption phenomena. Non-linear optics describes non-linear response of some properties like frequency, polarization and phase or path of incident light. Optical phenomena like frequency-mixing processes are given rise by non-linear optical phenomena.

Different frequency-mixing processes in non-linear optics are SHG, THG, HHG, SFG, DFG, OPA, OPO, OPG, SPDC, OR, etc. In second-harmonic generation (SHG) or it is also known as frequency doubling, generation of light in which frequency is doubled. Here, two photons are destroyed and single photon with double frequency is created. In third-harmonic generation (THG), generation of light in which frequency is tripled. Here, three photons are destroyed and photon with tripled frequency is created. In high-harmonic generation (HHG), generation of light with frequencies greater than the original light. In difference-frequency generation (DFG), generation of light with frequency which is different between two other frequencies.

Other non-linear processes are optical Kerr effect, Cross-phase modulation (XPM), Four-wave mixing (FWM), Cross-polarized wave generation (XPW), modulation instability, etc.

Non-linear optical phenomena can be described by a Taylor series expansion of dielectric polarization density P(t) which is in terms of electric field E(t):

$P = \varepsilon_0 \chi E$

$\chi = \chi_1 + \chi_2 E + \chi_3 E^2 + \cdots$

$P(t) = \varepsilon_0(\chi_1 E(t) + \chi_2 E^2(t) + \chi_2 E^3(t) + \cdots$

Where coefficients χ_n are n-th order susceptibilities of medium.

Second-order Nonlinear optics ($P_2 = \varepsilon_0 \chi_2 E^2$)

Second-harmonic generation (SHG)

$E = E(\omega)_{optical} \rightarrow P_2 \propto E^2(\omega) \rightarrow P_2(\omega \pm \omega) = P_2(2\omega)$ → Frequency doubling

$P_2(0)$ → Rectification

Electro-optic (EO) effect (Pockell's effect)

$E = E(\omega)_{optical} + E(0)_{electrical\ DC}$

$\rightarrow P_2 \propto E^2$

$\rightarrow P_2(0)\{\propto E^2(0)\}, P_2(\omega)\{\propto E(0)E(\omega)\}, P_2(2\omega)\{\propto E(\omega)E(\omega)\}$

$\rightarrow P_2(0), P_2(\omega)\{\propto E(0)E(\omega)\} \rightarrow \Delta n \propto E(0)_{electric\ DC}$

Third-order Non-linear optics ($P_3 = \varepsilon_0 \chi_3 E^3$)

Non-linear optical processes in non-linear medium occur due to the third order non-linear optics.

Intensity dependent refractive index

Non-linear optical material's refractive index depends on intensity of light.

Intensity dependent refractive index $n = n_0 + \bar{n}_2 \langle \bar{E}^2 \rangle$

Relation between linear and non-linear refractive indices with linear and non-linear susceptibilities respectively can be shown in the equations

$$n_0 = (1 + \chi_1)^{1/2}$$

And $$\bar{n}_2 = \frac{3\chi_3}{4n_0}$$

Third-harmonic generation (THG)

In this three photons incident on material, resulting light having frequency triples the incident frequency of one photon

$E=E(\omega)_{optical} \rightarrow P_3 \propto E^3(\omega) \rightarrow P_3(\omega)\{\propto E(\omega)^2 E(\omega)\}, P_3(3\omega)\{\propto E^3(\omega)\}$

→Frequency tripling

Non-Linear Absorption

Absorption is non-linear, if the total amount of power absorbed by sample has non-linear dependence with intensity of incident light. That is absorption coefficient depends on incident irradiance. There are many absorption mechanisms that have non-linear absorption. In triple photon absorption (TPA) or multi photon absorption (MPA), photons excite molecules in a single transition. Absorption increases quadratically for TPA and to nth power for MPA with intensity of incident light.

When saturation occurs, where absorption decreases with increase in intensity of incident light, non-linear absorption happens. Saturation absorption (SA) behaviour occurs due to the strong excitation process where excited states depopulate due to stimulated emission and it limits further absorption. This also occur due depletion of population of ground state, it is because of the long-lived meta states, this effect is known as optical bleaching.

Most commonly used method measuring non-linear absorption is to measure the dependence of absorbance with incident light intensity. One of the methods used is Z-scan technique. In Z-scan technique, incident light varies by moving the sample in the path of light. A plot of transmission verses irradiance is obtained. By observing it non-linear behaviour can be measured.

2.3 Non-linear optical applications

Non-linear optics allow us to transform the colour of a light beam, to transform its shape in space and time, and to create the shortest inventions made by humans. Non-linear optical phenomena are the fundamental of optical communication systems, optical sensing and materials research. The most common non-linear optical processes include self-focusing, self-trapping, sum-and difference-frequency generation, harmonic generation, parametric application and oscillation, stimulated light scattering (SLS), and four-wave mixing (FWM). Also, NLO provides coherent light of various wavelengths; multi-photon absorption for plasma-materials interaction; advanced spectroscopy and materials analysis. The realization of single- photon non-linear optics enable numerous applications, which include low-energy electro-optics, non-classical generation of light, etc. self-assembled quantum dots in semiconductors provide a powerful resource as medium for single-photon optical nonlinearities. Just like atoms, quantum dots have optical transitions which can absorb only one photon at a time, which is the origin of optical non-linearity. Further, quantum dots exhibit greater oscillator strength than trapped atoms and can directly couple with nanophotonic structure which confine light in the sub-wavelength dimensions. All these characteristics lead to the very largest bandwidth observed in any optical cavity or waveguide quantum electrodynamics systems.

CHAPTER 3
CHARACTERIZATION TECHNIQUES

3.1 Structural Characterization

X-Ray Diffraction (XRD)

X-Ray Diffraction is a major technique for determining the atomic and molecular structure of a crystal. It is a non-destructive method, in which the crystalline structure causes a beam of incident X-rays to diffract into many specific directions.

Crystals have periodic arrangement of atoms and X-rays can be regarded as electromagnetic waves. Because of their shorter wavelength, X-Rays are scattered by adjacent atoms in crystals which can interfere and give rise to diffraction patterns. When X-rays enter a crystal, each atom acts as a diffraction center and crystal acts as a three-dimensional diffraction grating.

X-ray diffraction is based on constructive interference of monochromatic x-rays and a crystalline substance. When the X-rays are made to fall on a sample, it gets scattered from different planes pf the crystal lattice. i.e., there is a path difference between the scattered rays. If the rays are in phase, they interfere constructively, and we get diffraction peaks.

The Bragg's law relates the wavelength of the electromagnetic waves to the diffraction angle and the lattice spacing in a crystalline sample.

$$n\lambda = 2d\sin\theta \qquad (3.1)$$

were

n- order of diffraction,

λ- wavelength of the incident X-rays,

d-inter-planar distance,

θ-angle between the incident rays and lattice.

