

**SYNTHESIS AND CHARACTERISATION OF MAGNETIC
GRAPHENE-NANOPARTICLE COMPOSITES FOR WATER
PURIFICATION.**

Nduduzo Nkanyiso Malinga

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University of KwaZulu-Natal

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Supervisor: Dr A. L. L. Jarvis

Declarations

As the candidate's Supervisor I agree/ do not agree to the submission of this thesis.

Signed:

..... (Dr. A.L.L. Jarvis)

Date:

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.....

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ABSTRACT

The synthesis of reduced graphene oxide is investigated in this work, with a focus on water purification. The work stems from the interest gained from the discovery of graphene and its high surface area. The study focused on the synthesis of reduced graphene oxide. This afforded the synthesis of reduced graphene oxide nanoparticles composites and doped reduced graphene oxide. The composites were produced with magnetic nickel, cobalt and cobalt ferrite nanoparticles. The doped reduced graphene oxide was synthesized using nitrogen and boron as dopants. The prepared samples were rGO, N-rGO, B-rGO, Co-rGO, Ni-rGO and FeCo-rGO. All the samples were characterized using Transmission Electron Microscopy (TEM), Fourier Transform Infra-red (FTIR) spectroscopy, Thermal Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Raman Spectroscopy and X-ray Diffraction (XRD). All the samples were found to have magnetic properties. The composites have superparamagnetic properties and FeCo-rGO had the highest magnetization at 12.54 emu.g^{-1} . The conductivity results showed that the doped samples and composites had better conductivity than rGO with the Ni-rGO having the highest conductivity of $62695.82 \text{ S.m}^{-1}$. All samples had conductivity which were similar to semiconductors. The prepared samples have high surface area and a large number adsorption sites and thus were used in applications of water purification in the removal of Cr(VI) ions from solution. The Co-rGO was found to have the ability to adsorb the Cr(VI) in form of CrO_4^{2-} while other samples catalysed reduction of Cr(VI) to Cr(III). Thus Co-rGO was used in the removal of Cr(VI) ions from solution. The adsorption of Cr(VI) ions occurs through electrostatic interaction between CrO_4^{2-} and Co-rGO. The optimum conditions for the removal of chromium ions were experimentally determined. The conditions, were a dosage of 300 mg.L^{-1} , a pH of 8, contact time 90 minutes and temperature was 298 K. The removal efficiency was affected by the concentration of chromium ions and there was 90 % removal efficiency for the concentration of 20 mg.L^{-1}

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List of Symbols

μ	Carrier mobility ($\text{cm}^2.\text{V}.\text{s}^{-1}$)
ρ	Resistivity ($\Omega.m$)
σ	Conductance ($\text{S}.\text{m}^{-1}$)
σ_{xy}	Hall conductivity ($4e^2.h^{-1}$)
χ	magnetic susceptibility ($\text{cm}^3.\text{g}^{-1}$)
χ_g	mass susceptibility ($\text{G}^{-1}.\text{g}^{-1}.\text{Oe}^{-1}$)
χ_{mol}	molar susceptibility ($\text{G}^{-1}.\text{mol}^{-1}.\text{Oe}^{-1}$)
λ	wavelength (nm)
θ	angle ($^\circ$)
e	Charge of electron ($1.602 \times 10^{-19} \text{ C}$)
ε	is the Polanyi constant
ε_r	is the dielectric constant
f_r	is the resonant frequency (GHz)
B	Magnetic induction
β	is the constant of the sorption energy ($\text{mol}^2.\text{J}^{-2}$)
h	Plank's constant ($6.626 \times 10^{-34} \text{ J.s}$)
E	Energy (eV)
E_y	Young's modulus ($\text{N}.\text{m}^{-1}$)
l	orbital angular momentum ($\text{kg}.\text{m}^2.\text{s}^{-1}$)
H	magnetic field intensity (Oe)
H_c	coercive fields (Oe)

V_g	gate voltage (J.C ⁻¹)
μ_l	orbital magnetic momentum (A.m)
m	mass (kg)
m	magnetic moment (erg.G ⁻¹ $\equiv$ emu)
M	magnetization (A.m ⁻¹)
M_s	saturation magnetization (emu.g ⁻¹)
M_r	remnant Magnetization (emu.g ⁻¹)
M_m	maximum magnetization (emu.g ⁻¹)
μ	magnetic permeability (G.Oe ⁻¹)
μ_r	relative permeability
μ_0	vacuum permeability (G.Oe ⁻¹)
μ_B	Bohr magneton
μ_0	permeability of free
k_1	is the rate constant (min ⁻¹)
k_2	is the second order rate constant (mol ⁻¹ .dm ³ .min ⁻¹)
q_e	amounts of Cr (VI) adsorbed at equilibrium (mg g ⁻¹)
k_2	Second order rate constant (g.mg ⁻¹ .min ⁻¹)
G	Gibbs free energy (kJ.mol ⁻¹)
R	Ideal gas constant (8.314 J.mol ⁻¹ .K ⁻¹)
H	Enthalpy (kJ.mol ⁻¹)
γ	Gyromagnetic ratio (s ⁻¹ .Oe ⁻¹)

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Chapter 1: Introduction

Chapter 1: Introduction

1.1. Graphene

Graphene is a mono layered arrangement of carbon atoms which are fused benzene rings and thus the graphene exhibits two dimensional properties. Graphene was first isolated in 2004 by Andre Geim and Konstantin Novoselov [1]. Upon its discovery, it was characterized to show that it had remarkable electrical conductivity, thermal conductivity and good mechanical strength. The high conductivity is attributed to the electronic structure of the graphene. Properties are influenced by the manner in which the graphene was fabricated [1].

1.1.1. Synthesis of Graphene

Graphene can be obtained by mechanical exfoliation of pyrolytic graphene. This method uses 'scotch tape' to cleave off multi-layered graphite, to which the processes is repeated until mono-layered is obtained [1]. The short comings of this method it produces graphene sheets with different sizes and shapes which lead to low yields of graphene sheets [1]. The other methods used in producing graphene, are Chemical Vapour Deposition (CVD), solvothermal and chemical exfoliation [2]. Chemical Vapour Deposition is method used to grow graphene sheets on metal substrates. The operating temperature of the CVD is about 900 °C, where a carbon source is decomposed to vapour form and carbon atoms nucleate and grow on a metal substrate and forms graphene sheets [3]. Thermal CVD is used to grow graphene on metal substrates like Ni, Co and Fe [3]. The process yields few-layered graphene instead of single-layered graphene [3].

The most common method of producing is common method to produce graphene is through chemical exfoliation [2, 4]. This method produces an intermediate product which is known as graphene oxide (GO). Graphene oxide is produced from the oxidation of graphite using sulfuric acid and potassium permanganate as oxidants [5]. The graphene oxide is then reduced using a reducing agent such as hydrazine hydrate forming reduced graphene oxide [4]. Figure 1.1 shows the structure of graphene oxide and graphene. The other method of producing graphene is using carbon nanotubes [6, 7]. This method uses chemicals to unzip the nanotubes into graphene sheets. Single walled carbon nanotubes (SWCNT) are unzipped using a palladium compound to form mono-layered graphene sheets [6]. Multi-layered graphene is produced from unzipping multi-walled carbon nanotubes using a mixture of sulfuric acid and potassium permanganate as oxidants [7]. The oxidation unzips the layers of carbon nanotube to form multi-layered graphene sheets[7]. Figure 1.2, is the schematic unzipping of single walled carbon nanotubes into mono-layered graphene. The drawback of this method is that materials are expensive to buy.

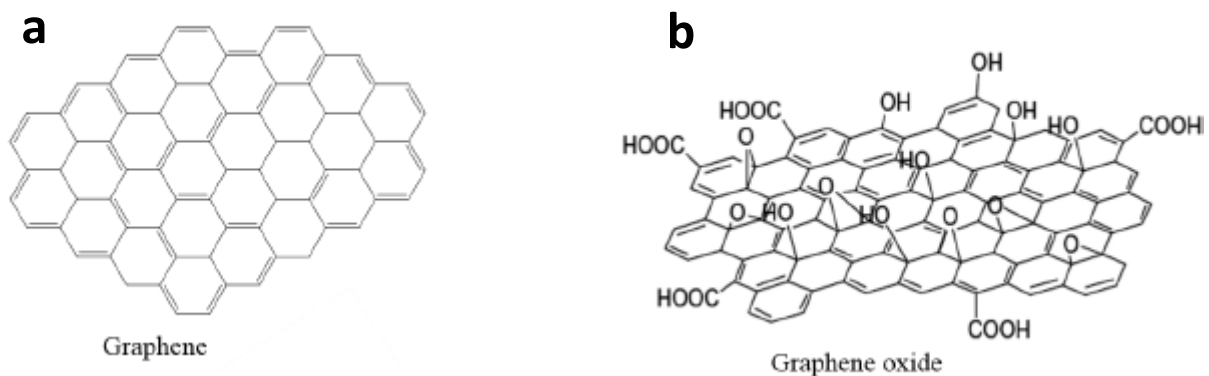


Figure 1.1: Chemical structure of (a) Graphene and (b) Graphene oxide [5].

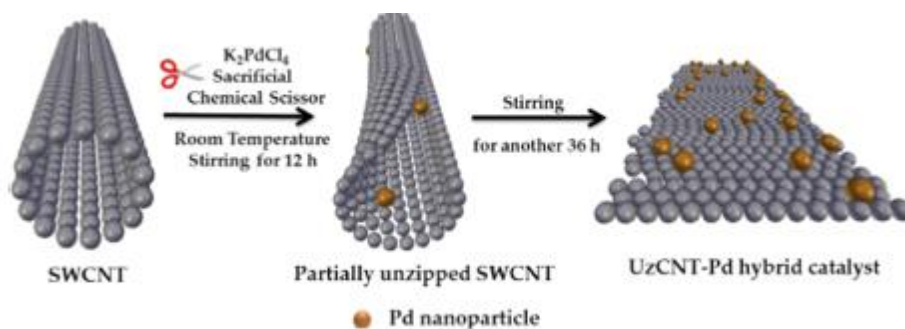


Figure 1.2: Schematic diagram of the unzipping of SWCNT into graphene sheet [7].

1.1.2. Application of graphene

The applications of graphene are found across several fields which include energy related applications [2], water purification [8] and sensors [9]. The research in this thesis is split into two parts: (1) the production of magnetic reduced graphene oxide and (2) study of the applications of the magnetic reduced graphene oxide. The magnetic reduced graphene oxide is produced via doping and secondly using reduced graphene oxide as a 'scaffold' for magnetic nanoparticles. Here graphene was doped with nitrogen and boron, the other is the production of graphene nanometal composites.

The fabricated graphene composites in this study are magnetic nanoparticles which are 'decorated' on graphene. Internationally there has been a focus on magnetic nanoparticles since the 1990s [10]. Magnetic nanoparticles are superparamagnetic, which is dependent on the size of the nanoparticles [11]. The combination of the nanoparticle and graphene united both properties of graphene (large surface area) and magnetic nanoparticles which will be useful as bulk material. Magnetic nanoparticle composites applications have been recently commercially manufactured, for examples Schottky barrier devices [12], nonlinear optical materials [13] and antenna material [14].

The aims of the thesis are to explore the methods of making magnetic graphene and investigate its use in pollution control. The synthesis of bulk doped graphene and the graphene composites are produced from the chemical exfoliation of natural flake graphite [2] with appropriate modifications. Graphene production, or more strictly speaking reduced graphene oxide, is a result of graphene oxide, an intermediate of the exfoliation process. The exfoliation process makes use of the oxidation of graphite in strong concentrated acid, such as sulfuric acid, in the presence of potassium permanganate. Graphene oxide was subsequently used in the production of graphene in the form of reduced graphene oxide, reduced doped graphene oxide and nanometal reduced graphene oxide composites. The prepared samples were characterized by a variety of techniques.

1.1. Aims and Objectives.

The central aim was the production of a magnetic graphene nanomaterial with a large surface area which could adsorb pollutants effectively.

The central aim is split up as follows:

1. The synthesis and characterization of graphene oxide: this is done by use of the Tour's and modified Hummer's method. The synthesized graphene oxide was characterized using a variety of methods.
2. The synthesis and characterization of reduced graphene oxide: the reduction of graphene oxide uses hydrazine hydrate as a reducing agent.
3. The synthesis of magnetic reduced graphene oxide:
 - (i) Doping and characterization of nitrogen doped reduced oxide and boron reduced oxide.
 - (ii) The synthesis and characterization of metal nanoparticle reduced graphene oxide composites. The formed samples are cobalt nanoparticle-reduced

graphene oxide (Co-rGO), nickel nanoparticle-reduced graphene oxide (Ni-rGO), cobalt ferrite nanoparticle-reduced graphene oxide (FeCo-rGO).

- (iii) The characterization of all prepared samples using the following techniques: Fourier Transform Infrared spectroscopy (FTIR), powder X-Ray diffraction spectroscopy (XRD), Raman Spectroscopy, Elemental Analysis and Transmission Electron Microscopy (TEM), Vibrating Sample Magnetometer (VSM) and conductivity studies.
4. Conductivity studies on rGO, N-rGO, B-rGO, Ni-rGO, Co-rGO and FeCo-rGO.
 5. Removal of chromate ions from solution using Co-rGO. This is an application of nanometal reduced graphene oxide composite. Co-rGO was selected for the ease removal with a magnet in an aqueous solution. The removal efficiency of the Cr(VI) was evaluated, with the effects of dosage of Co-rGO, pH of the solution, temperature and contact time. The adsorption kinetics was evaluated along with a variety of isotherms.
 6. The kinetic studies of the adsorption of Cr(VI) on Co-rGO. The adsorption kinetics was evaluated along with a variety of isotherms. The thermodynamic studies of the adsorption process and the regeneration of the Co-rGO.

1.2. Contributions and Publications

1.2.1. Contributions

The central contribution of this study is the proof that doped reduced graphene oxide has superparamagnetic response. There was a gap in the body of knowledge where the adsorption of Cr (VI) using Co-rGO. What was missing was conductivity in the relation to temperature changes. The other gap was in the use of rGO samples in antenna research which is given in Chapter 8:Appendices section The nanometal

graphene composites have superparamagnetic response and can be applied in water purification purposes with removal of heavy metal ions in aqueous solution.

1.2.2. Publications

1. Nduduzo Malinga, Leigh Jarvis, Magnetic Properties of Reduced Graphene Oxide-Nanoparticle Composites, *Journal of Nanostructure in Chemistry*, vol. 10, pp. 55 – 68, 2020.
2. Nduduzo Malinga, Leigh Jarvis, Adsorption of Cr(VI) from aqueous media using magnetic Co-reduced graphene oxide, *Korean Journal of Chemical Engineering*, vol. 37, pp. 1915 – 1925, 2020.

1.3. Outlines of the thesis.

The outline of the dissertation follows below:

Chapter 2 discusses the discovery and history of graphene and an introduction to nanoparticles. The properties of graphene, nanoparticles are highlighted in this chapter, as well as the different synthetic techniques. The applications of graphene are documented as well.

Chapter 3 discusses the theory of the magnetic properties of solids.

Chapter 4 outlines the experimental techniques used in this study. They include the synthesis and characterization of reduced graphene oxide, doped reduced graphene oxide and nanoparticle reduced graphene oxide.

Chapter 5 outlines the results and discussion of the study, where the objectives of this thesis are discussed.

Chapter 6 details the application of Co-rGO in the removal of Cr(VI) in aqueous media. The study focuses on the performance of the Co-rGO as a sorbent material. The adsorption isotherms, kinetic and thermodynamic studies are also investigated to evaluate the performance of the Co-rGO in the removal of Cr(VI).

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Chapter 2: Literature Review

Chapter 2: Literature Review

2.1. Graphene

2.1.1. History of Graphene

Graphene was first discovered in 2004 by Andre Geim and Konstantin Novoselov, by the mechanical exfoliation method [1]. The fabrication process involves the cleaving of the layers off from graphite. In 2010 the researchers received the Nobel Prize for Physics for their pioneering work on graphene. Since then, there has been an intensification in graphene research. The graphene work by Geim *et al* also gave rise to research of two-dimensional materials such as graphyne, hexagonal boron nitride and bismuth telluride, which were thought to be unstable [2]. The work on graphene was seen before in literature prior to the work done by Geim and Novoselov. In 1998 Forbeaux worked on multi-layered graphite material, which was crystalline upon annealing [3]. The experiment resulted in the formation epitaxial multilayered “graphene”. Since the multi layered graphene was on substrates, it was hard to characterize and the technique that ended up being used was angular resolved inversed photo emission spectroscopy, which is a surface technique used to characterize thin films. Up until Geim’s research, work on 2D materials were limited to theoretical research [2, 4], which was based on the theory that multi-layered materials have weak van der Waal’s interlayer coupling, and that thin films decomposed when below a certain thickness [4].

Throughout the years people have been “cleaving” bulk material into thin films, such as writing on blackboard with chalk [4] and writing with pencil (graphite) on paper, yielding “pseudographene” [5]. Eventually graphene was made from the mechanical exfoliation of graphene from graphite. The mechanical exfoliation of the graphite resulted in few-layered graphene [1]. The graphene obtained was found to be two-dimensional and was stable at room temperature. The most significant find was that

it can be used in field-effect (gated) electronics from the study of its electronic properties by the multi-terminal Hall bar device [1]. This sparked interest in the science research community, and graphene has been produced in a variety of ways to date.

2.1.2. Synthesis of Graphene

Graphene is synthesized using several different methods from different starting materials. The most widely known method is mechanical exfoliation which is popularly known as the “Scotch tape method” mechanical exfoliation, results in pristine graphene [1]. The method is called the Scotch tape method, because the method peels off multilayered graphene from graphite using sticky tape. The other methods include chemical vapor deposition (CVD) [6, 7], chemical exfoliation [8] and ultrasonic exfoliation [9], which are discussed in detail below.