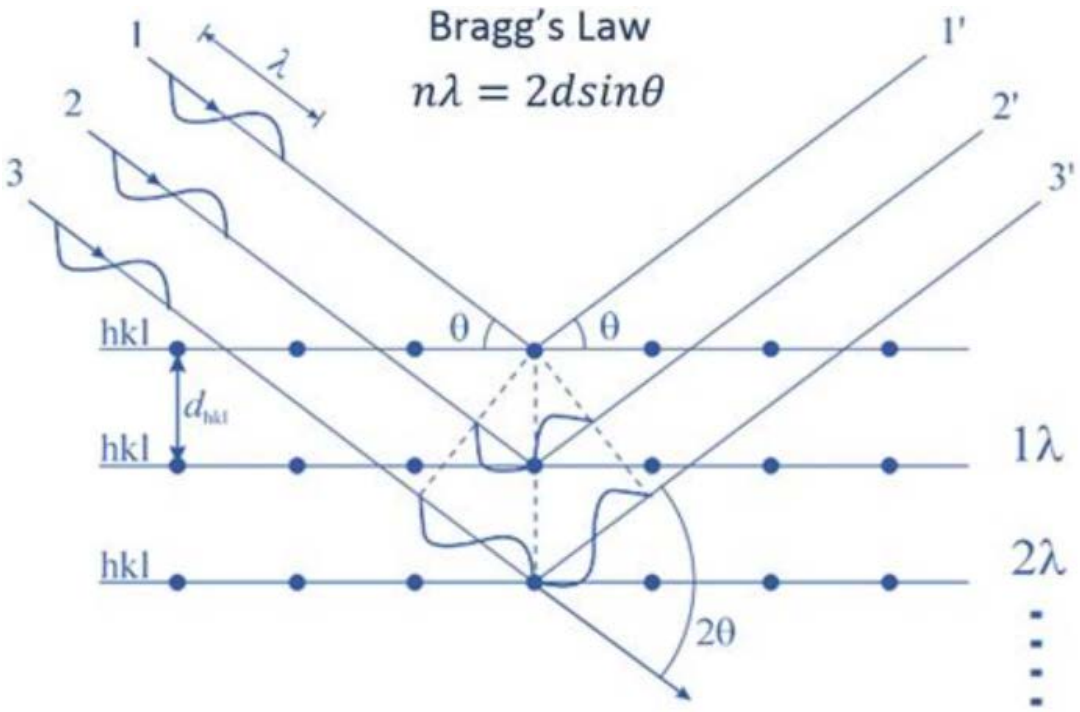


Figure 3.1: Bragg's diffraction

The generated X-rays were collimated and directed to a nanosized substance, where the interaction of these rays with the sample produces a diffracted ray, which will be detected, processed and counted. The intensity of the diffracted rays scattered at various angles are plotted. XRD can be used to determine crystal structure, crystallite size and strain.

The Debye Scherrer equation,

$$\beta = {K\lambda}/{L\ cos\theta} \qquad (3.2)$$

It is used to find the crystallite size.

In this equation,

β is the peak width (full width at half maximum),

L – the crystallite size,

λ – wavelength of the incident ray,

K – the Scherrer constant (0.9)

One of the most important advantages of X-ray diffraction is that it is a rapid and powerful technique for identifying samples. One disadvantage of XRD is that X-rays do not interact very strongly with lighter elements.

XRD Instrumentation:

A typical X-Ray diffractometer consists of three basic components: an X-ray tube, a sample holder and a detector. X-rays are generated in a cathode ray tube by heating a filament in order to produce electrons, which will be accelerated through a potential and collided with a target material. When the incident electrons have sufficient energy, they remove the inner electrons of the target substance. The empty space so created will be filled by the outer electrons. This will release characteristic X-ray spectra, which consist of several components, such as K_α and K_β. The X-rays so generated are collimated and directed towards the material. The sample rotates in the path of the collimated X-rays at an angle θ while the detector kept on an arm collects the diffracted rays. Goniometer is an instrument, able to keep the required angle between the sample, detector and source.

Figure 3.2: Bruker AXS D8 advance X –ray Diffractometer

Applications:

X-ray Diffraction is a non-destructive method, which is mainly used to determine the crystallographic structure of a substance and can give information on the dimensions of unit cell. This technology can be used to measure both physical and chemical properties of thin films, bulk solid particles. It can be used for the characterization of crystalline samples and to determine lattice parameters such as strain, grain size, epitaxy, composition. It also plays an important role to assess the weathering and degradation of natural and synthetic minerals.

3.2MORPHOLOGICAL CHARACTERIZATION:

Scanning Electron Microscope (SEM)

Scanning electron microscopy is a surface imaging technique, done by scanning of an electron beam across the surface of specially prepared samples. The SEM image provides visually impressive and approximately three-dimensional images of the sample. Here, the electrons from the electron gun are focused using condenser lenses and made to fall on a small spot on the sample surface. SEM utilizes electrons reflected from the surface. The focused beam is scanned, and the information collected from each spot is assembled to form the final image of the sample.

Unlike the optical microscope, the resolution provided by SEM is very large and hence they can be used for the identification of electronic channels, determining the size and shape of nanoparticles etc. In the case of a SEM, two kinds of electrons, namely, backscattered electrons and secondary electrons are detected. The former type was reflected after elastic collisions between the rays and the specimen, while the latter were originated from the atoms of the specimen; they are generated due to the inelastic collision between the rays and the specimen.

Backscattered electrons

Backscattered electrons are highly energetic electrons, which are used to produce high-resolution images that provides the distribution of various elements that construct a specimen. Also, they give brighter spots if there exist heavier atoms. Therefore, it is more sensitive to the composition of the specimen.

Secondary electrons

In contrast with backscattered electrons, secondary electrons are generated from the surface of the sample. They are the result of inelastic collision between the electron beam and the specimen, and they have relatively lower energy than the backscattered electrons. Secondary electrons can be used to analyze the topography of the sample's surface.

Characteristic X-rays

Characteristic X-rays are generated when the valence electrons fill a vacancy in the inner orbit of an atom, thereby releasing X-rays in a way which is "characteristic" to each element. They can be used for the investigation of the crystal structure using X-ray diffraction.

SEM- construction

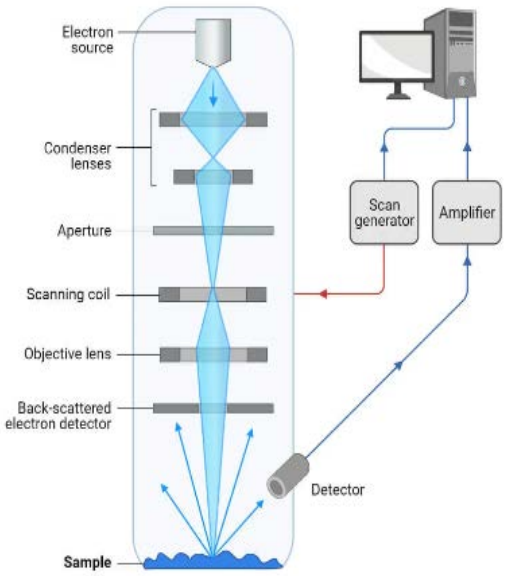


Figure 3.3: Basic construction of SEM

The key components of a SEM are, the electron source, lenses, scanning coil, sample holder and detector.

- **Electron source**

Electrons are generated at the source by thermionic heating, which are then accelerated to a potential of about 1-40 kV and condensed into a narrow beam, which will be used for imaging.

- **Lenses**

Just as optical microscopes, SEM use lenses to produce clear images. The lenses are made of magnets, which can bend the path of electrons. By doing so, the lenses focus and control the electron beam, thereby ensuring that the electrons end up precisely where they need to go.

- **Scanning Coil**

After the beam gets focused, scanning coils are used to deflect the beam along the X and Y directions, so that it scans in a raster manner over the sample surface.

- **Sample Chamber**

Specimens are placed on a container that is evacuated. The sample chamber includes a translation stage, tilt and rotation devices, temperature stages, optical cameras and a variety of other devices to assist for the sample imaging.

- **Detector**

When the incident electron beam interacts with a specimen in a SEM, multiple processes happen. In general, different detectors are required to differentiate the secondary electrons, backscattered electrons and characteristic X-rays.

One disadvantage of SEM is that it is limited to solid specimens.

3.3 OPTICAL CHARACTERIZATION

UV-Visible Absorption Spectrophotometry

Spectroscopy is the study of interaction of electromagnetic radiations with matter. When matter absorbs radiation, it undergoes excitation and de-excitation which results in the formation of spectrum. UV- Visible Spectroscopy is an analytical technique, which measures the number of discrete wavelengths of UV or visible light, which are absorbed or transmitted through a sample in comparison with a reference sample. This spectroscopy depends on the use of light. Ultraviolet (UV) radiations are electromagnetic, with wavelength ranges from 10nm to 400nm, which is shorter than that of visible light.

The principle of UV-visible spectroscopy is based on the absorption of UV or visible light by chemical compounds which leads to the formation of distinct spectra.

The absorption of UV or visible light by a molecule leads to the transition among energy levels. The difference in energies of ground and excited states of an electron is always equal to the amount of UV or visible radiations absorbed by it.

According to the molecular orbital theory, the molecule absorbs UV-visible energy and goes to the excited state by promoting its energy from a bonding or non- bonding orbital to an anti- bonding orbital.

The relation between the energy E and the frequency of the absorbed photon is given by,

$$\mathbf{E=h\nu} \qquad \mathbf{(3.3)}$$

where E is the energy of the photon, ν is the frequency of the photon and h is the Plank's constant.

According to Beer- Lambert law, there is a linear relationship between the concentration and absorption of the solution.

i.e**.,** $$\mathbf{A=\log(I/I_0)} \qquad \mathbf{(3.4)}$$

this means that the amount of light absorbed is directly proportional to the concentration of the solution. If there is no light is absorbed for a particular wavelength, then its absorbance will be zero. Hence, for a fixed path length, UV-visible Spectroscopy can be used to measure the concentration of the absorber.

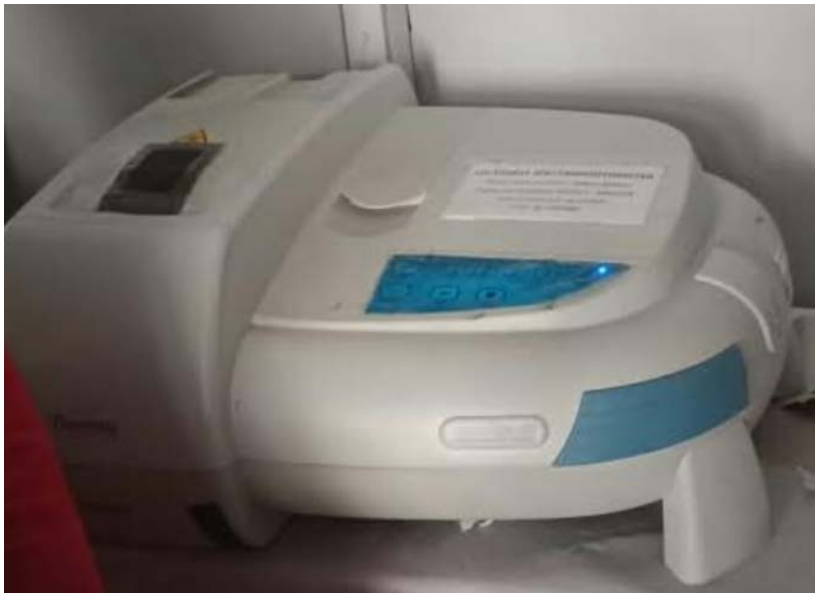


Figure 3.4: Evolution 201 UV-Visible Absorption Spectroscope

Photoluminescence Spectroscopy

Photoluminescence spectroscopy, also called PL Spectroscopy, is when electromagnetic radiations stimulate the emission of a photon from a matter. It is a non- contact process and non- destructive method for probing materials. It uses a laser source to collect light generated from a material when it falls from the excited state to the ground state. This process is called photoexcitation. During this process, light gets absorbed and imparts the excess energy into the material. The excess energy can be dissipated by the specimen in two ways: either by the emission of light or through luminescence.

PL Spectrum is entirely different from absorption spectrum. The absorption spectrum determines transitions from ground to excited state while PL spectrum determines transitions from excited to ground state. When the excitation spectrum is represented as intensity versus wavelength, it is like absorption spectrum. The wavelength at which the molecule absorbs energy may be equal to the excitation wavelength, which can provide intense emission at a red-shifted wavelength.

Photoluminescence- modes

- **Resonant radiation:** During this process, a photon of a particular wavelength gets absorbed with the immediate emission of an equivalent photon. The process does not involve any significant internal energy transitions between absorption and emission.

- **Fluorescence:** When the chemical substrate is undergoing the internal energy transition by emitting photon before return to ground state, certain amount of absorbed energy gets released such that the emitted light has lower energy when compared to that of the absorbed light.

- **Phosphorescence:** it is a type of photoluminescence related to fluorescence. It is the emission of light from a material exposed to radiation and persists as an overglow after the exciting radiation has been removed.