2.1.2.1. Chemical Vapor Deposition

Chemical vapor deposition (CVD) of graphene is carried out by the decomposition of carbon material on a substrate. In this technique the precursor material can either be solid, liquid or gas [6,7]. The first use of CVD to grow carbon materials on a metal substrate was done in 1966, where methane was decomposed at $T = 900^{\circ}\text{C}$ and formed graphite, which was used as a support material for electron microscopy [9]. In 1969 carbon rings, which were polycrystalline, were synthesized from the decomposition of acetylene and ethylene on platinum. It was also proposed that graphite formed, by first forming graphene as the initial monolayer on the metal surface [10]. The first graphene-like substance obtained by CVD was grown on an iridium substrate. At the time iridium was an ideal substrate, since it produced pristine graphene. However, it was difficult to transfer the graphene onto other substrates and iridium was expensive. More recently cost-effective base metals can be used instead [11, 12].

Thermal CVD is used to grow graphene on metal substrates like Ni, Co and Fe [6]. The process yields few-layered graphene instead of single-layered graphene. The growth of graphene is achieved by the carbon source in vapour form decomposing in a furnace and nucleating on a metal substrate with temperatures in the region of about 1000 °C [13]. The nuclei will grow and form thin graphene polycrystalline films.

The choice of substrate will determine the type of graphene produced (i.e. the number of layers) and thus substrates are chosen to suit desired applications. Copper is mostly used as a substrate, as it selectively yields single layered graphene. On the other, hand nickel (111) is suited for the production of mono- and bi-layered graphene and polycrystalline nickel produces few-layered graphene [6, 14 - 16]. The graphene obtained from the CVD experiment is transferred from the metal substrate to an etching solution, where the graphene is etched from the metal substrate [6]. When graphene is grown on a nickel substrate, the nickel is removed by firstly adding PPMA as a sacrificial layer and then nickel is removed by a diluted hydrochloric acid (HCl) [17]. Graphene that is grown on a copper substrate follows a similar approach; the difference is in the etching, where iron (III) chloride (FeCl_3) solution is used instead of hydrochloric acid [18]. Figure 2.1 shows the removal of graphene from a copper substrate.

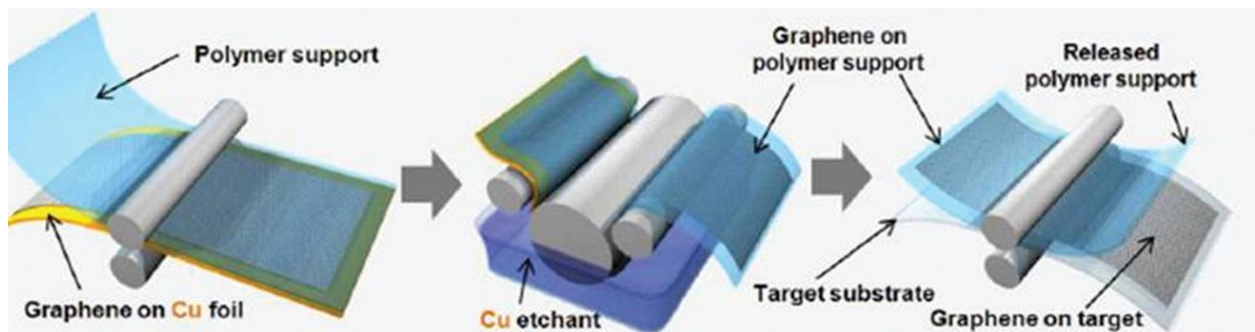


Figure 2.1: Diagram showing etching of copper from the graphene support [18].

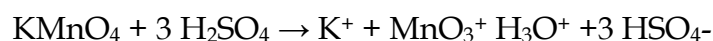
2.1.2.2. Chemical Exfoliation

The process of chemical exfoliation of graphite to graphene involves the use of chemicals as mechanical means. This widely used method is the production of graphene oxide, which is then reduced to “reduced graphene oxide”(rGO), and the method of choice for this research.

Graphene oxide was first synthesized by Brodie in 1859, which involved the addition of potassium chlorate (KClO_3) in a slurry of graphite with fuming nitric acid (HNO_3) [19]. The product he obtained was washed and dried. The product obtained was then subjected to the oxidation reaction several times, until a light yellow product was obtained, which was found to contain carbon, hydrogen and oxygen. His method was improved by Staudenmaier, which employed the addition of sulfuric acid and multiple additions of aliquots of potassium chlorate (KClO_3) over the course of the reaction [20, 21]. The product obtained is an oxidized product and one reaction was used. However, the drawbacks were that the process was time consuming and the reaction evolved chlorine dioxide which is both toxic and an explosive hazard [20, 21]. Both these methods were then improved by Hummer and Offerman in 1958, and the reagents used were sulfuric acid (H_2SO_4), sodium nitrate (NaNO_3) and potassium permanganate (KMnO_4) [22]. The elimination of the potassium chlorate in the preparation of graphene oxide resulted in a product obtained in a day. The Hummer's method however was found to produce a product that has incomplete oxidation of graphite and evolved toxic NO_x gases. Researchers thus focused on improving the method. The first improved method was introduced by Kovtyukhova, where a pre-oxidation treatment step was done. The pretreatment involved refluxing graphite with a mixture of H_2SO_4 , sodium thiosulfate ($\text{K}_2\text{S}_2\text{O}_8$) and phosphorus pentoxide (P_2O_5) for several hours [23]. The product was filtered, washed and dried before

Hummer's method was employed. Other improvements to the Hummer's method are the addition of extra amount of potassium permanganate [24], and Tour's method, which only uses sulfuric acid, phosphoric acid and potassium permanganate [24].

The oxidation of graphite from the Hummer's or the modified Hummer's method results in the formation of functional groups on the network of the graphite; the typical groups formed are hydroxyl, epoxide, carbonyl and carboxylic acid [24]. The graphite is oxidized by the activation of MnO_4^- by the acid, as described by the equations given below [25]:



The scheme shows how the formation of Mn_2O_7 aids in the oxidation graphite. The bimetallic form of manganese has been reported to detonate in the presence of organic compounds and at elevated temperatures [25, 26], thus it is important that the reaction is cooled. The order in which the reagents are added to the reaction vessel is also important. In Figure 2.2, the image compares the amount of the recovered graphite as the starting material. The Tour's method with is given as the improved method, had the least recovered graphite indicating the higher yields of graphene oxide than the other methods. In the comparison of the 3 methods, the Tour's method is the superior method when compared to the Hummer's and modified Hummer's methods in the production of graphene oxide.

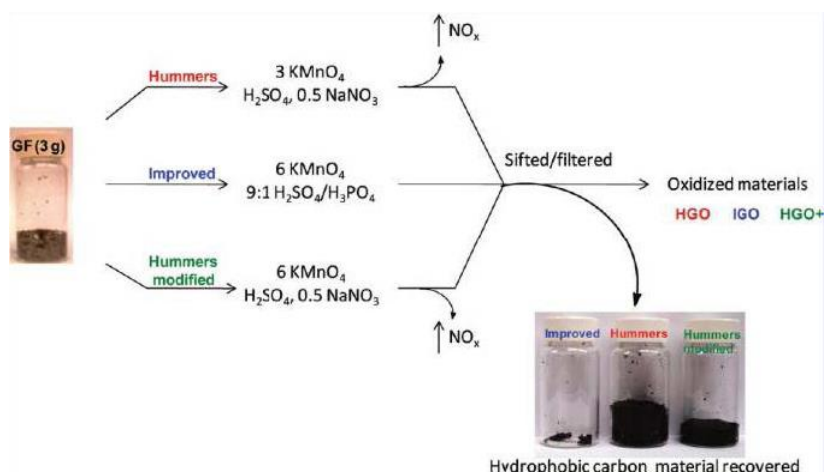
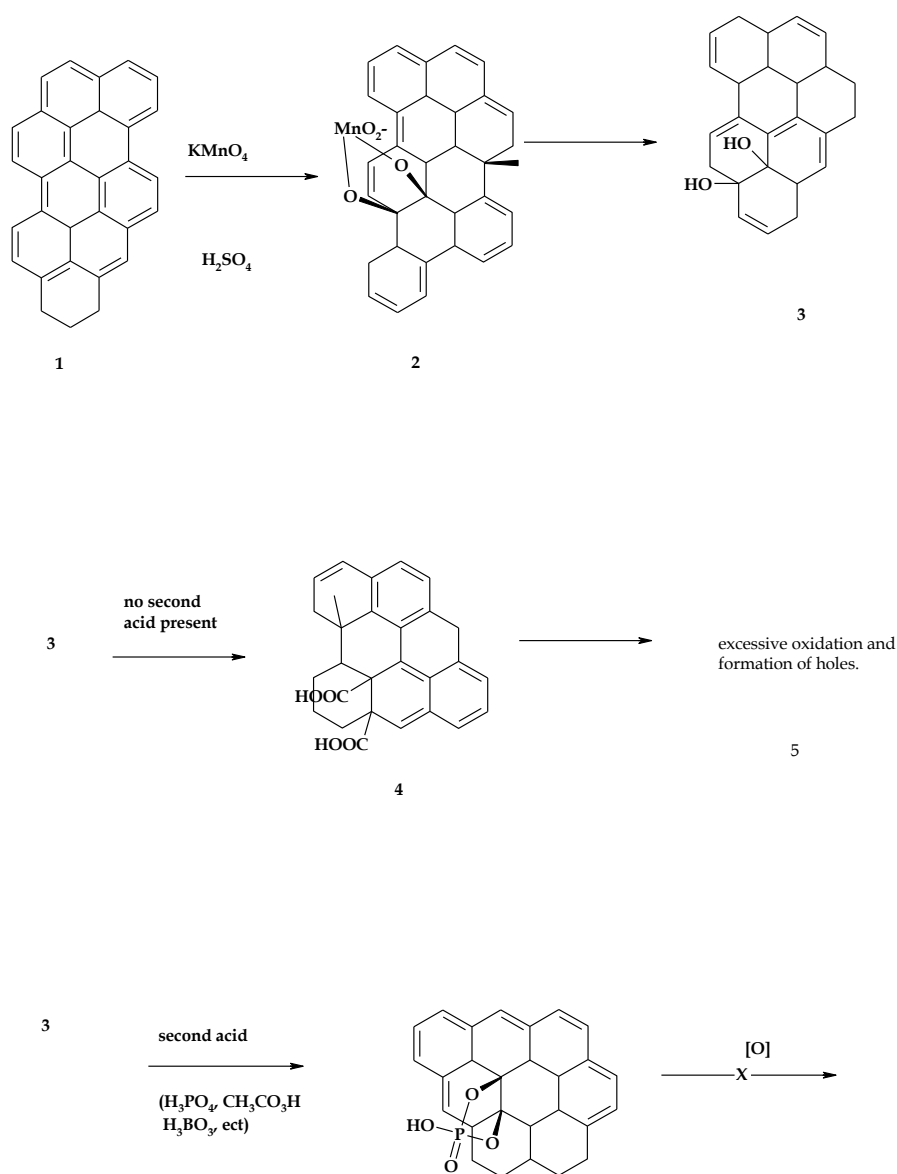


Figure 2.2: Comparison of the recovered starting material from the different methods of producing graphene oxide, with the Hummer’s method having the most recovered graphite [24].

The use of Tour’s method where phosphoric acid is used, has been shown to yield more of the graphene oxide product [24]. The products obtained from the addition of phosphoric acid have more intact 6-membered rings in the basal plane of the graphene oxide [27-28]. It has been proposed that the phosphate ions form 5-membered phosphor rings that prevent further oxidation of graphene oxide and thus preventing pores which is illustrated by Scheme 2.1. The pores in the graphene matrix are formed from over oxidation, which are defects in the graphene. The scheme outlines the advantage of using two acids in the oxidation of graphite, thus preventing over oxidation and g defects. The pores also degrade the electronic properties because of the break in electron delocalization. Table 2.1 shows the different methods and starting materials. The Hummer’s method and modified Hummer’s method have NO_x releasing compounds from NaNO₃ and HNO₃. Both methods also produce less yield of graphene oxide as outlined in Figure 2.2.



Scheme 2.1: Scheme proposing the use of two acids in the oxidation process to prevent over oxidation of the graphite (adapted from ref [25]).

Table 2.1: Table of different methods of producing GO, and starting materials

Methods	Graphite/g	H ₂ SO ₄ /mL	H ₃ PO ₄ /mL	KMnO ₄ /g	NaNO ₃ /g	HNO ₃ /mL	Yield/g
Hummer's	3	69	-	9	1.5	-	2.3
Modified Hummer's	3	90	-	9	-	30	3.2
Tour's	3	360	40	9	-	-	5.1

After the graphite is chemically exfoliated into graphene oxide, graphene can be produced from the reduction of the graphene oxide. The reduction serves to deoxygenate the graphene oxide, to form graphene, by reforming the carbon-carbon double bonds [29]. There are many reducing agents that effectively reduce graphene oxide which include anhydrous hydrazine [29], hydrazine hydrate [30] and sodium borohydride [31]. It was demonstrated by Gilje that reduced graphene oxide exhibits p-type semi-conductive behavior [29]. The conductivity of the reduced graphene oxide is higher than to graphene oxide, but fails when compared to pristine graphene, which is a factor of 10 to 100 better [32 - 34]. The significant difference in the conductivity of pristine graphene and reduced graphene oxide is due the residual functional groups and vacancies which are introduced during the oxidation process which are not removed in the reduction process [27]. The defects from the chemical exfoliation degrade the electronic properties of graphene when compared to graphene obtained from mechanical exfoliation [35]. The reduced graphene oxide has a high surface area for the anchoring of nanoparticles [36].

2.1.2.3. Ultrasonic exfoliation

Graphene can be obtained by using ultrasonic energy to exfoliate different layers of graphite in an organic solvent which is viscous. The solvents include dimethylformamide, N-methyl-pyrrolidone [37], tetraethyleneglycol diacrylate [38] fluorobenzonitrile and pentafluoropyridine [38]. The method employing liquid exfoliation is a soft method of the production and thus the graphene flakes obtained have less defects and the electronic properties are maintained [37]. The ideal solvent for the ultrasonic exfoliation of graphite, must be one with a surface tension of less than 40 mN m^{-1} . This allows for the graphite flakes to be easily separated and the solvent to stabilize the graphene [37]. The mechanism proposed is that there is an implosion of cavity bubbles, which then produce high pressures and temperatures. This results in violent collisions between particles, which give rise to radicals that break up C-C bonds [38]. The graphite is exfoliated into graphene and increasing the sonication time, increases the concentration of graphene dispersed in the solvent. The graphene can be separated from the un-exfoliated graphite by washing and centrifugation, which will separate the layers. Spectroscopic analysis of the graphene flakes obtained shows low defects and are of high quality.

2.1.3. Properties of Graphene

2.1.3.1. Physical structure

As mentioned before, graphene was first isolated from the mechanical exfoliation of graphite. The parent material of graphene is graphite and the properties of the two entities are different. Graphite is composed of multi layered carbon sheets that are weakly coupled to form a 3D crystal lattice [2]. The graphite is made up of 2D layers of sp^2 hybridized carbon that are arranged in a honeycomb lattice [39]. Every carbon bonded has sigma (σ) bonds and pi (π) bonds. The pi bonds make up the delocalized

π -electrons network [40]. A single layer of the carbon matrix of fused honeycomb lattice is graphene [40].

Graphene is composed of a monolayer of carbon atoms and displays a long-range crystalline order [10]. Even though graphene is defined as a monolayer of fused benzene rings, graphene can be defined as having up to 10 layers of carbon matrices. The 10 layer graphene was found to have the graphene properties compromised, as it exhibits the properties of graphite. The limit of multilayered graphene is thus 10 layers [41]. The structure of graphene is shown in Figure 2.3. The figure shows that graphene is 2D material with high crystal quality and is the building block for carbon materials such as nanotubes, graphite and fullerenes [40].

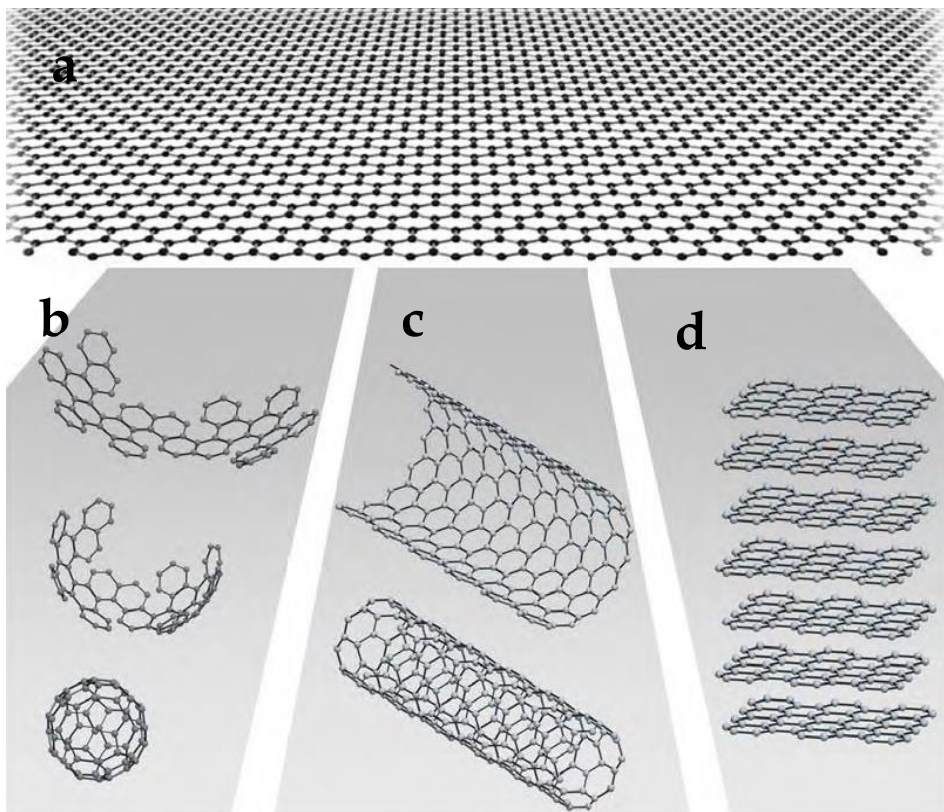


Figure 2.3: (a) Graphene, as the basic building block of carbon materials such as (b) fullerenes, (c) carbon nanotubes and (d) graphite [40].