One of the most important limitations of PL Spectroscopy is that several optical centers may possess number of excited states which are empty at low temperature.

Figure 3.5: RF-6000 Spectro Fluorophotometer

3.4 NON-LINEAR OPTICAL CHARACTERIZATION

Z-scan Technique

Nonlinear optics (NLO) is a branch of Optics, which deals with the behavior of light in nonlinear media, i.e., the media in which the polarization density **P** responds nonlinearly to the electric field **E** of the light. Nonlinear optical phenomena are the basis of many components of optical communication systems, optical sensing and materials research.

Z-scan is a well- known sensitive technique for measuring nonlinear absorption. It often measures the Kerr nonlinearity and third order non-linearity of a material. In this method, a single Gaussian laser beam is tightly focused on the sample and the transmittance is obtained as a function of the sample position with respect to the focal plane. Sample is moved through the path of laser beam and intensity of beam is measured using detector.

Z-scan technique have two different methods, closed and open apertures. To measure non-linear refractive index of optical material, z-scan setup is used in closed aperture method. Where as to measure non-linear absorption coefficient of optical material, z-scan setup is used in open aperture method. In close aperture method, a far-field aperture is used to detect the beam distortions in the beam. In the case of open aperture method, the far-field aperture is removed and whole beam could be measured by the detector.

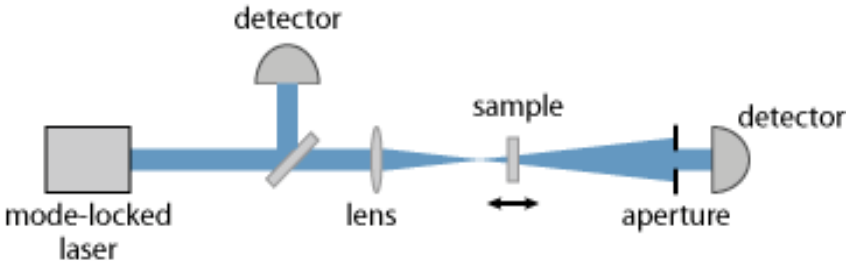


Figure 3.6: Z-scan measurement setup

In closed-aperture z-scan technique, aperture is placed to prevent most of the light reaches the detector. Lens focuses laser to certain point and after that point beam defocuses. After some distance aperture is placed and detector is placed behind it. Detector is sensitive in focusing and defocusing light that induced by the sample. Sample is mainly placed at the focus point of lens and it is moved along z-axis with a distance $\pm z_0$. Normalized transmittance is mainly between 0.1< S<0.5.

In open-aperture z-scan technique, aperture is removed or enlarged to allow most of the light to the detector. In this case normalized transmittance is S=1. Non-linear absorption due to two-photon absorption can be measured used in this. In this project, we use open-aperture method to find non-linear absorption coefficient of the samples.

CHAPTER 4

EXPERIMENTAL PROCEDURE

Graphene oxide was synthesized using modified Hummer's method by chemical exfoliation of graphite powder. Reduced graphene oxide was synthesized from this graphene oxide by thermal reduction of Graphene oxide.

Desired structure and properties of graphene and its derivatives depends upon size, shape and functional groups attached to the surface. During the synthesis we must consider these factors. Perfect structure of graphene is a single atom thick layer with sp^2 hybridised carbon structure. For industrial applications, it is difficult to synthesis these structures by bottom-up approaches. Bottom-up approaches in this synthesis found to be time consuming and difficulties in scalability. Top-down approach is used to produce highly oxidised form of graphene, graphene oxide, and reduced graphene oxide.

Materials

The chemicals used are graphite powder, $NaNO_3$, H_2SO_4, $KMnO_4$, H_2O_2, HCl.

4.1 Synthesis of Graphene oxide by Modified hummer's method

Modified hummer's method is the method used for the synthesis of graphene oxide from graphite by oxidation. Synthesis of graphene oxide from oxidation of graphite is found out by many scientists, one among them was Hummers. Hummers modified method by including the use of $KMnO_4$ as an oxidizer and use of $NaNO_3$ for exfoliating the layers. In modified hummer's method, Oxidation of graphite powder was done vigorously using H_2SO_4 and $KMnO_4$ as oxidising agents by this method. $NaNO_3$ was used to exfoliate graphite layers. H_2O_2 and HCl were used to rinse product obtained from oxidation. It was washed continuously with distilled water to remove impurities like unwanted ions.

Graphene oxide was synthesized using modified hummer's method from graphite powder. 2g of graphite powder and 2g of $NaNO_3$ mixed with 90 mL of H_2SO_4 were stirred continuously for 1 hour in an ice bath (0-5℃) in a round bottomed flask. 12g of $KMnO_4$ added slowly and stirred for 1 hour in an ice bath in a temperature less than 15℃. Then slowly added 180 mL of distilled water. It was kept around at 10℃ and stirred for 2 hours. After that we removed ice

bath and stirred for 2 hours around 35℃ and stirred for 10 minutes above 90℃. After that we added 40 mL of H_2O_2 and stirred for 40 minutes around 25℃. Further it was diluted by adding 400 mL of distilled water and stirred for 30 minutes around 25℃. At last, it was kept aside for 24 hours. We obtained graphene oxide solution. To purify it was washed with HCl and then washed with distilled water several times. Graphene oxide gel like substance dried in oven at 60℃ for 6 hours. It was then grinded using mortar and pestle and we obtain graphene oxide powder. Figure 4.1 shows the steps of synthesis of graphene oxide.