2.1.3.2. Electronic properties of graphene

Graphene is described to be both a 2D zero-overlap semimetal [1, 42], and a semiconductor with zero band gap [43]. The honeycomb lattice in the graphene, from the fused benzene rings forming the backbone, impart the π delocalized electrons in the graphene matrix. As a result 2D graphene is gapless, which in turn makes the material to have ballistic conduction and higher carrier mobility [1]. The electronic properties of graphene were studied initially through the Hall effect, using graphene films to which a gate voltage was applied. That is how the electronic properties of graphene were characterized. The graphene thin films that were analyzed had few layers of graphene and had electronic properties typically associated with that of a 2D semimetal. A device that was made from thicker layers of graphene had properties that were a cross between 2D and 3D electronic properties [1]. This shows that the electronic properties of single, double and multilayered graphene are distinctly different due to the presence of higher numbers of charge carriers in thicker layers of graphene [1, 4].

Graphene has an electronic structure that follows the tight-binding approximation. The unit cell of the graphene has two atoms, which amounts to two conical points per Brillouin zone, where the band crossing occurs (Figure 2.4) [43]. At crossing point the electron energy is linearly dependent on the wave vector [44]. The energy states of the sigma bonds are removed from the energy at the point of contacts of the conduction and valance bands. This implies that the Fermi level of graphene lies on the pi bands [43]. The behavior exhibited is from symmetry considerations and thus has robust long-range hopping processes.

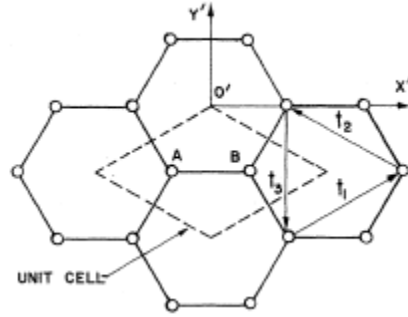


Figure 2.4: Sketch showing the graphite lattice, with the 2 carbon atoms and vector planes [44].

The surface of the Fermi level for graphene is characterized by having six double cones and the position where the cones touches each other, is a the Fermi level. The Fermi level is at $E = 0$, where the valence and conduction bands meet, and this proves that graphene is a zero band gap semiconductor. The Fermi level of the graphene can be changed by application of an electric field, which can create localized charge carriers either electron or holes, depending on the polarity of the electric field. This effect gives the structure and properties of doped graphene [5]. Monolayer graphene has a cosine-like energy bands and as is shown in Figure 2.5. The bands intersect at the K point of the Brillouin zone and the insert in the figure shows that the energy spectrum is linear around the Fermi level [44].

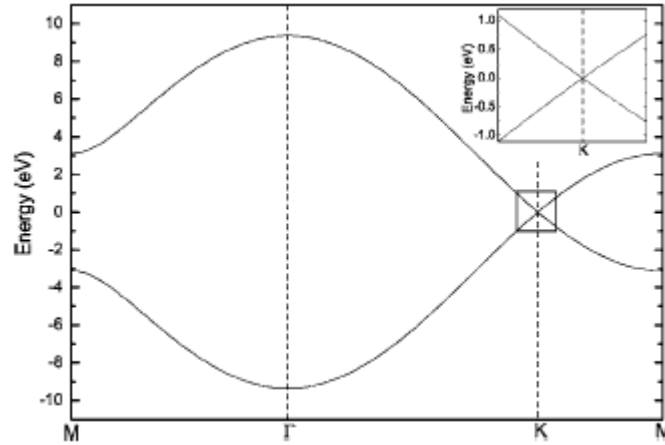


Figure 2.5: Sketch showing the energy band of graphene with the insert showing the intersection at the K point [51].

The curvature in the energy band spectrum of the conductive and valence bands indicates the effective mass and the linear behavior at the Fermi level suggests that the graphene has a band structure with zero effective mass [5]. The graphene has an electronic spectrum that closely resembles the Dirac spectrum for massless fermions. The Dirac equation is used to describe a particle with a spin of $\frac{1}{2}$ with relativity [43]. Since the electron has a spin of half, the Dirac equation applies to them as well. The crystal structure of graphene can be used to explain the phenomenon that the charge carriers of graphene can be described by a Dirac-spectrum, rather than Schrödinger's equation. The mechanism is explained by that there are two equivalent carbon atoms in the sublattice, which leads to quantum-mechanical tunneling between sublattices. The result is the formation of two energy bands, which intersect near the edge of the Brillouin zone, yielding a conical energy spectrum [43].

The phenomenon that graphene has an electronic spectrum which can be described by a Dirac-spectrum allows for parallels to be drawn between graphene and particle physics, and it thus can be studied further by studying the physical properties of the graphene. One method that can be used is Klein tunneling which uses the Klein paradox [43]. The Klein paradox is defined as “the unimpeded penetration of

relativistic particles through high and wide potential barriers” [45]. A potential barrier is usually smaller than the gap that separates the electrons from the holes band in semiconductors. This means that the probability of penetration is affected by the barrier height and width [44]. However, in graphene the width and the height have no effect on the probability of penetration. Graphene can thus be subjected to a counterintuitive relativistic process, where an incident electron penetrates through a potential barrier and the transmission will be weakly dependent on the barrier height [43]. In this relativistic effect, the incident electron creates a positron inside the barrier and by matching the electron and positron wave functions across the barrier, it leads to the probability tunneling of the Klein paradox [43]. In graphene the Klein paradox can be studied using bench top experiments.

Multilayer graphene has a different energy band diagram, which can be seen in Figure 2.6. The figure shows the band diagram of double layer graphene. It is observed that the two levels in the valence and conduction band do not intersect at the K point, but overlap. The insert in the figure shows that the spectrum is nonlinear around the K point and parabolic in nature [44]. The overlap is small in the conduction and valence bands, which is also characteristic of bulk graphite [44]. This indicates that double layered graphene is a semimetal, just like graphite. Therefore, we can conclude that when the number of layers of graphene are increased, the band structure will resemble that of graphite [44].

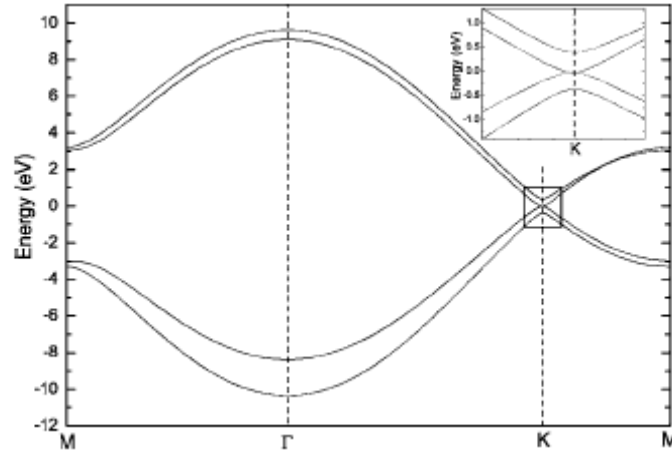


Figure 2.6: Diagram showing the band energy spectrum of double layer graphene [44].

Mono-layer graphene has unique transport properties when compared to those of few layered graphene. The 2D nature of mono layer graphene forces charge carriers to be contained within the plane and the quantum Hall effect may be observed [43]. The quantum Hall conductivity is a function of the charge carrier concentration, n , in an applied constant magnetic field [43] at low temperatures. By changing the magnetic field or the electron concentration, the Fermi energy can be tuned to coincide with Landau levels. This can change the properties of metals and semiconductors [43]. The quantum Hall Effect of graphene follows a half-integer quantum Hall Effect, unlike in traditional semiconductors [46, 47]. The evidence can be found in the period of the quantum Hall effect plateau occurrences. The plateaus were expected to occur at Hall

conductance, $\sigma_{xy} = \frac{4e^2}{h}N$, $N \in \mathbb{Z}$, however they occur at $\sigma_{xy} = \frac{2e^2}{h}(N + \frac{1}{2})$, $N \in \mathbb{Z}$ [46].

This is caused by the presence of an electron and a hole at Landau state at zero energy. The Landau level follow quantum mechanics and therefore they are the discrete, quantized energy levels that a charged particle may occupy in the presence of an applied magnetic field [43]. In Figure 2.9, the quantum hall conductivity is plotted as a function of n , in magnetic field. It should be noted that the quantum Hall effect, decreases with the corresponding increase in the number of graphene layers. In the case of double layer graphene, the plateaus occur at full integer values. This is because

fermions in double layer graphene have a non-zero mass at $n = 0$ which can also be seen in Figure 2.7 [43, 47].

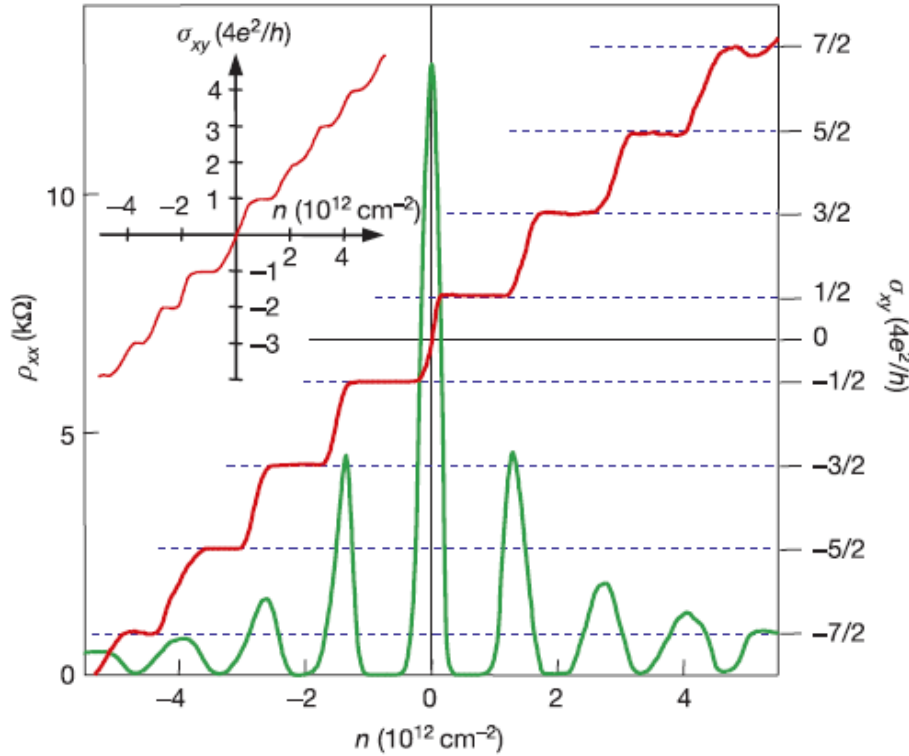


Figure 2.7: Diagram showing the quantum Hall effect. The sketch shows σ_{xy} , of monolayer graphene as function of the number of charge carriers. (n is depicted in red and the longitudinal resistivity is depicted in green) [47].

2.1.3.3. Conductivity.

Graphene has ambipolar electric field effect which means that in graphene the charge carriers can be easily tuned between electrons and hole with concentration up to 10^{13} cm^{-2} [40]. Under ambient conditions, graphene has a charge carrier mobility, μ , of $15\,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [1, 46 - 48]. The mobility has been shown to be affected by temperature [48]. This is important, because μ in graphene is very high for $n > 10^{12} \text{ cm}^{-2}$ in

electrically and chemically-doped devices [48]. There is an occurrence of ballistic transport at micron range [48]. In the nanometer range the electron transport becomes ballistic where the length of the conductor becomes extremely small compared to the mean free path and the electron transport has negligible electrical resistivity caused by scattering [49]. The mean free path of electrons are relatively large which reduces energy losses.

Graphene electronic properties were studied first with multi terminal Hall bar devices that supply a gate voltage (V_g) to graphene [1]. Figure 2.8 shows that the sheet resistivity of few layer graphene (ρ) is dependent on V_g . The resistivity shows a peak and the Hall coefficient R_H displays a reversal of its sign at the same V_g value. This is a typical ambipolar field effect of semiconductors [1]. In graphene the zero conductance area is absent, which is caused by the pinning of the Fermi level inside the band gap and the electron transport occurs in 2D [1].

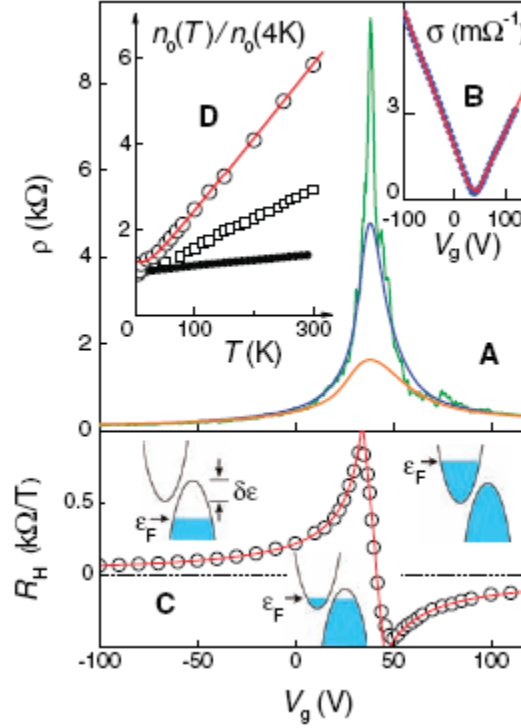


Figure 2.8: Diagram of the electric effect in few-layer graphene. (a) Shows the few layer graphene resistivity ρ on V_g for different temperatures in Kelvin ($T = 5, 70$ and 300 K). (b) Shows the changes in the films conductivity, (c) shows the Hall coefficient versus the V_g at $T = 5$ K and (d) shows the charge carrier dependence on temperature [1].

The electric field effect of the material allows its conductivity to be controlled. Since graphene has a distinct ambipolar electric field effect, it can rival or replace silicon transistors [50, 28]. Graphene also has a linear current-voltage characteristic and currents greater than 10^8 A cm^{-2} can be sustained [1]. We can quantify the planar conductivity as,

$$\sigma = en\mu, \quad (2.1)$$

where the mobility, μ , is limited by acoustic phonons of $n = 10^{12}$ cm^{-2} and since $\mu = 200$ 000 cm^2 V^{-1} s^{-1} , therefore the 2D sheet resistivity is calculated 31 Ω m [47]. Graphene has a high thermal conductivity equal to ≈ 5 000 W mK^{-1} which is higher than metallic

conductors (copper is $\approx 401 \text{ W.mK}^{-1}$). Graphene can also withstand higher current densities than copper [50, 51].

2.1.3.4. Mechanical properties

Graphene has an extremely high specific strength, equal to $48\,000 \text{ kN.m.kg}^{-1}$, which is significantly higher than that of steel (154 kN.m.kg^{-1}). The mechanical properties of any material stem from the crystal structure of the material [52]. The contributing factors are mostly the characteristics of the pristine crystal lattice, grain boundaries and structural defects, such as dislocations [52]. The elastic properties of a solid will be affected by ideal intra-atom interactions, a defect free crystal lattice and lattice geometry [52]. The strength will be affected by the defects, i.e. the strength of a solid with defects will decrease dramatically when a mechanical load is applied when compared to the ideal strength it can possess without defects. In the case of nanomaterials, defects can be absent, while on a microscale they are always present. On the nanoscale, the defects can be absent in the matter which they are fabricated and thus a non-deformed state can be thus obtained, which then causes the nanomaterial to have superior strength close to its ideal strength [52].

In the case of graphene, small pristine graphene membranes can be obtained without defects. They were analyzed for mechanical properties by Lee and coworkers where single layer of graphene was transferred to a substrate with holes. The mechanical properties were studied with Atomic Force Microscopy (AFM) and the process is illustrated in Figure 2.9 [53].

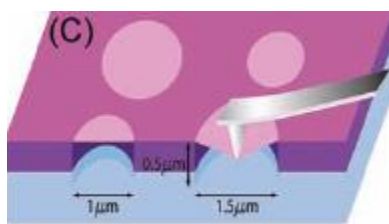


Figure 2.9: Diagram showing the mechanical strength testing of graphene using AFM with a diamond cantilever [53].

The AFM study was used to determine or measure the elastic properties and intrinsic breaking strength of graphene, using the non-indentation method [60]. The graphene membrane was modelled as a 2D membrane. The Young's modulus was determined to be 342 N.m^{-1} , with a standard deviation of 30 N.m^{-1} [53]. To compare value with other materials, the parameter can be now expressed by dividing with the interlayer spacing of its parent material, graphite, which is 0.335 nm [1, 52, 53]. The intrinsic strength of graphene correspond brittle fracture of graphene and determined to be 42 N.m^{-1} or 130 GPa [52, 53].

2.1.3.5. Doping of Graphene

There are several methods of doping graphene, which is the addition of group elements, in small quantities, to graphene. The main elements that are used to dope graphene are nitrogen, boron and sulfur, to name a few [11]. The doping of graphene is used to create a band gap for a specific application. The methods used to dope graphene are CVD [54], hydrothermal [57] thermal [58], solvothermal [59] and ball milling [60].

2.1.3.5.1. Chemical Vapour Deposition

CVD has been used to dope graphene using a copper film as catalyst and a silicone substrate, upon which the graphene sheets are deposited. The production of nitrogen doped graphene produces pyrrolic, pyridinic and graphitic nitrogen on graphene. This method utilizes graphene as carbon source and ammonia as nitrogen source in the presence of methane, hydrogen and argon [54]. The nitrogen gas forms a plasma, which replaces carbon atoms. It has been recorded to form ~3 % nitrogen. Figure 2.10, shows the three types of nitrogen in a graphene matrix, where the pyrrolic nitrogen leads to the formation of pores in the graphene sheet.

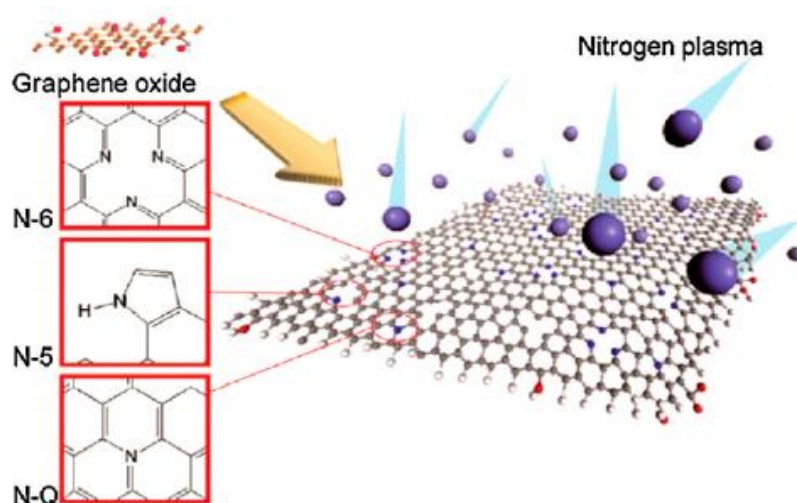


Figure 2.10: Illustration of nitrogen doping using CVD, N-6 is pyridinic nitrogen, N-5 is pyrrolic nitrogen and N-Q is graphitic nitrogen [54].

2.1.3.5.2. Hydrothermal doping

Hydrothermal doping of graphene is the reduction of graphene oxide using hydrazine or ammonia [57]. The method produces doped reduced graphene oxide, which is a

multilayered graphene. The method has challenges of scaling up the process, as well as the high costs of reagents. Another method is to form nitrogen doped graphene hydrogels, where the graphene oxide is reacted with urea. The reaction takes place inside an autoclave and as the name suggests, the hydrogel is 97 % water. The water is removed by freeze drying and the doped graphene formed is 6 % nitrogen.

2.1.3.5.3. Thermal doping

Thermal doping is a widely used method to form boron doped reduced graphene oxide. Graphene oxide is mixed with boric acid or ammonia and the mixture is thermally annealed at 900° C [54,58]. In the case of boron doping, a slurry of graphene oxide, deionized water and boric acid are used. The slurry is freeze dried and heated for thermal reduction of graphene oxide. Figure 2.11 illustrates the process and shows that the method produces a porous graphene sheet [61].

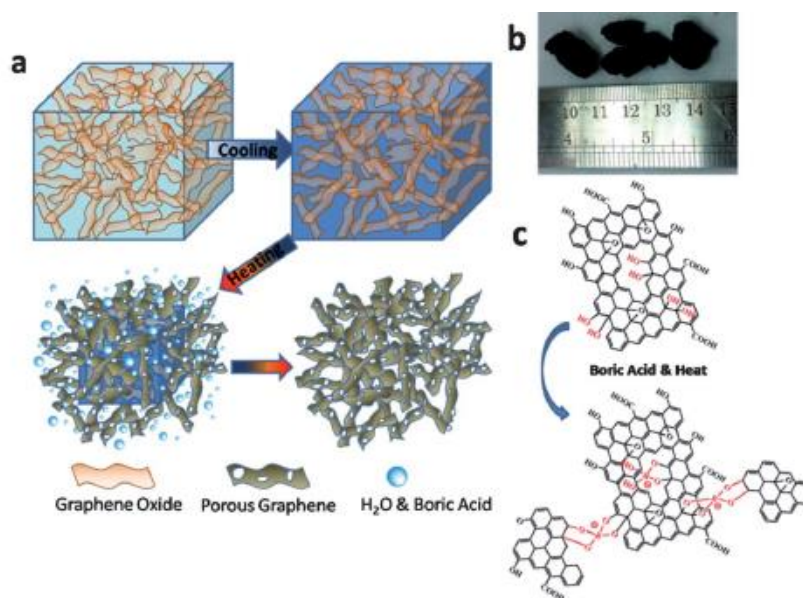


Figure 2.11: Illustration of the formation of B-rGO, (a) is the schematic diagram of the method, (b) is the formed product and (c) reaction mechanism [61].

2.1.3.5.4. Solvothermal doping

Solvothermal doping is a technique that requires graphene oxide and a solvent to be sonicated for 30 minute, or until graphene oxide is thoroughly dispersed in the solvent forming a 1 mg.mL⁻¹ dispersion [54]. The dispersion is then mixed with ammonia borane, which is source for nitrogen and boron. The method can be used in both aqueous and organic media. The dispersion is further diluted with 1 L of solvent and then refluxed for 12 hours.

2.1.3.5.5. Ball milling doping

Ball milling doping is the technique mostly used to form edge carboxylated graphite (ECG), which is a low cost method of producing oxygen doped graphene. The technique uses graphite and dry ice as reagents with the ball milled at 500 rpm and for 48 hours [60]. Figure 2.12, illustrates the formation of oxygen doped graphene.



Figure 2.12: Illustration of the formation of ECG [60].

2.1.3.6. Other Properties

2.1.3.6.1. Magnetic properties.

Graphene itself has been reported to have an intrinsic magnetization property which is a result of the extensive delocalized π electrons which align with the applied field [54]. Graphene has been labelled a weak ferromagnetic magnetic material, while doping with heteroatoms improve the magnetic properties of graphene [54, 24]. The intrinsic graphene magnetization is 0.1 emu.g^{-1} and doping with boron increases it to 1 emu.g^{-1} [54, 24]. This is further explored in this thesis, where graphene is doped with nitrogen. Most of the magnetization data was done at 5 K, where as in this thesis it is done at room temperature.

2.1.1.3.6.2. Optical properties

Mono layer graphene is an electron transparent material. It was discovered by Nair *et al* that graphene exhibits an opacity of $2.3 \pm 0.1 \%$, therefore suggesting that graphene is transparent [55]. However, the opacity of the material is directly proportionally to number of layers, with each layer contributing 2.3% . This implies that the transparency is lost as more layers of graphene is increased. Even though graphene is one atomic layer thick when white light is shone on it, the incident light causes $\pi \rightarrow \pi^*$ interaction, [55] and transmit $97 - 98 \%$ [56, 39]. This property has allowed graphene to be applied in solar cells and flexible electronics [6].

2.1.4. Methods of Characterization.

Graphene can be characterized by the following techniques: Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Raman, Thermal Gravimetric Analysis and X-Ray Diffraction (XRD).

2.1.4.1. Electron Microscopy.

Electron microscopy is a tool to view the structure of nanomaterials. TEM is widely used to confirm the 2D structure of graphene [39]. TEM can also show the defects the structure of the graphene. High Resolution TEM has a higher accelerating voltage which allows for better resolution [62]. HTTEM can offer more information about the structure of graphene, including the number of layers in multilayer graphene. In Figure 2.13, TEM image shown in (a), shows an image of monolayered graphene sheet and (b) shows the multi-layered graphene using HRTEM. HRTEM image may be used in counting the number of graphene sheets in multilayered graphene.

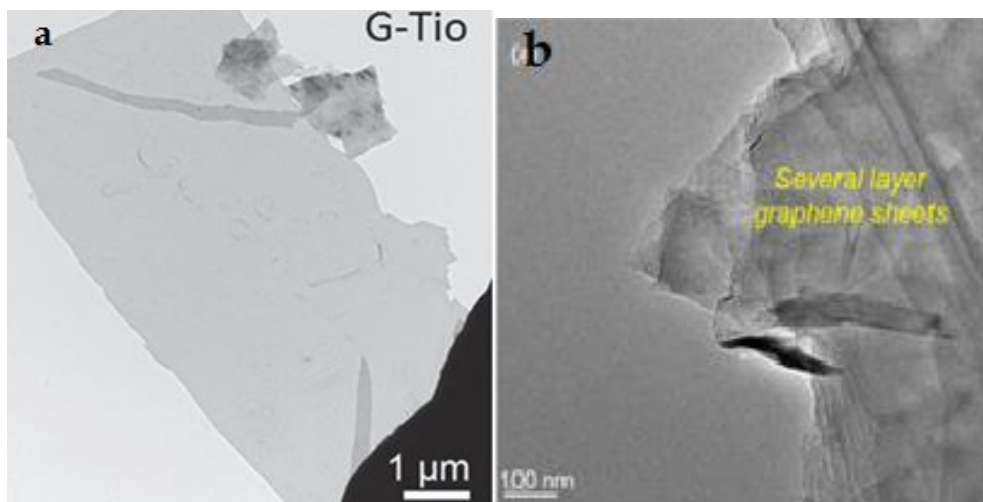


Figure 2.13: Micrograph of graphene from (a) TEM [38] and (b) HRTEM [63].

2.1.4.2. X-Ray Diffraction.

X-ray diffraction has been used to analyze the crystal structure of materials. In this method, a sample is irradiated by X-rays which is diffracted by crystalline samples [63]. The relation between the incident X-ray and the spacing between the planes is given by Bragg's Law which is expressed by

$$n\lambda = 2d \sin \theta, \quad (2.2)$$

where n is an integer, λ is the wavelength of the X-ray, d is the spacing between the crystal planes and θ is the angle of diffraction. Most crystals have a characteristic diffraction pattern and therefore XRD can be used for qualitative purposes [59]. XRD can be used to determine the characteristic peak for graphite, graphene and graphene oxide [65, 66]. It has also been used to get the number of layers of graphene [67]. Figure 2.14 shows the diffraction patterns of graphene, graphite and graphene oxide. The graphite and graphene peaks occur at 26° but the graphite has sharp peaks indicating bulk crystal structure and graphene broad peak indicating nanocrystal structure.

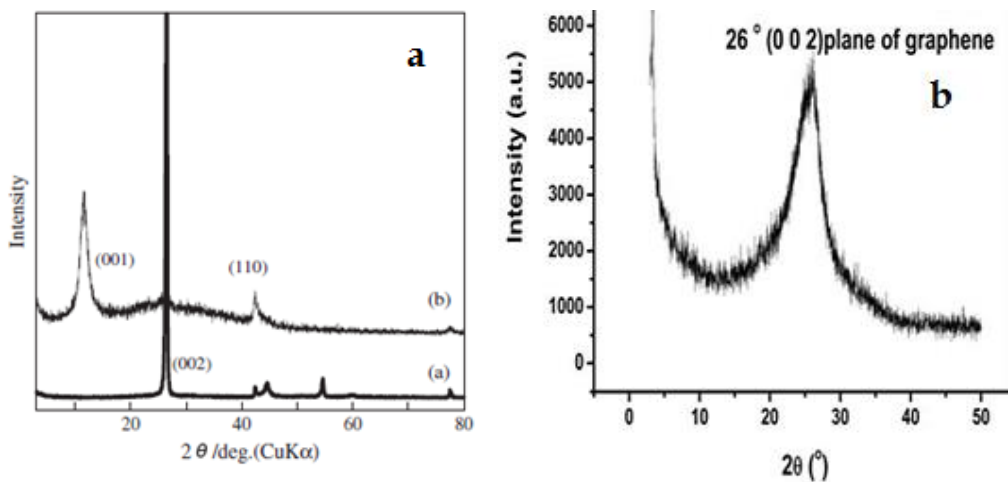


Figure 2.14: X-ray diffraction pattern showing graphite and (a) GO and graphite [67], (b) graphene [68].

Figure 2.15 shows the XRD spectra of multilayered graphene. The technique is used to the number of layers in multilayered graphene. The sizes of the peaks of the diffractogram can be used to determine the number graphene layers in multi-layered graphene.

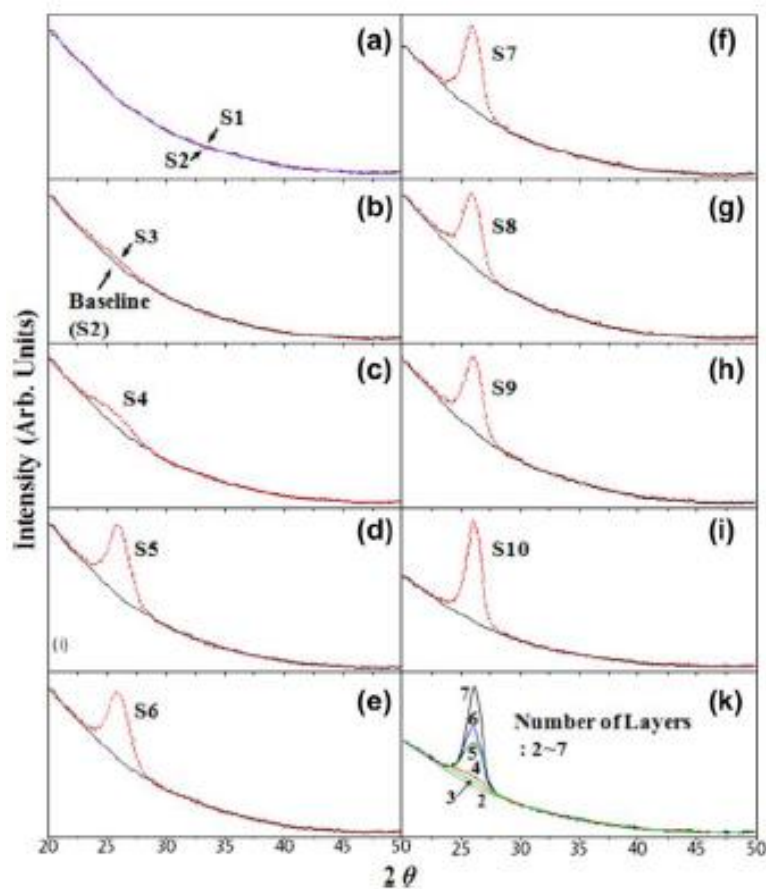


Figure 2.15: Diffractogram pattern showing multi layers of graphene [62], where (a) are mono and double layers, (c) – (k) are multilayered. S is the number of layers of graphene.

2.1.4.3. Thermal Analysis.

Figure 2.16 shows the results from Thermogravimetric analyser (TGA) and differential scanning calorimetry (DSC). Thermal analysis techniques are used to determine the thermal characteristics and thermal stability of graphene [66]. TGA is mainly used for the thermal stability of graphene, and DSC shows thermal processes [67]. The thermal analysis of graphene is usually done at a range of 40 - 900 °C. Graphene usually decomposes at ~ 490 °C, which is shown by TGA and the DSC shows the thermal heat energy for the decomposition of graphene, which can be observed Figure 2.17 [68]. The spectrum (a) shows the degradation of GO is shown, the first decomposition (between 100 - 230 °C) is associated with the loss of water and labile function groups such as C=O, COOH, the TGA show the mass that is lost whilst DSC shows the heat energy absorbed by the degradation process. Both in spectra (a) and (b) the degradation of graphene occurs at temperatures from ~ 500 - 650 °C, the TGA shows the spectra shows the mass that is lost in the degradation and DSC shows the heat absorbed by the degradation [68].

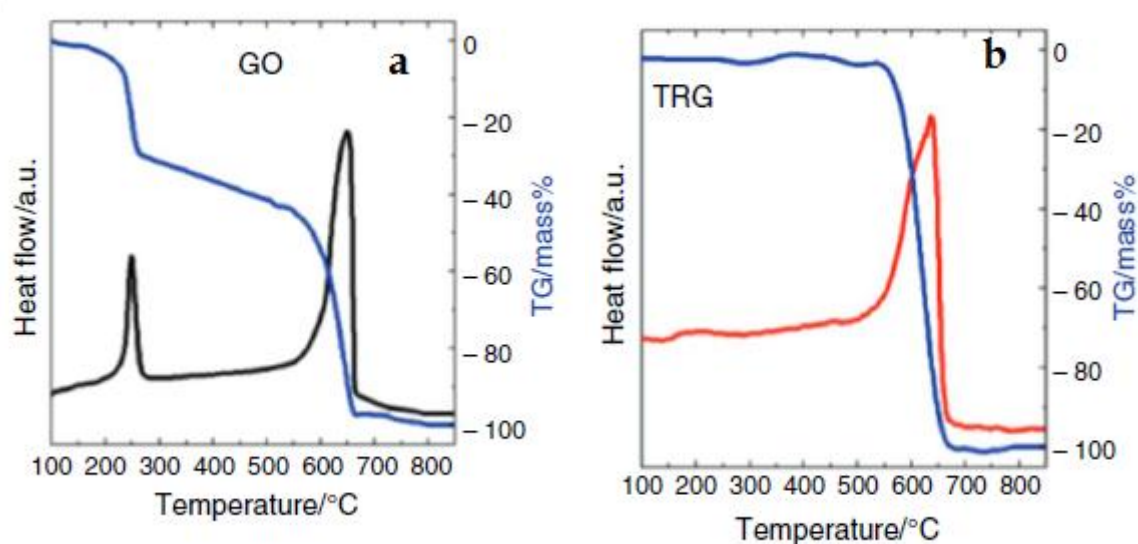


Figure 2.16: Thermogram showing TGA and DSC spectra of (a) graphene oxide and (b) thermally reduced graphene oxide [68].

2.1.4.4. Raman Spectroscopy

Raman is a non-destructive analytical technique used to determine the number of layers of graphene [69 – 71]. The method is versatile and can also be used for the analysis of molecules. Unlike other spectrophotometric techniques, Raman uses scattering of light rather than absorption. The technique uses a monochromatic laser which is shone on the sample being analysed and the light is scattered [70]. The scattered light has a different frequency compared to the incident beam, this allows the detector to register a reading. The molecular bonds of the sample interact with the incident beam, which causes a shift in the frequency of the scattered light. Carbon based material have been analysed by Raman Spectroscopy because of the different characteristic bands that are observed. Graphene, graphene oxide and graphite all have different characteristic bands from the Raman analysis. The characteristic bands are D, G and 2D which occurs when the samples are analysed using a laser excitation of $\sim 513/514$ nm. The D peaks are found in graphene, graphene oxide, and carbon nanotubes [71, 72]. A D peak is a measure of the disorder and defects found in the samples analysed, which is normally caused by impurities and disorder in sp^2 hybridised atoms in the samples [71, 72]. The G-Band is found in most carbon materials and it arises from the stretching vibrations of sp^2 hybridized C – C bonds in graphitic materials. The 2D peak and its shape can be used to determine the number of layers of graphene. The ratios of ID/IG is used to measure the degree of disorder in graphitic material. Figure 2.17 shows typical Raman spectra of different carbon materials.