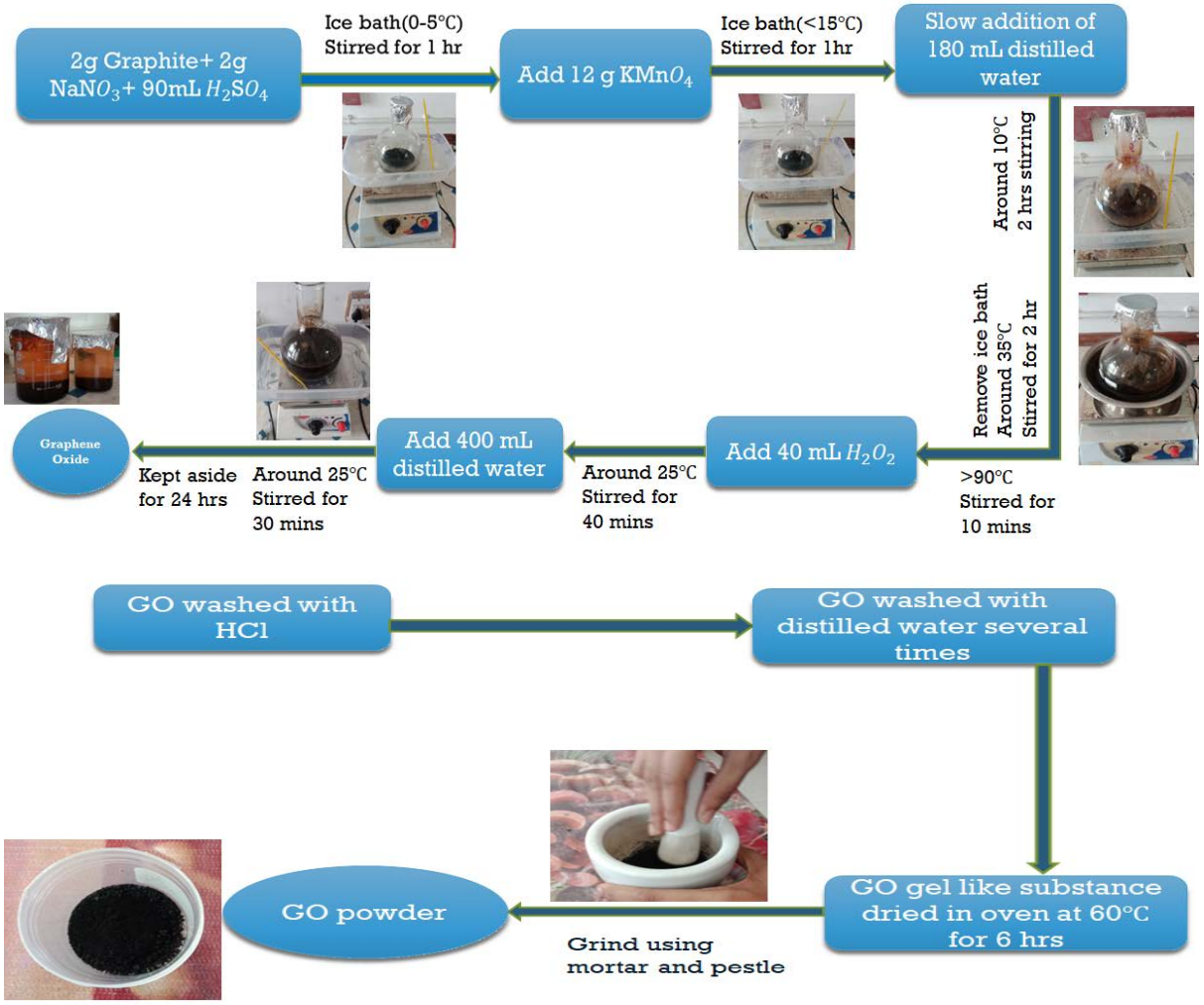


Figure 4.1: Flow chart of synthesis of GO

4.2 Synthesis of Reduced graphene oxide by Hydrothermal method

Hydrothermal reduction method was used here in the synthesis of reduced graphene oxide over many chemical reduction methods. It is because of its simplicity, scalability and low defects content.

Reduced graphene oxide was synthesized from the graphene oxide prepared earlier using hydrothermal method. Graphene oxide was diluted using diluted water. 100 mg of graphene oxide and 50 mL of distilled water were mixed together and it was then sonicated for 30 minutes. Then the solution was then sealed in a Teflon coated autoclave at 170℃ for 6 hours. We obtained reduced graphene oxide solution. Then it was then dried at 40℃ for 6 hours and it was then grinded using mortar and pestle. We obtained reduced graphene oxide powder. Figure 4.2 shows the steps involved in the synthesis of reduced graphene oxide with a flowchart.

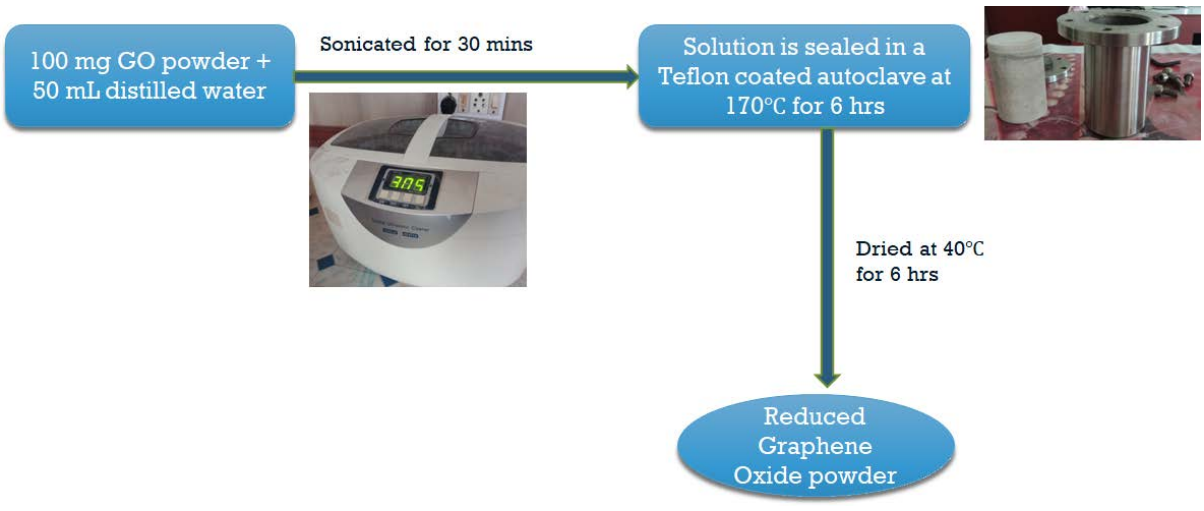


Figure 4.2: Flowchart of synthesis of RGO

CHAPTER 5

RESULTS AND DISCUSSIONS

Graphene oxide and Reduced graphene oxide are characterized by different techniques described in the 3rd chapter. Structural and morphological analysis is done by X-Ray Diffraction Analysis (XRD) and Scanning Electron Microscope (SEM) analysis respectively. Optical analysis of the samples is done by UV-Visible Absorption Spectroscopy and Photoluminescence Spectroscope. Nonlinear optical analysis is done by Z-scan Technique.

5.1 Structural and Morphological Analysis

X-Ray Diffraction Analysis

XRD Analysis is carried out by Bruker AXS D8 advance X-Ray Diffractometer. It is the most widely used technique for general crystalline material characterization which is a non-destructive method. It is based on constructive interference of monochromatic X-rays and the crystalline sample. Bragg's law relates wavelength of electromagnetic radiation to diffraction and lattice spacing in crystalline sample.

$$n\lambda = 2d\sin\theta \quad (5.1)$$

where n is the order of diffraction, λ is the wavelength, θ is the diffraction angle and d is the interplanar spacing. XRD analysis is used to measure the average spacing between layers or rows of atoms, determine the orientation of a single crystal or grain. Graphite, Graphene oxide and Reduced graphene oxide test using XRD is done with a range of 2θ angle between 0-80° and wavelength of 1.54 Å. It is performed to determine whether the sample is graphite, graphene oxide or reduced graphene oxide. XRD pattern obtained for Graphite, Graphene oxide and Reduced graphene oxide is shown as in the figure 5.1.