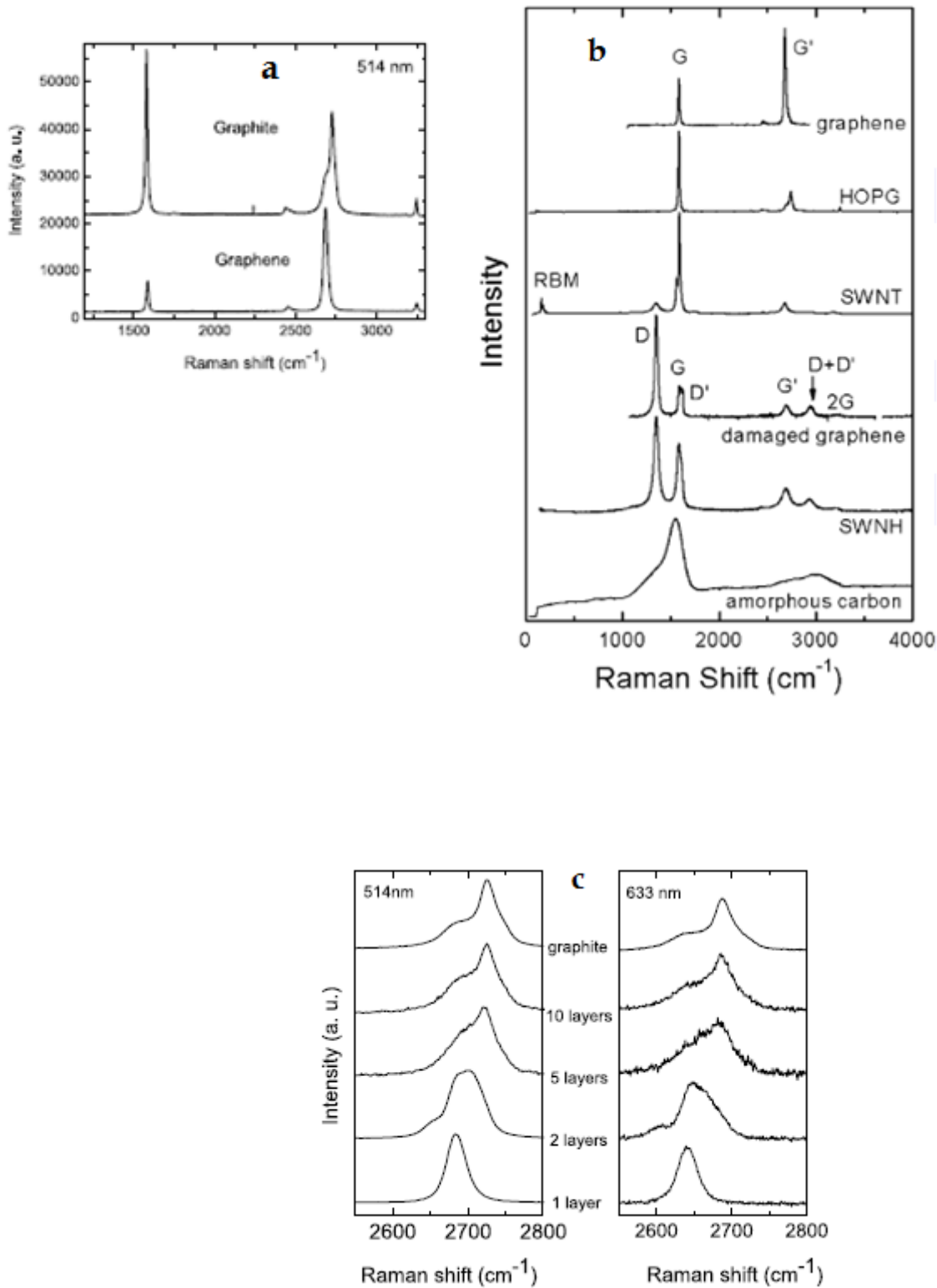


Figure 2.17: Raman spectra of different carbon materials showing different characteristic vibrational modes. (a) Raman spectra of graphite and graphene [69] , (b) Raman spectra of different carbon materials with the different characteristic vibrational modes labeled [71] and (c) Raman of graphite and graphene showing the

2D peaks of different layers graphene and how the shape changes as the number of layers are increased [69].

The spectra shows that the graphite has D peaks because graphitic usually has no defects in the graphene matrix as it has no functional groups in the graphene matrix, building up the graphite. G peak occurs at around 1580 cm^{-1} and is common to most graphitic materials. 2D peaks occur for graphene and reduced graphene oxide, and normally occurs 2700 cm^{-1} .

2.1.4.5. Magnetization Measurements

A vibrating sample magnetometer (VSM) is used to determine the magnetic characteristics of a sample. The magnetization of the sample is determined under the influence of an applied external ramping magnetic field (which is called a sweeping field). The magnetization data gives the magnetic properties of the samples, such as the magnetic state and the nature of the interactions of the magnetic moments [68]. The sample holder was suspended into a Janis model cryostat in an applied magnetic field of 14 kOe. The VSM operation is based on Faraday's law of induction, which states that the induced voltage in the coil is proportional to the magnetization of the sample. Figure 2.18 shows the magnetization of nitrogen doped graphene, where at 2 K doped is superparamagnetic and at 300 K it is paramagnetic, the insert shows the initial magnetization done at 300 K.

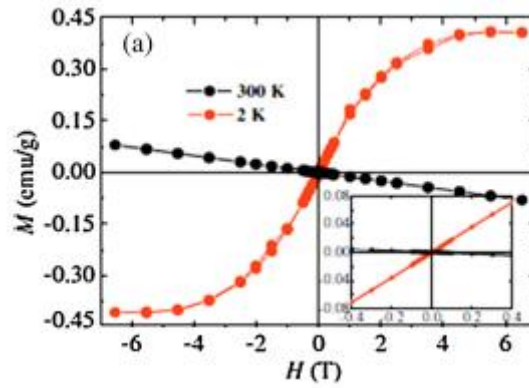


Figure 2.18: VSM magnetic response of nitrogen doped graphene [54].

2.1.5. Applications

Graphene has the potential to be used in a number of technological applications [6], from flexible electronics [39, 75], solar cells [75], to supercapacitors [76]. In the United Kingdom there are 2585 filed patents on graphene, as reported by the U.K. Intellectual Property Office [77].

2.1.5.1. Flexible electronics applications

Graphene thin film is usually on a substrate such as a thin polymer [6]. The method of fabrication was the use of CVD on a copper-coated flexible PVC substrate. The copper was removed by etching [74]. The fabricated device is a graphene touch-sensitive capacitor, interfaced to CMOS circuitry. The combination of graphene and silicone electronics yields high-sensitive electronics, which can be used in wearable electronics and interactive e-skin [74].

Other uses of flexible electronics are in solar cells and transparent conductive films [6]. In most cases the transparent conductive thin films were generally constructed from inorganic semiconductors [78]. The mostly used semiconductor in transparent

conductive thin films has been Indium tin oxide [6]. The fact is that the semiconductor is metallic makes it prone to attacks from acidic and basic species [78]. However graphene has a higher transparency than metallic semiconductor and more chemically resistant [2]. In solar cells the transparent conductive thin films are used [79]. Graphene is useful since it has a transparency of about 90 % and a sheet resistance of $10 \Omega \text{ sq}^{-1}$ [79]. This makes graphene an ideal candidate in solar cell applications. Other application includes organic light emitting diodes [6].

2.1.5.2. Energy applications

Graphene has been used in energy storage devices, such as supercapacitors, batteries and it has also been used in fuel cell applications [6]. Mostly, electrochemical capacitors have been widely explored. The uses extend to hybrid vehicles and power supply devices, which is due to its high-power density and cost effectiveness [66]. Graphene, with its high electrical conductivity, high electron mobility and high surface area makes it an ideal candidate for supercapacitors [54]. The first graphene-based supercapacitor showed to have a specific capacitance of 117 F.g^{-1} in an aqueous solution and 75 F.g^{-1} in ionic liquid electrolytes [54]. It has been reported that doping graphene with hetero atoms such as nitrogen can improve the capacitance [80]. The graphene was doped with nitrogen and had a nitrogen content of 10 % by weight. The doped graphene supercapacities had a specific capacitance of 326 F.g^{-1} and the sheets were found to have superior cycling stability with a columbic efficiency of 99 % after 2000 cycles. The energy density of doped graphene is high and peaks at 25 W.h.kg^{-1} and a power density of 7980 W.kg^{-1} [80].

In fuel cells graphene is used in oxygen reduction electrode [81]. The cathode material is usually expensive metals such as platinum, gold and ruthenium [81]. The metals are a limited resource, while graphene production is cheap. Graphene having a high conductivity and a high surface area it will be ideal alternative for the noble metals

[81]. Mostly, to be more efficient, graphene is used in conjunction with platinum nanoparticles. The nanoparticles also have high catalytic activity and can be anchored on the graphene films [82].

2.2. Graphene Composites.

2.2.1. Nanoparticles

Nanoparticles offer new approaches in tackling innovative design and novel products with the potential to have a variety of technological applications [83]. Metal nanoparticles present a new approach in the design of new products. The size of the nanoparticles can be tuned to suit applications [82 - 85]. Nanoparticles tend to have different properties that form the bulk material. This is seen in Co_2B , where bulk Co_2B is ferromagnetic and Co_2B nanoparticles are superparamagnetic [83]. Other nanoparticles which are semiconductors are the quantum dots [84]. These nanoparticles are well researched in the field of photophysics. These nanoparticles such as CdTe display a property called quantum size effect [84]. This effect occurs when exciton is confined in 3 dimensions resulting smaller particles emitting high energy photons and larger emitting lower energy photons and applications in LEDs, solar cells and photocatalysts [84]. Magnetic nanoparticles have also been looked at for applications in medicine, electronics and recording media [85].

Magnetic properties are dependent on the size and shape of nanoparticles [83,85]. Magnetic nanoparticles, unlike other nanoparticle have unique mechanical and magnetic properties [85]. The most frequently studied magnetic nanoparticles are the ferrite spinel type particles. They generally have hard and soft magnetic materials [83, 85]. The hard magnetic materials are characterized by large values of saturation

magnetization and higher coercivity while soft magnetic materials have low values of saturation magnetization and coercivity [85].

2.2.1.1. Synthesis and Characterisation of magnetic nanoparticles

Magnetic nanoparticles are synthesized using a hydrothermal method, and a co-precipitation method for bimetallic nanoparticles [86]. Mono-metallic nanoparticles are synthesized by the reduction of metallic ions, followed by the chemisorption of ligands to stabilize the nanoparticles. The ions of interest in this study are Ni^{2+} , Co^{2+} and Fe^{3+} . The simplest method in making nickel nanoparticles is the addition of cobalt acetate to a solution of sodium citrate and hydrazine [86]. The sodium citrate is the stabilizing agent and the method was adopted for the synthesis of other cations by substituting the cobalt acetate with FeCl_3 and NiCl_2 respectively.

Other nanoparticles are nanometal oxides particularly dysprosium oxide and cobalt iron oxide nanoparticles. Dysprosium oxide nanoparticles are synthesized from the calcination of dysprosium hydroxide nanorods [87], while cobalt ferrites nanoparticles are made from the co-precipitation method. The cobalt acetate and iron (III) chloride are added to a boiling basic solution and then the stabilizing agent is added [88]. The nanoparticles are used to make magnetic graphene composites.

Nanoparticles and composites are characterized by TEM, HRTEM and XRD. TEM analyses the shape of the nanoparticles and HRTEM are used in to analyse defects in the structure of the particles. Both these techniques can be used to estimate the particle size of the nanoparticles. XRD is the most accurate technique for the determination of average particle size.

2.2.2. Graphene Composites

Graphene composites have received significant attention in the research space. The most cost effective method of producing graphene in the laboratory is in the form of reduced graphene oxide. However, reduced graphene oxide (rGO) does suffer from restacking from the π - π interaction [89]. Restacking occurs when the π bonding orbitals in the graphene sheet interact with π anti-bonding orbitals in the adjacent sheet, which can lead to multilayered rGO to amorphous carbon. This severely impedes the surface area of the rGO and limits the number of applications [89]. To overcome this problem researchers have introduced nanoparticles between the graphitic sheets, thereby forming graphene nanoparticle composites [90]. The composites can be formed using both metallic and metallic oxide nanoparticles [90]. Graphene has a high surface to volume ratio, which allows it to be a suitable substrate to disperse nanoparticles. It has been shown that the formation of the composite changes magnetic properties, for example in the formation of graphene- Co_3O_4 composite, where the composite is superparamagnetic and the pure Co_3O_4 are anti ferromagnetic [91].

The nanocomposite can easily be synthesized using the hydrothermal method. This means that it is a very economical and a scalable process. Depending on the target application, the concentration of the nanoparticles can be varied to meet the specifications of the desired application. The combination of nanoparticles with reduced graphene oxide improves the dispersion of nanoparticles. Therefore, the surface area of the composites is high. There is a charge transfer between the nanoparticles and the reduced graphene oxide. The charge transfer between graphene and metallic nanoparticles changes the electronic and magnetic properties in the metal graphene composite [92].

2.2.2. Synthesis and characterization of magnetic graphene nanocomposites

The most common method of synthesizing nanocomposites is the hydrothermal method [89 - 92].

The method is done using a solution of graphene oxide with metal salt and a reducing agent. Graphene oxide is mixed with a metal salt in a basic solution and refluxed for 3 to 12 hours with a reducing agent. For example, graphene oxide is dispersed in water by ultra-sonication to form a graphene oxide suspension usually about 0.5 mg.mL^{-1} . Nickel chloride solution of about 17 mg mL^{-1} and 4 % graphene oxide solution are mixed together the pH is set to 10 and reducing agent is added dropwise. The solution is refluxed for 3 hours in inert atmosphere [93].

The composite are characterized by TEM, HRTEM, Raman and XRD. The TEM analyses the shape of the nanoparticles and HRTEM are used in the analysis of defect in the structure of the particles. Both these techniques can be used to estimate the particle size of the nanoparticles. XRD is the most accurate technique for the determination of average particle size.

2.3. Applications of graphene oxide composites.

2.3.1. Removal of pollutants in aqueous media.

The earth is water rich planet, making water the most abundant substance on the earth's crust. It has been stated by the Food and Agriculture organization that the estimated water content on earth is roughly $1.351 \times 10^6 \text{ km}^3$. Only 0.003 % is fresh water suitable for human consumption, agricultural uses, hygiene uses and industrial uses. The challenge is to distribute the water for human consumption without

harming the environment [94]. The world's population is constantly climbing at a rate about 1.2 % per annum. Freshwater remains a limited resource and the water quality is important for drinking, cooking, animal farming and crop production. The World Health Organization (WHO) and United Nation (UN) declared access to fresh drinkable water a basic human right [95]. Thus, the preservation of water quality is of the utmost importance. Water quality is greatly affected by the pollutants, which are toxic chemicals, human domestic waste and medical waste, which render the water unsafe for human consumption and the environment at large. Rapid urbanization, informal settlement and population growth increases the demand for fresh water [96]. It was also discovered by A. van Leeuwenhoek, while using a microscope, that water contains micro-organisms [97]. The microorganism contamination of drinking water brings about the outbreaks of diseases, such as cholera and diarrhea. Chemical pollution is a major cause of contamination which causes problems in the environment. The toxicity caused by chemical pollution may cause environmental problems, because some chemicals have high toxicity which in humans and animals disturbs endocrine systems. In some cases, the exposure leads to teratogenic and carcinogenic effects. This affect organism reproduction and causes vegetation damage [98]. Cost effective methods are thus needed to be developed for water remediation.

Most commons method for water remediation have been filtration, biological treatment and adsorption [99]. However filtration and biological treatment have drawbacks, such as high operating costs and production of side products. Adsorption is a versatile cost-effective method that utilize of activated carbons and magnetic graphene nanocomposites sorbent materials for adsorption. Magnetic composites such as Fe_3O_4 /graphene have been shown to remove organic dyes, methylene blue, Pb (II) and Cr(VI) ions in aqueous solution [99 - 100]. The magnetic composite can be easily removed from solution using an external magnet. Methylene blue has positively charged centres which are attracted to the negatively charged oxygens of the Fe_3O_4 . The zeta potential is an important factor when using adsorption experiments. It is the point where the net charge of the absorbent material is zero and thus determines the

electrophoretic mobility of adsorbates [101]. Fe_3O_4 /graphene is negatively charged at pH values higher than 3.7 [101]. This means that in naturally occurring water, Fe_3O_4 /graphene would be ideal in the removal of positively charged pollutants. Figure 2.19 illustrates how Fe_3O_4 /graphene is used in the removal of methylene blue and $\text{Pb}(\text{II})$ ions [101]. The Fe_3O_4 /graphene is easily removed using a hand held magnet which means that it can be easily regenerated.