Figure compares XRD patterns of Graphite, Graphene oxide and Reduced graphene oxide. For graphite in figure 5.1.a, it shows the diffraction sharp peak at 28.6° indicates ordered structure having interplanar spacing(d) 0.3119 nm. For graphene oxide in figure 5.1.b, it shows the diffraction peak at 8.19° having interplanar spacing(d) 1.0784 nm. Graphene oxide's diffraction peak shifted to lower values and there is disappearance of peak at 28.6° and it has an increased interlayer distance between the carbon planes than graphite. It may be due to the intercalation of functional groups between the layers of graphite and it confirms the production of graphene oxide. For reduced graphene in figure 5.1.c, oxide it shows the diffraction peak at

22.86° having interplanar spacing(d) 0.3887 nm. In this case diffraction peak shifts to higher 2θ values and disappearance of peak at 8.19° and corresponding interplanar spacing decreases from that of graphene oxide. It may be due to the removal of functional groups from graphene oxide during reduction process. Reduced graphene oxide has similar interplanar spacing that of graphite. The XRD results show that the synthesis of graphene oxide and reduced graphene oxide has been successful.

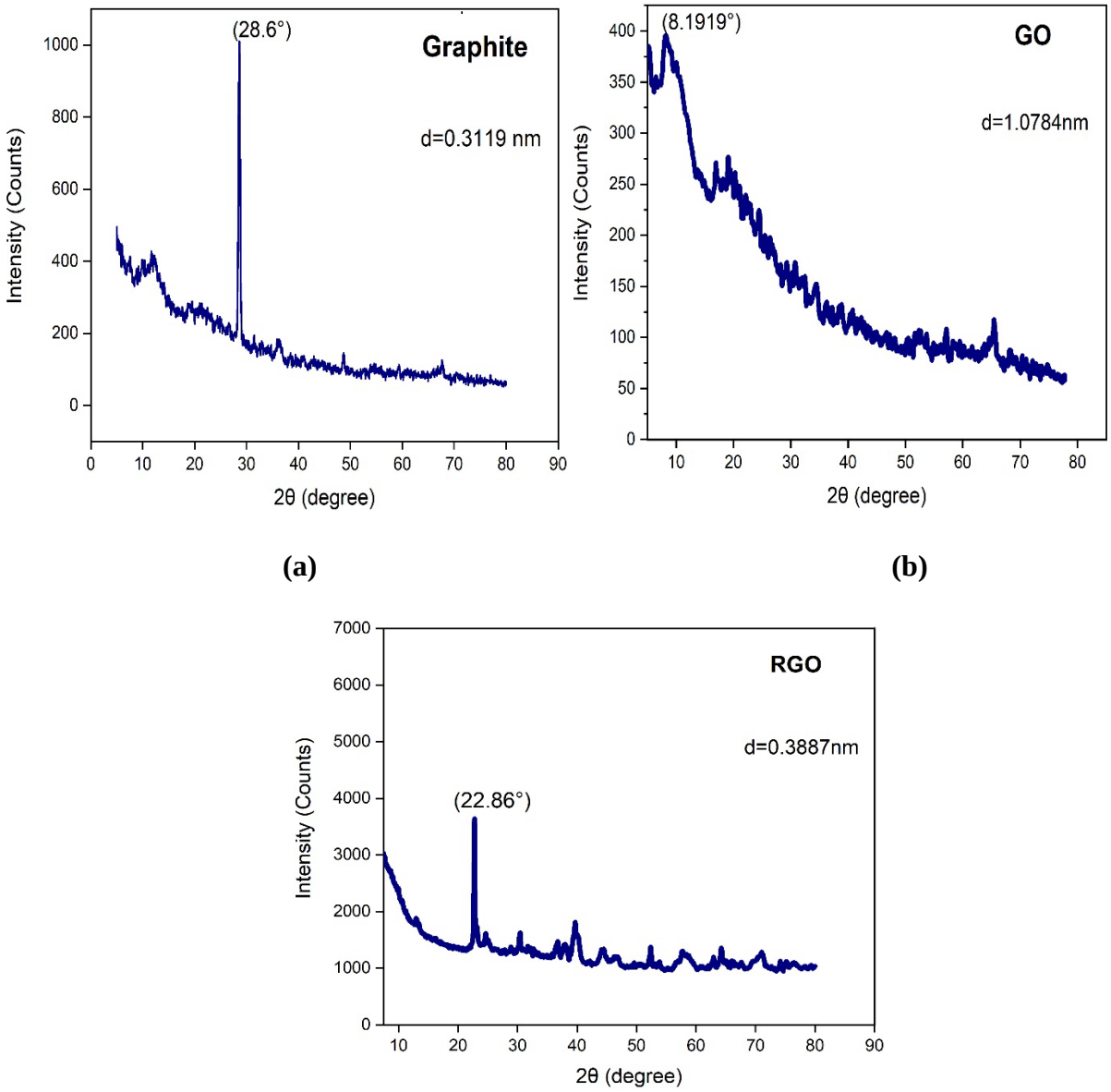
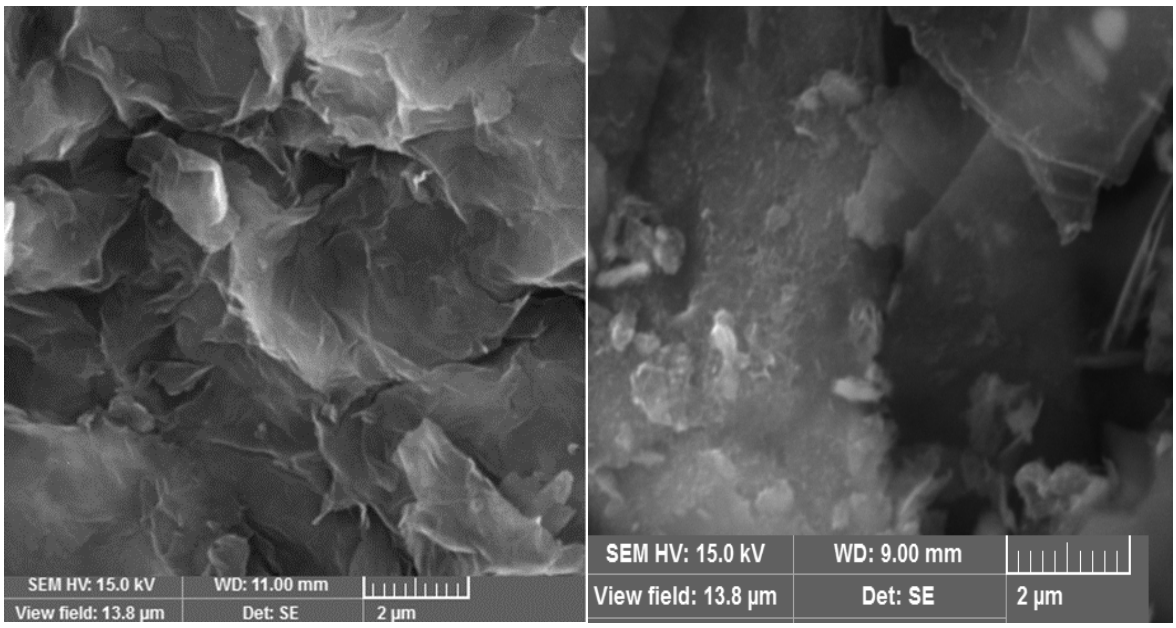