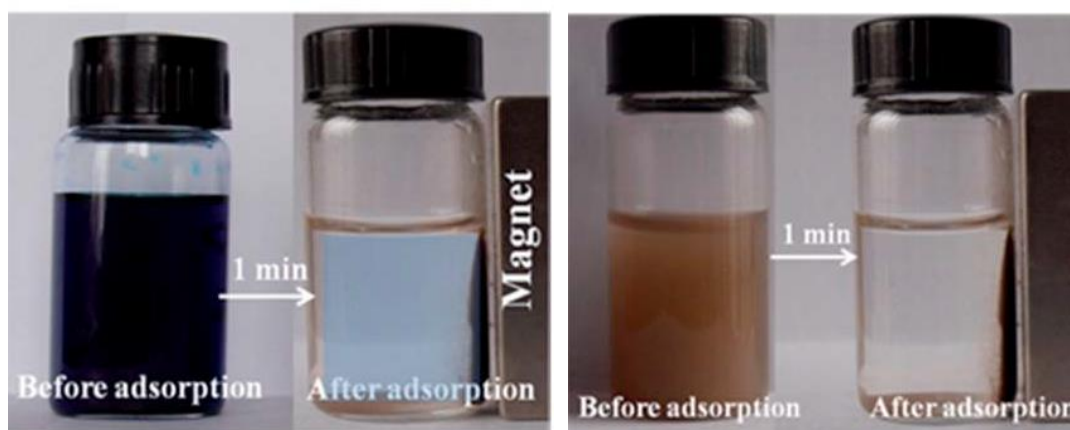


Figure 2.19: Pictures showing the use of Fe_3O_4 /graphene in the removal of $\text{Pb}(\text{II})$ and methylene blue [101].

The other method of water purification in the removal of dyes is using CoFe_2O_4 -rGO as a catalyst in sonar luminescence [102]. A solution of an organic dye and CoFe_2O_4 -rGO are placed in an ultrasonic cleaner. The ultrasonic irradiation of the composite produces sonar luminescence hot spots on the surface of the reduced graphene oxide and the light emitted is absorbed by the CoFe_2O_4 , which creates electron (e^-) and hole (h^+) pairs. The electrons produced react with dissolved oxygen forming reactive oxygen species which can degrade organic dyes [102].

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Chapter 3: Theory

Chapter 3: Theory.

This chapter discusses magnetic moments in materials, and the influence of temperature and applied magnetic field on reduced graphene oxide samples. It focuses on the doping techniques used in the formation of doped reduced graphene oxide samples.

3.1. Origin of Magnetism.

The magnetic property of a material originates from the circulation of the electrons around the atoms and their intrinsic spin which gives rise magnetism [1]. The atomic structure of materials gives insight to how the electrons move around the nuclei, which are assumed to be responsible for the magnetic behavior. The electron movement in the orbitals has been assumed to constitute a current, I [2]. This is illustrated in Figure 3.1, showing the existence of a magnetic moment due to an electron moving in a closed orbit.

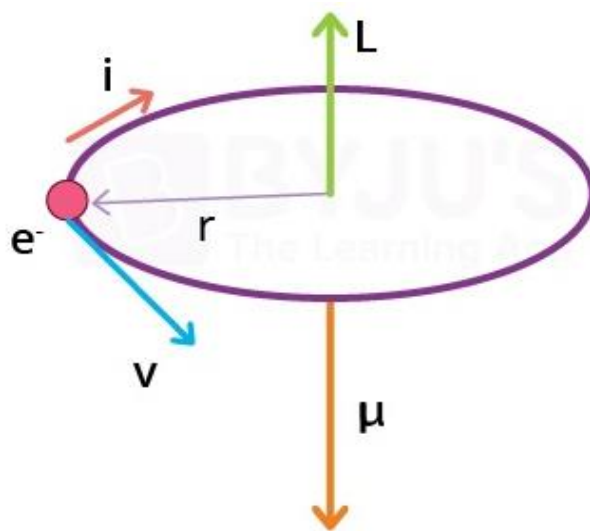


Figure 3.1: Illustration of an electron moving in a closed orbit [3].

We consider an electron of mass, m_e , moving in a closed orbit of radius r as shown in figure below. The current I is induced from the movement of the electron associated with a magnetic moment, defined as

$$\mu = IA, \quad (3.1.1)$$

where A is the area of the orbit with a magnitude of πr^2 [2,3]. If the electron is moving with an angular speed of ω then the current can be defined as

$$I = -ef = -\frac{e\omega}{2\pi} \quad (3.1.2)$$

where f is the frequency of rotation. The magnetic moment then becomes

$$\mu = -\frac{e^2}{2} \omega = -\frac{em_e r^2}{2m_e} \omega = -\frac{e}{2m_e} l, \quad (3.1.3)$$

where l is the orbital angular momentum and equal to

$$l = m_e \omega r^2. \quad (3.1.4)$$

Now the orbital magnetic moment μ_l of an electron can be expressed in terms of the angular momentum as

$$\mu_l = l \frac{-e\hbar}{2m_e}. \quad (3.1.5)$$

Angular momentum of an electron is quantized in the z direction, given by

$$L_z = m_l \hbar \quad (3.1.6)$$

$\hbar$ is related to Planck's constant by the expression $\hbar = h/2\pi$ since $l = m_l \hbar$, the magnetic quantum number is $m_l = 0, \pm 1, \pm 2$. Therefore the magnetic moment in the z direction is given by

$$\mu_{lz} = -\left(\frac{eh}{2m_e}\right) m_l = -m_l \mu_B, \quad (3.1.7)$$

where μ_B is the Bohr magneton which defines the natural unit for magnetic moment, which can be expressed by $\mu_B = e\hbar/2m_e$ [1]. In the presence of a magnetic field in the z-direction μ_z the spin is also quantized, which now gives

$$\mu_B = -2\mu_B m_s, \quad (3.1.8)$$

where the magnetic spin quantum number $m_s = \pm 1/2$. In a multi electron system the assumption is made that the orbital momenta couple together to give the total orbital momentum

$$L = \sum l_i,$$

and for the spin we similarly get

$$S = \sum s_i.$$

Finally, L and S are coupled to give the total angular momentum

$$J = L + S \quad (3.1.9).$$

The total magnetic momentum of an atom can therefore be shown to be

$$\mu_J = -g\mu_B J, \quad (3.1.10)$$

where the parameter g is called the Landé g -factor which is defined as

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \quad (3.1.11)$$

For ideal orbital motion $g = 1$ and for pure spin $g = 2$ [2]. From the above equation, the total magnetic momentum of an atom can be calculated from the total angular momentum induced by both the spin and orbital angular momenta of the electrons.

3.2. Magnetization.

The magnetization $\vec{M}$ of a sample is the total magnetic moments per unit volume determined usually under the influence of a magnetic field [2]. This is expressed as

$$\vec{M} = \frac{1}{V} \sum_{i=1}^n \vec{\mu}_i, \quad (3.2.1)$$

where V is the volume of the sample of mass m . The volume of a sample varies with temperature. This implies that the magnetization is affected by temperature if expressed in volume. It makes more sense to define the magnetic moment per unit mass $\vec{\sigma}$ which is expressed as,

$$\vec{\sigma} = \frac{1}{m} \sum_{i=1}^n \vec{\mu}_i. \quad (3.2.2)$$

The response of magnetization of a sample under the influence of a magnetic field is called magnetic susceptibility χ which is defined as

$$\chi = \frac{\mu_0}{B_0} M, \quad (3.2.3)$$

where μ_0 is the permeability of free space and B_0 is the magnetic induction related to the applied magnetic field H_0 by $B_0 = \mu_0 H_0$.

3.3. Classification of magnetic order in solids

The classification of magnetic order in solids occur from the interaction of microscopic magnetic moments. Thus, the magnetic order is dependent on the internal arrangement and orientation of the magnetic moments [4]. The most common types which will be outlined are ferromagnetism, diamagnetism, paramagnetism and superparamagnetism.

3.3.1. Diamagnetism

Diamagnetism, which is displayed weakly by materials (except for superconductors), is classified to be when a material repels an applied magnetic field. This is due to the electrons in motion creating a small current which induces a magnetic field that opposes the applied magnetic field. The magnetic order follows Lenz's law, where the electrons in the atomic orbitals will adjust their orbit in a way to create current loops that opposes the applied magnetic field [5].

3.3.2. Paramagnetism

Paramagnetism occurs in materials that have permanent magnetic moments. These material usually have partly filled inner 'd' and 'f' shells, which include transition, lanthanides and actinides [5]. This causes the magnetic order to be characterized by random orientation of magnetic moments, which is expressed in Figure 3.2. Paramagnetic materials have non-interacting or weakly interacting magnetic moments. Thus it corresponding susceptibility is positive and temperature dependent. When a magnetic field is applied, the magnetic moments align themselves towards the direction of the applied magnetic field.

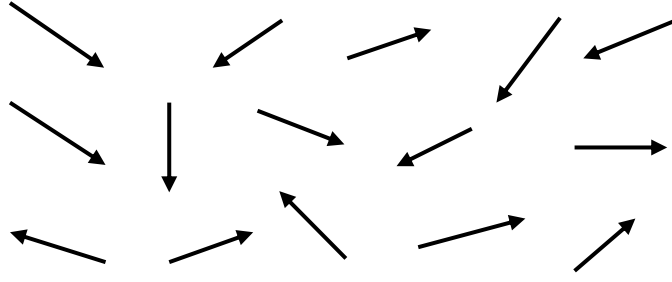


Figure 3.2: Sketch of the magnetic ordering of paramagnetism showing random orientation of magnetic moments.

The magnetic field intensity H causes the splitting of energy levels [6],

$$E_J = \mu_J \cdot H = -g m_J \mu_B H \quad (3.3.1)$$

where m_J is the azimuthal quantum number with values $-J, -J + 1, \dots, J - 1, J$. The average magnetic moment of an atom in the field direction is given by

$$\langle \mu_J \rangle = \sum g m_J \mu_B P(E_J) \quad (3.3.2)$$

where $P(E_J)$ is the probability for the occupation of a given energy level E_J . This is expressed in terms of the Maxwell-Boltzmann distribution as

$$P(E_J) = \frac{e^{-g \mu_B m_J / k_B T}}{\sum e^{-g \mu_B m_J B_0 / k_B T}} \quad (3.3.3)$$

where k_B is the Boltzmann constant. The average magnetic moment is given by

$$\langle \mu_B \rangle = g\mu_B J F(J, x) \quad (3.3.4)$$

where $F(J, x)$ is the Brillouin function defined as

$$F(J, x) = \left(1 + \frac{1}{2J}\right) \coth \left[\left(1 + \frac{1}{2J}\right) x \right] - \frac{1}{2J} \coth \left(\frac{x}{2J} \right). \quad (3.3.5)$$

The parameter x is a dimensionless ratio of the Zeeman energy to the thermal energy and is given by

$$x = \frac{g\mu_B J B_0}{k_B T}. \quad (3.3.6)$$

Under the condition $T = 300$ K and a low field, x becomes minute, i.e. $x \ll 1$ to the point that the Brillouin function is approximated as

$$F(J, x) \cong \frac{x(J+1)}{3J}. \quad (3.3.7)$$

The magnetization for n non-interacting magnetic moments per unit volume take the following expression,

$$M = \frac{n\mu_0 g^2 \mu_B^2 J(J+1)}{3k_B T}. \quad (3.3.8)$$

Since the magnetic susceptibility is given by

$$\chi = \frac{\mu_0 M}{B_0} \quad (3.3.9)$$

and when substituting for M we get

$$\chi = \frac{n\mu_0 g^2 \mu_B^2 J(J+1)}{3k_B T} = \frac{C}{T}. \quad (3.3.10)$$

This is known as the Curie law for susceptibility where

$$C = \frac{n\mu_0 g^2 \mu_B^2 J(J+1)}{3k_B}. \quad (3.3.11)$$

C is called the Curie constant. However, in many instances interactions between magnetic moments occur which lead to the Curie-Weiss law expressed by

$$\chi = \frac{C}{T - \theta_p}. \quad (3.3.12)$$

θ_p is known as the paramagnetic Curie temperature [5 , 6].

3.3.3. Ferromagnetism

Ferromagnetism is a form of magnetic ordering where the atoms of the ferromagnetic material possess magnetic moments which spontaneously align parallel to each other below a critical temperature called the Curie temperature T_c . The magnetic moments have strong interaction between them, at $T = 0$ K. Materials that are classical ferromagnets are Fe, Ni and Co. The ferromagnets will display a net spontaneous magnetization even in the absence of an applied magnetic field. The alignment of the magnetic moments will decrease with a corresponding increase in temperature.

Figure 3.3 shows the alignment of magnetic moments in a ferromagnetic sample. The temperature at which the alignment is destroyed due to thermal agitation is the Curie temperature [3]. This means that at the point where is $T > T_C$, the ferromagnetic material will display properties of a paramagnetic species, because the disorder of the magnetic moments becomes complete. At this point the magnetic susceptibility will obey the Curie-Weiss law. In the vicinity of T_C the law fails. In the Weiss mean field theory the ferromagnetic orders originate from the assumption that a strong internal magnetic field B_{in} is responsible for the ordering of magnetic moments. The magnitude of the internal magnetic field is assumed to be proportional to the magnetization M_S , therefore,

$$B_{in} = \lambda M_S, \quad (3.3.13)$$

where λ is the molecular field coefficient. The effective magnetic field in an externally applied magnetic field in a sample is generally given by

$$B_{eff} = B_0 + B_{in} = B_0 + \lambda M_S. \quad (3.3.14)$$

Similar to a paramagnetic species, the magnetization $M_S(B_0, J)$ of a ferromagnetic species can be expressed in terms of the Brillouin function $F(J, x)$ where

$$M_S(B_0, T) = ng\mu_B J F(J, x). \quad (3.3.15)$$

The ratio of the Zeeman energy to thermal energy y in a ferromagnetic material is now defined as

$$x = \frac{g\mu_B J(B_0 + \lambda M_S)}{k_B T}. \quad (3.3.16)$$

Spontaneous magnetic order exists even without application of an external field i.e $B_0 = 0$ since $B_{in} \gg B_0$. At $T = 0$ K, the spontaneous magnetization per unit volume is

$$M_S(0,0) = ng\mu_B J. \quad (3.3.17)$$

For zero applied field ($B_0 = 0$) and $T > 0$, the spontaneous magnetization of a ferromagnetic material can be expressed by

$$M_S(0,T) = M_S(0,0)F(J,x), \quad (3.3.18)$$

where $M_S(0,T)$ is the saturation magnetization and x is expressed as

$$x = \frac{g\mu_B J \lambda M_S(0,T)}{k_B T}. \quad (3.3.19)$$

Using equation 3.15 the spontaneous magnetization of a ferromagnetic material can be written in terms of the reduced magnetizations as

$$\frac{M_S(0,T)}{M_S(0,0)} = F(J,x) \quad (3.3.20)$$

and

$$\frac{M_S(0,T)}{M_S(0,0)} = \left(\frac{k_B T}{ng^2 \mu_B^2 \lambda J^2} \right) x. \quad (3.3.21)$$

In Figure 3.4 the variation of the reduced magnetization as a function of x , is shown by equation 3.3.21 is represented by curve C_1 . The point of intersect (P) between the C_1 and the Brillion function defines the magnetic state of the material. At temperatures above T_C , the assumption that $B_{in} \gg B_0$ is no longer valid. The magnetic moments are randomly oriented. This means that the sample has paramagnetic properties above T_C . The magnetic susceptibility of a paramagnetic material above T_C is given by the Curie-Weiss law. The Weiss theory predict the collapse of the magnetization at T_C . Figure 3.5 shows the dependence of the saturation magnetization M_S on the temperature T and the inverse magnetic susceptibility dependence on temperature T . The solid line shows the temperature dependence due to itinerant electrons, while the broken line represents that due to localized moments. Examples of ferromagnetic materials are iron, cobalt, nickel, gadolinium and their oxides.

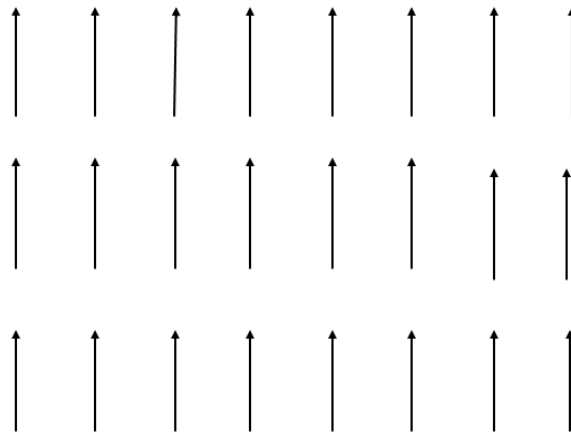


Figure 3.3: Magnetic ordering of ferromagnetic species.

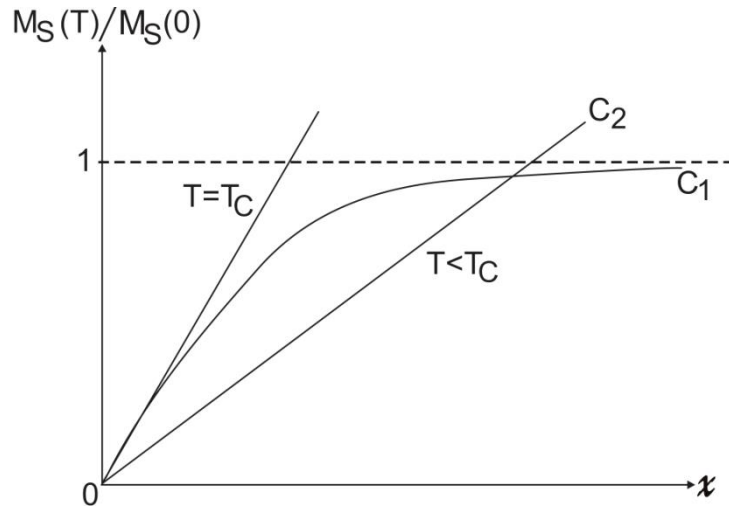


Figure 3.4: Graphical illustration of the solution of equation 3.3.19 and 3.3.20 [1].