Figure 5.1: XRD pattern Of Graphite, Graphene oxide, Reduced graphene oxide

Scanning Electron Microscope (SEM) Analysis

Surface morphology and structure of graphene oxide and reduced graphene oxide were observed by JEOL JSM 7600F scanning electron microscope (SEM). SEM images of graphene oxide and reduced graphene oxide are shown in the figure 5.2. In figure 5.2.a can be observed the morphological form of graphene oxide. It is like a folded sheet structure. In figure 5.2.b can be observed the morphological form of reduced graphene oxide. It is like a layered structure.



(a) **(b)**

Figure 5.2: SEM images of graphene oxide(a) and reduced graphene oxide(b)

5.2 Linear Optical Analysis

UV-Visible Absorption Analysis

The characterization using UV-Visible Spectroscope Evolution 201 with wavelength range of 200-800 nm is performed to identify the conjugated double bond of carbon from the graphene oxide and reduced graphene oxide sample structures formed. The conjugated double bond is due to transition of $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ of conjugated system in a molecule. Figure 5.3 shows the UV-Visible Absorption Spectrum of graphene oxide and reduced graphene oxide.

Graphene oxide and reduced graphene oxide is more active in UV region. Graphene oxide UV-Visible spectrum shows an absorption peak at 230 nm. It is due to the $\pi \rightarrow \pi^*$ transition of aromatic C-C and C=C bonds in sp^2 hybrid regions. Reduced graphene oxide UV-Visible spectrum shows an absorption peak at 260 nm. When graphene oxide reduced to reduced graphene oxide, absorption peak shifted to higher wavelength side, this indicates the formation of reduced graphene oxide. Maximum absorption value of graphene oxide is smaller than reduced graphene oxide. This is due to the functional groups affecting the aromatic C=C bonds. In the case of reduced graphene oxide functional groups are removed and the effect of it disappears so that C=C bond will increase.

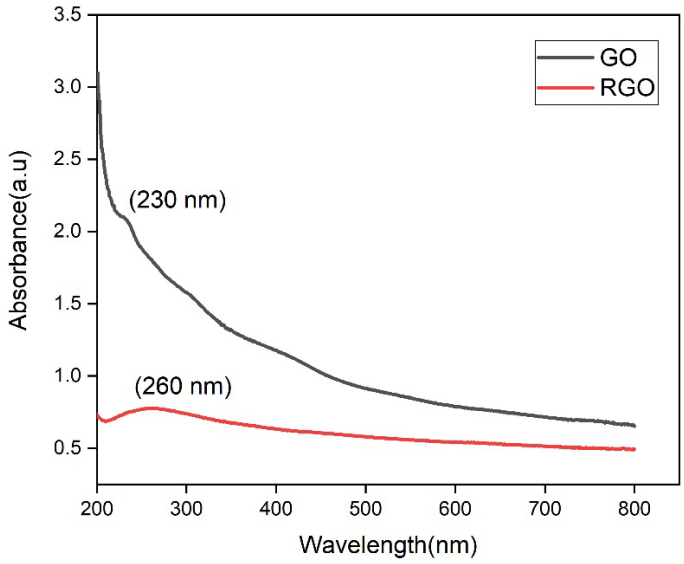
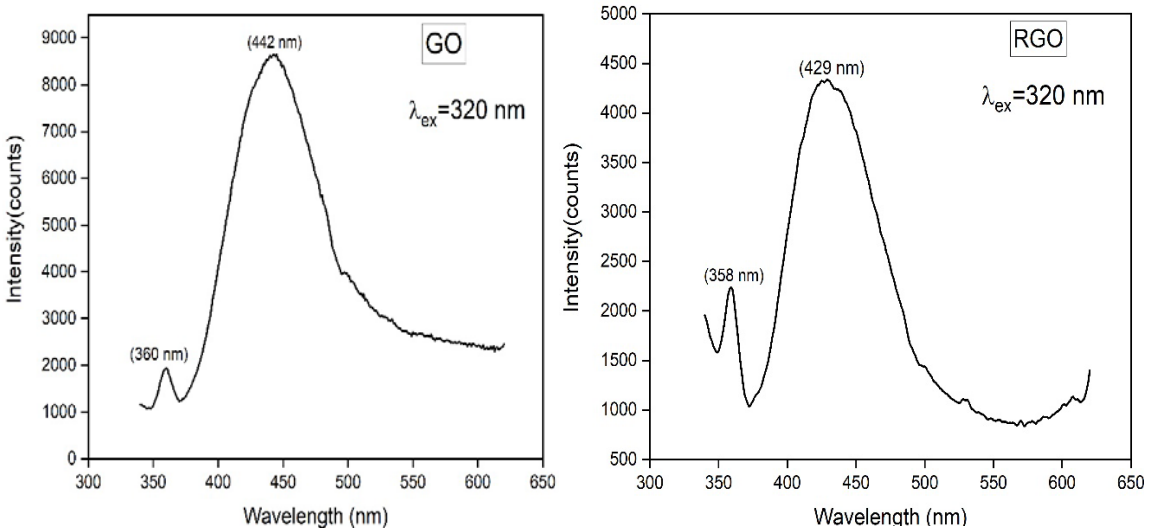


Figure 5.3: UV-Visible Absorption Spectrum of Graphene Oxide (GO) and Reduced Graphene Oxide

Photoluminescence Spectroscopy analysis

Characterization using Photoluminescence spectroscope (RF-6000 Spectro Fluorophotometer) is done for graphene oxide and reduced graphene oxide. PL emission spectrum of graphene oxide and reduced graphene oxide recorded by using an excitation wavelength of 320 nm is shown in the figure 5.4. An emission peak at 360 nm is obtained for graphene oxide due to oxidation of graphite and formation of crystallite graphitic sp^2 C atoms presented in graphene oxide. There is an additional broad peak around 442 nm may be attributed to $\pi - \pi^*$ transitions. $\pi \; and \; \pi^*$ states of sp^2 clusters determine the optoelectronic

properties of C based materials. In reduced graphene oxide emission peak was blue shifted to 358 nm and 429 nm. It is mainly attributed to restoration of sp^2 C domains results highly structured ordering because of elimination of O functional groups.



(a) **(b)**

Figure 5.4: PL Emission Spectrum of Graphene oxide and Reduced graphene oxide

5.3 Non-Linear Optical Analysis

Open aperture Z-Scan Analysis

Open Aperture Z-Scan technique used for the measurement of the nonlinear optical properties of materials. It is a simple technique for measuring the change in phase induced on a laser beam upon propagation through a nonlinear material. Open-aperture Z-Scan technique is done by continuous wave Nd: YAG laser at an intensity of 370 MW/cm^2 and 532 nm wavelength. The measurements of normalized transmittance versus sample position curve are obtained by open aperture Z-Scan technique which results in calculating nonlinear absorption coefficient. According to an open aperture Z-Scan plot, saturable absorption behaviour of the material dominates the nonlinear absorption process and results in an asymmetrical peak with regard to the lens's focus. Open aperture Z-scan measurements of graphene oxide and reduced graphene oxide is as shown in the figure 5.5.

Open aperture Z-scan plot of graphene oxide and reduced graphene oxide exhibits peak at focal point due to maximum transmittance which steadily decreases on both sides of the focus. It is the saturable absorption behaviour. The strong saturable absorption behaviour and absence of reverse saturable absorption of graphene oxide and reduced graphene oxide, implies the absorption cross section of ground state is much larger than the absorption cross section of excited state. When laser irradiance is on these samples, electrons in the lower energy levels absorb photon energy and jump to higher energy levels. When majority of higher electron energy levels are occupied, prevents further absorption even when the laser intensity is high known as Pauli Blocking effect. Saturable absorption of graphene oxide and reduced graphene oxide is the result of this particular effect.

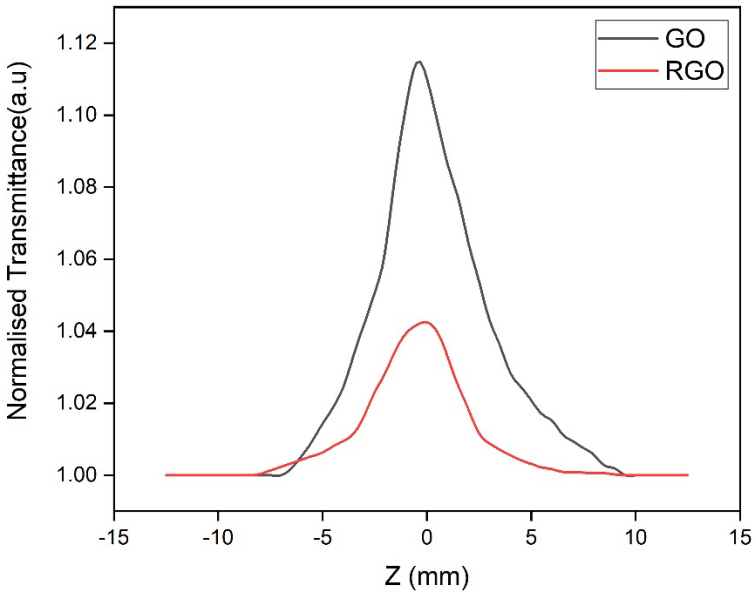


Figure 5.5: Open Aperture Z-Scan plot of graphene oxide and reduced graphene oxide

Nonlinear absorption coefficient β of graphene oxide and reduced graphene oxide can be obtained from the experimental open aperture Z-scan data by fitting the normalized transmittance data to the open aperture formula given by

$$T(z, S = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}} \qquad (5.2)$$

where m is an integer

$$q_0(z,t) = \frac{\beta I_0(t) L_{eff} z_0^2}{z^2 + z_0^2}$$

where $L_{eff} = \frac{[1-\exp(-\alpha L)]}{\alpha}$ is the effective film thickness.

Nonlinear absorption coefficient can be estimated using relation below,

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}} \quad (5.3)$$

L is the film thickness, α is the linear absorption coefficient. The parameter q_0 can be obtained by fitting the experimental results to open aperture formula, where $z_0 = \frac{k\omega_0^2}{2}$ and z are Rayleigh range and translated length parallel to beam propagation respectively where k=$\frac{2\pi}{\lambda}$ (λ is the wavelength of laser), I_0 is the intensity of incident beam at focal point, ΔT is the peak value at open aperture Z-scan curve.

Nonlinear absorption coefficients of graphene oxide and reduced graphene oxide is shown in the table 5.1. From the open-aperture z-scan plot as shown in the figure 5.5, we can see that that both samples have saturable absorption behaviour. That is, it has maximum transmittance at the focal point. Saturation absorption behaviour in graphene oxide and reduced graphene oxide can be used for optical switching and mode locking lasers.

Sample	**Nonlinear absorption coefficient (β)**
	(cm/W)
Graphene Oxide	0.57 *10^-4
Reduced Graphene Oxide	3.22 *10^-4

Table 5.1: Nonlinear absorption coefficient of graphene oxide and reduced graphene oxide

CONCLUSION

Graphene oxide was successfully synthesized by modified hummer's method from oxidation of graphite. Reduced graphene oxide is also synthesized by hydrothermal reduction method. We studied structural, linear and non-linear optical properties of them. XRD analysis shows the production of graphene oxide and reduced graphene oxide was successful on looking at the difference in interplanar spacing. SEM results gives the morphological structure of both samples. From UV-Visible absorption analysis and Photoluminescence spectroscopy analysis, we can see the structure and properties of the C-C bond in both graphene oxide and reduced graphene oxide. Non-linear optical property was studied by the open-aperture z-scan technique. It shows the saturable absorption behaviour of both samples and we calculated non-linear absorption coefficient of both the samples. Saturable absorption behaviour of graphene oxide and reduced graphene oxide leads to applications such as optical switching and mode locking lasers.

FUTURE SCOPES

We can synthesize nanocomposites of graphene oxide and reduced graphene oxide and study the difference in structural, linear and non-linear optical properties of them from that of graphene oxide and reduced graphene oxide in its pure form. We can look for various applications in optoelectronics and non-linear optics.

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