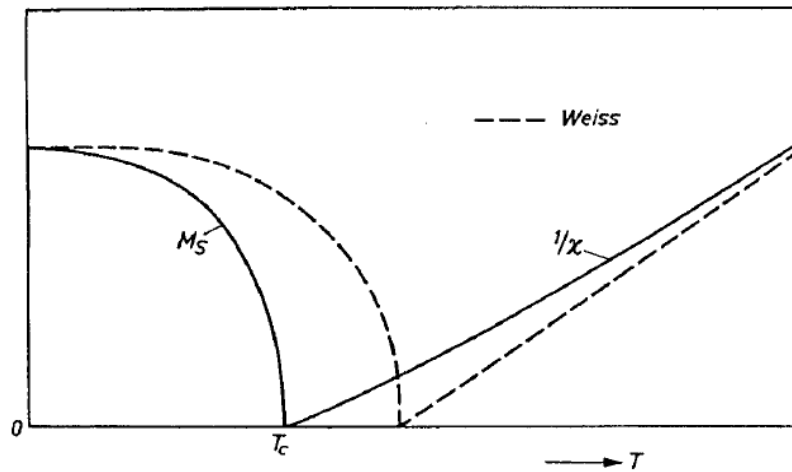


Figure 3.5: Temperature T dependence of the saturation magnetization M_S and the inverse susceptibility above the Curie point of a ferromagnetic material. The solid line shows the temperature dependence due to itinerant electrons while the broken line represents that due to localized moments [1].

3.3.4. Superparamagnetism

Superparamagnetism is the form of magnetic ordering that occurs below the Curie temperature in nanosized ferromagnetic materials [5]. The nanoparticles have a single magnetic domain which are aligned in a ferromagnetic pattern. The magnetic momenta of the nanoparticle are roughly about 10^5 greater than that of a single atom [5]. There is energy required to overcome the crystal field anisotropy of the material as a result of thermal fluctuations that exist within the moments at a microscopic level. This energy is expressed as

$$\Delta E = KV \sin^2 \theta, \quad (3.3.22)$$

where V represent the volume of the nanoparticle, K is the uniaxial anisotropy energy density and θ is the angle between the direction of the moments and the magnetic axis. The magnetization of the nanoparticles can randomly flip direction caused by the influence of temperature. The average time between two flips is known as the Neel relaxation time (τ_N), which is expressed as

$$\tau_N = \tau_0 \exp\left(\frac{KV}{k_B T}\right), \quad (3.3.23)$$

where τ_0 is the length of time characteristic of the material, k_B is the Boltzmann constant and T is the temperature. When the temperature is below a certain temperature, which is called the blocking temperature T_B , the time-scale measurement $\tau_m \gg \tau_N$. This causes the magnetic moment to appear to be frozen. The blocking temperature of a superparamagnetic material occurs at a temperature where $\tau_m = \tau_N$. The Langevin classical function $L(x)$ that describes the magnetic behavior of superparamagnetism is expressed as

$$L(x) = \coth x - \frac{1}{x}, \quad (3.3.24)$$

where

$$x = \frac{\mu B_0}{k_B T} \quad (3.3.25)$$

and μ is the magnetic moment of single domain particles. The $L(x)$ function is the classical analog of the Brillouin function, which describes the nanoparticles and small particles [2].

3.4. Magnetic Hysteresis loop

The magnetization process that gives rise to the shape of a magnetic hysteresis loop comes from the displacement of domain walls. The magnetization is usually uniform inside a domain and non-uniform across a domain wall [7]. The hysteresis loop is a graphical representation of the magnetization of a sample against applied magnetic field H , of the other expression of the applied magnetic field, M . Hysteresis loops consists of the curves are found in four quadrants depending on the direction of the magnetic field and magnetic domains of a sample. The hysteresis loop is usually referred as a B-H curve or a M-H curve. The loop traces the response of the domains caused by an applied magnetic field. The magnetic properties of a sample can be deduced from the loop. The shape of the hysteresis loop is affected by impurities, defects or grain boundaries present in the sample [3]. An example of a hysteresis loop is shown in Figure 3.6

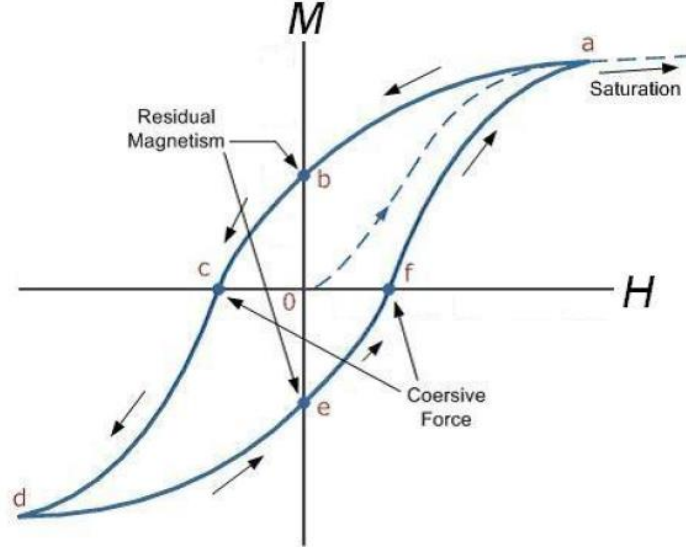


Figure 3.6: Typical hysteresis loop of a sample undergoing magnetization [8].

The curve '0a' shows the gradual increase of the initial magnetization of the sample under the magnetic field. At point a it is assumed that the sample is subjected to a saturation magnetic field. The magnetization can be described by the equation

$$M(H) = M_s(0) \left(1 - \frac{a}{H} - \frac{b}{H^2} - \dots \right) + \chi H, \quad a \quad (3.3.27)$$

where a and b are fit parameters and χ is the high-field susceptibility [9]. When the applied field is reduced to zero and increased in the reverse direction, we get the curve a, b, c, d. When the field is reduced to zero and increased in the reverse direction, we get points d, e, f and a, which completes the hysteresis loop. If the field decreases from the maximum to 0, the magnetization reduces to a finite value M_R (0b). This becomes the retentivity, remanence or remanent magnetization of the sample. This is a parameter used in applications such as random-access memory in computers. The coercivity or coercive field H_C ('0c' and '0f') is another magnetic property. Materials with a large coercivity usually possess a large maximum energy product $(BH)_{max}$.

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Chapter 4: Experimental

Chapter 4: Experimental

This chapter discusses the experimental techniques used in the scope of this thesis, namely, the synthesis of graphene from chemical exfoliation. The method yields graphene oxide as intermediate, which is used in the synthesis of reduced graphene oxide, doped reduced graphene oxide and reduced graphene oxide-nanoparticles composite. The chapter also lists the equipment used in the scope of the thesis, such as FTIR, XRD, TEM, DSC, TGA and VSM.

4.1. Materials

Phosphoric acid (H_3PO_4) 85%, sulfuric acid (H_2SO_4) 98%, potassium permanganate (KMnO_4) 99%, ethanol 99.9 %, hydrogen peroxide (H_2O_2) 35 % and hydrochloric acid 35% (HCl) were purchased from Associated Chemical Enterprise. Iron chloride (FeCl_3) 98%, sodium borohydride (NaBH_4), hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) 65% and iron sulphate heptahydrate ($\text{FeSO}_4\cdot 7\text{H}_2\text{O}$) 98 % were purchased from Sigma Aldrich. Cobalt acetate 98% (CoAc) was purchased from BDH Chemicals and nickel chloride (NiCl_2) 98%, urea and boric acid were purchased from Saarchem. Expandable graphite (98 %) was donated by Richards Bay minerals.

The acids and KMnO_4 were used in the oxidation of graphite into graphene oxide. The $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and NaBH_4 were used as reducing agents to reduce graphene oxide into reduced graphene oxide and reduced graphene oxide- nanoparticle composites. Urea and boric acid were used in the synthesis of doped reduced graphene oxide.

4.2. Equipment

1. Fourier Transform Infrared (FTIR) spectra were recorded on a Perkin Elmer Spectrum 100 ATR FT-IR spectrometer. The background spectrum was run as air to enable background correction of the sample run.



Figure 4.1: FTIR ATR, Analytical Lab (WC)

2. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM 1010 TEM with an accelerating voltage of 18 kV. Samples were sonicated in a volatile solvent such as THF and drop dried on a copper grid (sample holder).
3. Scanning tunneling electron microscopy (STEM) images were recorded on HRTEM JOEL JEM 2100 with an accelerating voltage of 200 kV. Samples are sonicated in a volatile solvent, such as THF and drop dried on a plastic grid (sample holder).

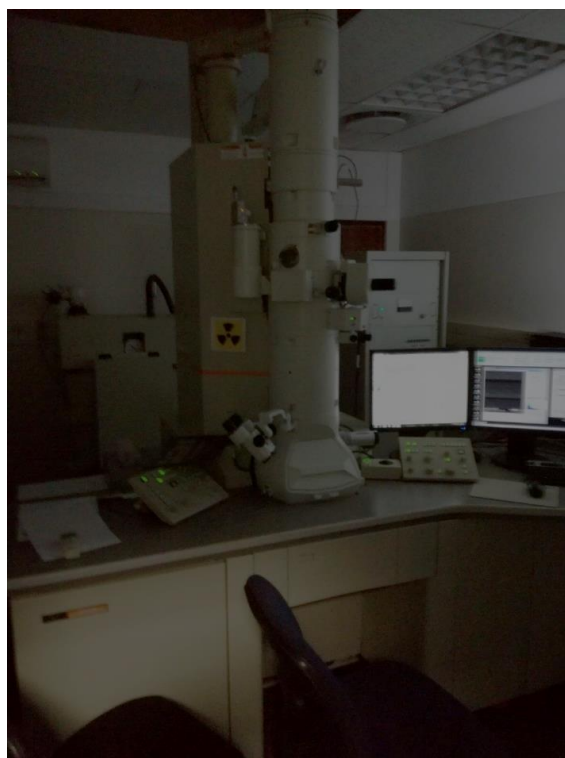


Figure 4.2: High Resolution TEM JOEL JEM 2100, Microscopy & Microanalysis Unit (WC).

4. Thermogravimetric analysis (TGA), together with differential scanning calorimetry (DSC), was recorded on Q600 SDT TA Instruments. The samples were placed in a ceramic pan and measurements were conducted under a nitrogen flow ($20 \text{ mL} \cdot \text{min}^{-1}$) from room temperature to 1000°C , at a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$.



Figure 4.3: Simultaneous DSC-TGA, Q600 SDT TA Instruments.

5. Magnetization experiments were recorded on the Lakeshore Magnetometer System 735S. The samples were placed in a sample holder and stoppered with cotton wool to prevent the sample from having torque, while vibrating. The sample was then vibrated in the presence of 1.5 T electromagnet. The instrument was calibrated using a nickel sphere. The sample of interest was weighed and placed in a cylindrical sample holder. The sample holder was screwed to the bottom of a vibrating rod. The rod was lowered in the sample chamber, between two pick up coils. The measurements were performed at room temperature and the magnetization range is from -1.4 T to 1.4 T. A computer was used to data collect.



Figure 4.4: Lakeshore 735 vibrating sample magnetometer (VSM), Condensed matter Physics Lab.

6. Electrical conductivity and temperature measurements were carried out using the following instruments: Lakeshore 336 temperature controller, Keithley G221 current source, Keithley 2182A nanovolt meter and Cryomech CP819 cooler. The sample, in a pellet form, was introduced to a cryostage sitting inside a vacuum chamber. The temperature controller is set to a temperature loop with a ramp rate of 0.4 K.min^{-1} and a settling time of 70 s. LabVIEW software was used for automation of the different instruments, simultaneous data collection and plotting of data, and a four wire conductivity was employed.

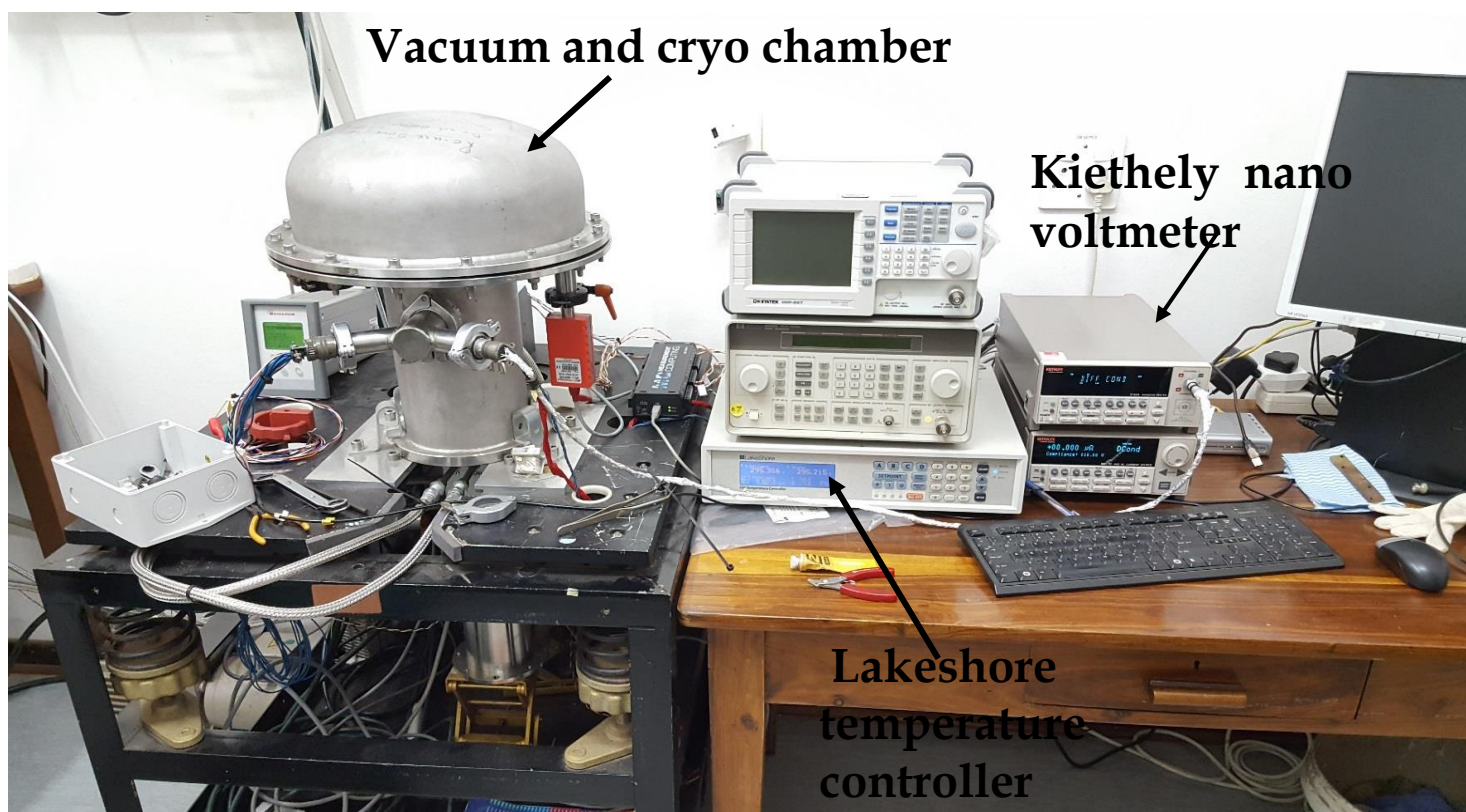


Figure 4.5: Cryochamber, Keithley G221 current source, Keithley 2182A nanovolt meter and Lakeshore 336 temperature controller, Materials Lab (HC).

7. X-ray Diffraction was carried out on a Bruker D8 Advanced. The sample was placed on a silicon wafer. The instrument was equipped with a graphite monochromator with a Vantec detector. The radiation source was a CuK X-ray beam with a wavelength, $\lambda = 1.5406 \text{ \AA}$. using Cu-K α radiation ($1.5405 \text{ \AA}$, nickel filter). Data were collected in the range from $2\theta = 5^\circ$ to 90° , scanning rate of $1^\circ.\text{min}^{-1}$ with a filter time-constant of 2.5 s per step and a slit width of 6.0 mm.



Figure 4.6: Bruker D8 Advanced Chemistry department (WC).

4.3. Synthesis

4.3.1. Synthesis of graphene from chemical exfoliation

The method uses natural flake expanded graphite. The expanded graphite helped minimise the amount of oxidants (sulfuric acid and potassium permanganate) required. The expandable graphite was irradiated with microwaves in a conventional 1000 W microwave oven, which caused the flakes to expand and initiated exfoliation. Figure 4.7 shows the formation of expanded graphite. The expanded graphite is more fluffy and amorphous when compared to flake graphite.

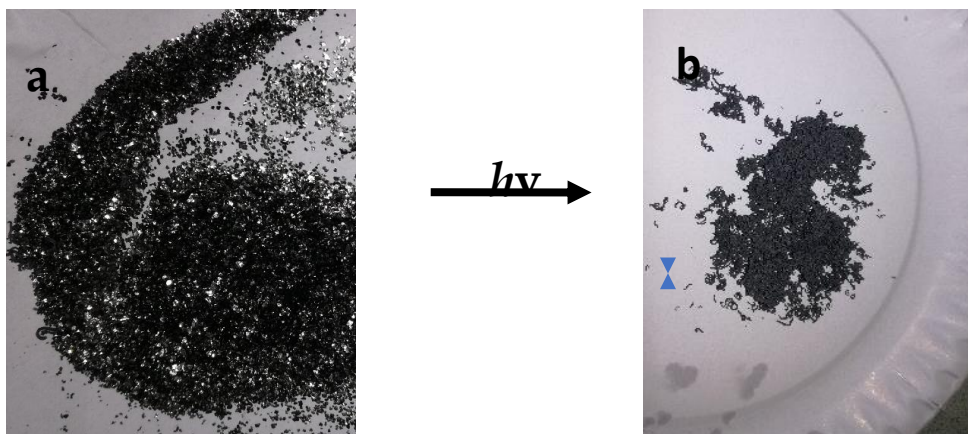


Figure 4.7: Diagram showing formation using expanded graphite, (a) expandable graphite and (b) expanded graphite.

4.3.1.1. Synthesis of graphene oxide.

The oxidation of graphite to graphene oxide was carried out using two methods. The methods used were Tour's and modified Hummer's. The methods differs in that the modified Hummer's method uses an acid mixture of sulfuric and nitric acids with a ratio of 3:1. The method is also exothermic which requires that the temperature be maintained below 0 °C using an ice-acetone bath. Tour's method uses sulfuric acid and phosphoric acid with a ratio of 9:1. The method takes a longer time (3 days), but yielded more product.

4.3.1.1.1. Modified Hummer's Method.

In the synthesis of graphene a modified Hummer's method was followed [1]. Expanded graphite (2 g) was transferred to a tall form beaker in an ice bath. Sulfuric acid (90 mL) and nitric acid (30 mL) were added while the temperature was kept at -5° C by making an ice - acetone bath. KMnO_4 (5 g) was added slowly to the reaction beaker and the temperature was then raised to room temperature and stirred for 2 hrs or to when the slurry had a brown 'cake' appearance. At this point deionized water (150 mL) was added to loosen the slurry and the temperature was raised to 100 °C. The solution was stirred for a further hour and was then allowed to cool to room temperature. The reaction was stopped by the addition of crushed ice (300 mL) and H_2O_2 (3 mL). The mixture was centrifuged and the brown product collected. The product was purified by washing with water, HCl, ethanol and diethyl ether.

4.3.1.1.2. Tour's Method.

Natural flake expanded graphite (3 g) was mixed with phosphoric acid (30 mL) in a 30 mL pill vial. The pill vial was sealed and placed in an ultrasonic bath and sonicated for 1 hr. The graphite was partially dispersed in the acid and then transferred to a 500 mL three neck round bottom flask. The flask was cooled to 0 °C and sulfuric acid (270 mL) was added dropwise and the heat evolved from the reaction forced the graphite sheets to exfoliate and separate into layers [2]. The solution was stirred and followed by the slow addition of potassium permanganate (13.5 g). The solution was stirred again for 12 hrs. The solution was then cooled to room temperature, followed by the addition of ice (400 mL) and H_2O_2 (3 mL). The mixture was sifted through a metal sieve with the filtrate collected. The filtrate was then centrifuged to collect the solid product, was washed with water, HCl ethanol and diethyl ether.

4.3.1.2. Reduction of Graphene oxide (rGO).

Graphene oxide (0.5 g) was mixed with deionized water (100 mL) in a 250 mL round bottom flask and sonicated until there was no visible particulate matter. The flask was transferred to a hotplate and hydrazine hydrate was added to the solution (3 mL) and the reflux set up was established [3]. The solution was refluxed for 24 hrs at 100 °C, which yielded a black product consistent with the formation of graphene. The solution was filtered and the product was washed with copious amounts of water and methanol.

4.3.2. Synthesis of Doped Reduced Graphene Oxide.

The synthesis of the doped reduced graphene oxide used the thermal reduction of graphene oxide. The method uses a tube furnace and the boron and nitrogen are introduced experimentally from chemical vapor deposition (CVD) on graphene oxide. A stainless-steel tube was placed in a tubular section of the horizontal tube furnace. Figure 4.8 shows the sample holder was a tantalum boat, which was placed on the stainless-steel tray, which is used to introduce the graphene oxide paste in to the furnace.

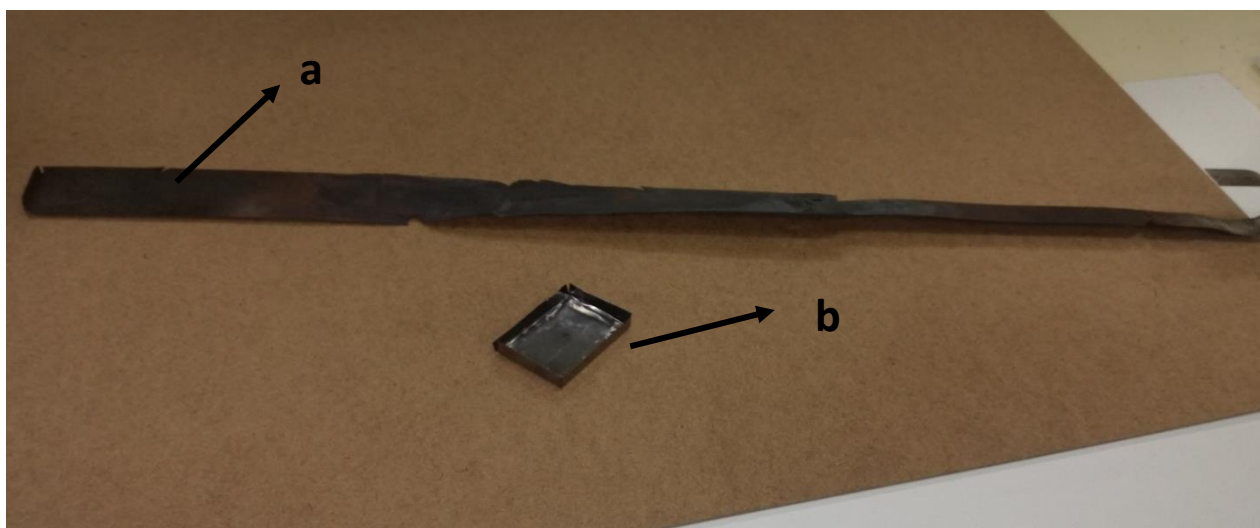


Figure 4.8: Apparatus for doping reduced graphene oxide, (a) stainless steel tray, (b) tantalum tray.

There is also a purpose built tubular stainless steel tube which was installed in the tube furnace. It had a small pipe, which was used to introduce inter gases into the stainless-steel tube, providing an inert atmosphere for the doping of reduced graphene oxide.

4.3.2.1. Boron doped Reduce Graphene Oxide (B-rGO).

Boron doped graphene was synthesized from the decomposition of a graphene solution, which was modified from literature [6]. Graphene oxide powder (0.4 g) and HBO_3 (0.3 g) were sonicated in 20 ml deionized water for 30 minutes. The solution was then transferred to a metal boat and heated in a tubular furnace in an inert nitrogen atmosphere. The solution mixture was heated from room temperature to $1000\text{ }^\circ\text{C}$ at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ and pyrolyzed for 1 hr. The furnace was then cooled down to room temperature, still under inert conditions. The product obtained was washed

with near boiling water (4×100 mL) to remove unwanted ions, followed by an ethanol wash. The colloidal powder was then dried in an oven.

4.3.2.2. Nitrogen doped reduced graphene oxide (N-rGO).

The synthesis was carried out from a modified literature method [7]. The modification was the addition of ethanolamine as nitrogen source. Graphene oxide (0.5 g) was mixed with deionized water (5 mL) in a 25 mL pill vial and sonicated until there was no visible particulate matter. Ethanolamine (0.5 mL) and urea (0.1 g) were added and sonicated for a further 10 minutes. The solution was then transferred to a tantalum boat and placed inside a furnace, which was heated 800 °C under an inert argon atmosphere. After cooling the furnace down to room temperature, the product was collected and washed with copious amounts of water and methanol.

4.3.3. Synthesis of metal nanoparticles on graphene.

4.3.3.1. Synthesis of graphene decorated with cobalt nanoparticles (Co-rGO).

Graphene oxide that was synthesized by Tour's method (Section 4.3.1.1.2), was used in this experiment. Graphene oxide (1.01 g) was mixed with 25 ml deionised water and sonicated until the graphene was well dispersed and formed a dark brown solution [8]. The solution was transferred into 250 mL volumetric flask. Cobalt acetate (2 g) and Potassium hydroxide (0.05 g) were weighed into the solution and refluxed for 2 hrs. Then, a sodium borohydride 0.6M (10 mL) solution was added dropwise to the solution, followed by the addition of trisodium citrate (3.5 g) and refluxed for

2 hrs at 90 °C. The solution was cooled and filtered. The filtrate was washed with hot water to remove unreacted cobalt ions followed by an ethanol wash and then was dried in a vacuum oven.

4.3.3.2 Synthesis of graphene decorated with nickel nanoparticles (Ni-rGO).

The synthesis was carried according to the literature method [9,10]. The modification was that NiCl_2 was used as magnetic source, sodium borohydride as reducing agent and sodium polyacrylate was used as stabilizing agent. Graphene oxide (0.4 g) was mixed with 25 ml dionised water and ultrasonicated until the graphene was well dispersed and formed a dark brown solution. The solution was transferred into a 250 mL volumetric flask. NiCl_2 (0.3 g) was weighed into the solution and refluxed for 1 hour. After the hour had passed, solutions of 0.1M sodium polyacrylate (5 ml) and 0.2 M sodium borohydride (2 mL) were added dropwise and refluxed for 2hr at 90 °C in an argon atmosphere. The solution was then centrifuged, and the supernatant was decanted away. The remaining solid was washed with copious amounts of hot water and ethanol. The solid was dried under vacuum at 40 °C.

4.3.3.3. Preparation of graphene decorated with cobalt ferrite nanoparticles (FeCo-rGO).

The synthesis was utilized a modified literature method [11]. The modification was the addition of graphene oxide and sodium citrate as stabilizing agent. Graphene oxide (0.6 g) was dissolved in deionized water (40 ml) in a 250 mL round bottom flask by ultrasonication. The graphene oxide solution was then refluxed at 150 °C with FeCl_3 (0.6 g), CoAc_2 (0.8 g), Na_3Cit and NaOH (0.2 g) in an argon atmosphere. The solution was refluxed for an hour to ensure the thorough solvation of the metal salts. A solution of NaBH_4 (0.04 M, 10 mL) was then added dropwise and refluxed for 30 min to which

the colour changed from brown to black, confirming the indication the reduction of the graphene oxide and metal salts. The solution was cooled to room temperature, centrifuged (4000 rpm) and the supernatant was decanted away. The remaining solid was washed with copious amounts of hot water, 1:1 HCl, ethanol and diethyl ether. The solid then was dried under vacuum at 40 °C.

4.3.4. Synthesis of metal nanoparticles.

4.3.4.1. Synthesis of cobalt nanoparticles (Co-NP).

Deionized water (50 mL) was added to a three neck, 250 mL round bottom flask. A reflux apparatus was set up with nitrogen air bubbled in the round bottom flask to remove excess air and to ensure that the reaction was done under inert conditions. Cobalt acetate (2 g) and potassium hydroxide (0.05 g) were weighed into the solution and refluxed for 2 hours. Then, a sodium borohydride 0.6M (10 mL) solution was added dropwise to the solution, followed by the addition of trisodium citrate (3.5 g) and refluxed for 2hr at 90 °C. The solution was cooled and filtered. The filtrate was washed with hot water to remove unreacted cobalt ions, followed by an ethanol wash and then dried in a 60°C vacuum oven.

4.3.4.2. Synthesis of cobalt nanoparticles (Ni-NP).

Deionized water (50 mL) was added to a three neck 250 mL round bottom flask. A reflux apparatus was set up with nitrogen air bubbled in the round bottom flask to remove excess air and to ensure that the reaction is done under inert conditions. NiCl₂ (0.3 g) was weighed into the solution and refluxed for 1 hour. After the hour had passed, solutions of 0.1M sodium polyacrylate (5 ml) and 0.2 M sodium borohydride (2 mL) were added dropwise, and refluxed for 2hrs at 90 °C in an nitrogen atmosphere.

The solution was centrifuged and the supernatant was decanted away. The remaining solid was washed with copious amounts of hot water and ethanol. The solid was then dried in a vacuum at 40 °C.

4.3.5.3. Synthesis of cobalt ferrite nanoparticles (FeCoO-NP).

Deionized water (50 mL) was added to a three neck 250 mL round bottom flask. A reflux apparatus was set up with nitrogen air bubbled in the round bottom flask to remove excess air and to ensure that the reaction is done under inert conditions. FeCl₃ (1.8 g), CoAc₂ (1.8 g), Na₃Cit and NaOH (0.2 g) was refluxed for 3 hr at 200 °C. The solution was allowed to cool and copious amounts absolute ethanol was added to the solution to precipitate out the FeCoO-NP. The solution and the precipitate was placed on top magnets and allowed to settle for 48 hrs. After the settling time, the solution was centrifuged and the supernatant was decanted away. The remaining solid was washed with copious amounts of hot water and ethanol. The solid was then dried in a vacuum at 40 °C.

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Chapter 5: Results and Discussion.

Chapter 5: Results and Discussion.

This chapter discusses the results of the synthesis and characterization of the reduced graphene oxide, doped reduced graphene oxide and reduced graphene oxide-nanoparticles composites. There were several deviations from literature in the manner in which the synthesis was carried out, such as using expanded graphite (expandable graphite was expanded using a microwave) in preparation of graphene oxide, and skipping the freeze drying step in the formation of the doped reduced graphene oxide.

5.1 Synthesis and characterization

5.1.1. Synthesis of graphene from chemical exfoliation

(a) Synthesis of graphene oxide

One of the graphene synthesis methods was the Tour method. The synthesis was modified by using expandable graphite, in order to reduce the amount of acids used. The expanded graphite was also sonicated in sulfuric acid. The traditional ratio of the acids $\text{H}_2\text{SO}_4 : \text{H}_3\text{PO}_4$ is (360 mL : 40 mL), but in this synthesis we found the following reductions to be more than enough (270 mL : 30 mL), a reduction of 25 %. When the reaction was over and a brown product was obtained, it was characterized with FTIR, which confirmed that the reduction of amounts of acid had no effect on the reaction. FTIR was used in conjunction with XRD for the confirmation of the formation of graphene oxide.

The graphene oxide obtain from the modified Hummer's method was also characterized. There were two methods used in the formation of graphene oxide as

evident in Figures 5.1 to 5.3. There was no observable difference between the graphene oxide samples, other than the graphene oxide obtained from Hummers method having a more intense brown colour, while the Tour method had a lighter colour. Figure 5.2 shows that the graphene oxide obtained from the Tour's method was wrinkled compared to the graphene oxide from the modified Hummer's method. The samples were then characterized with a spectroscopy technique. The data obtained from FTIR showed the typical characteristic peaks for hydroxyl and carboxylic groups. The oxidation of aromatic results in carbonyl groups (C=O) which is characterized by the carbonyl vibration as seen in Figure 5.1. The most prominent peaks on the spectra are the hydroxyl peaks, which are around the 3100 cm^{-1} to 3350 cm^{-1} region.

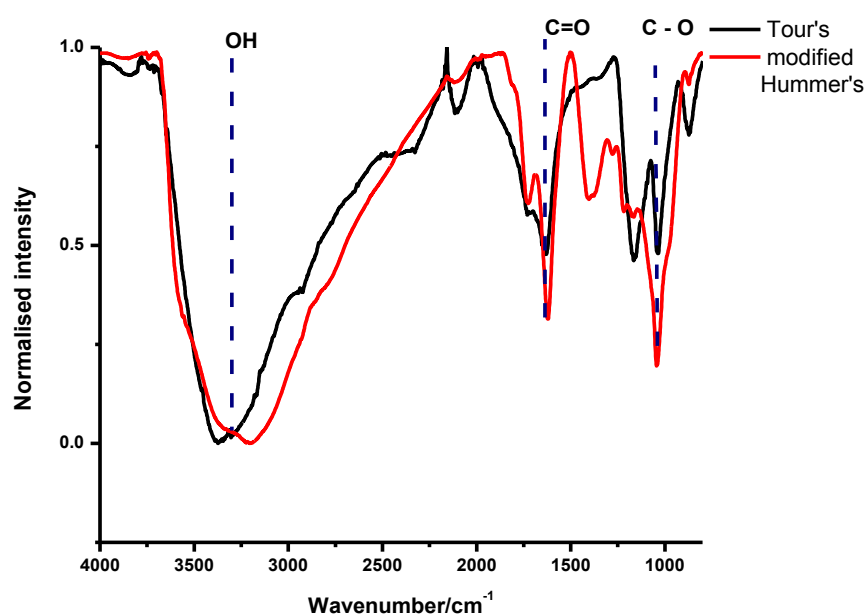


Figure 5.1: Graph showing the FTIR of graphene oxide from Tour's and Hummer's method.

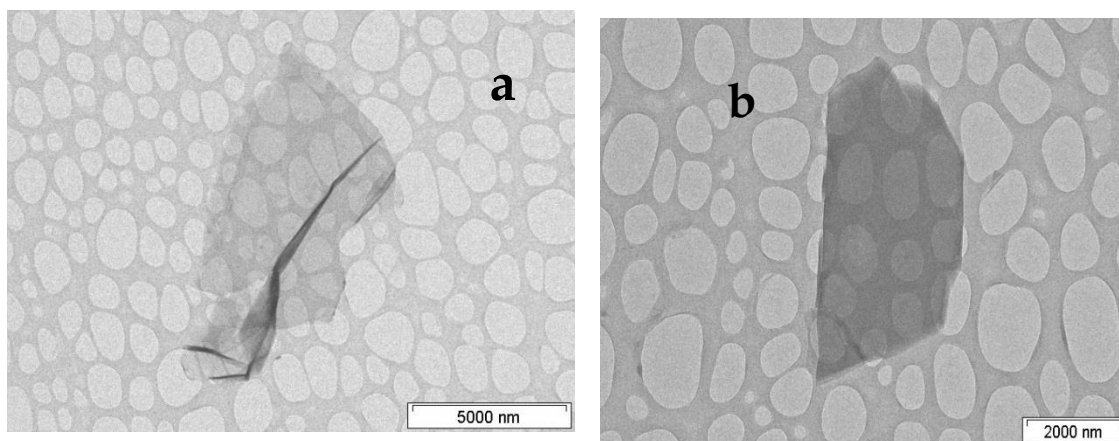


Figure 5.2: TEM data of graphene oxide from Tour's (a) and Hummer's method (b).

This confirms the oxidation of graphite into graphene oxide, with the appearance of the oxidated functional groups such as C=O (1635 cm^{-1}), O-H (3221 cm^{-1}) and C-O (1210 cm^{-1}) [1]. In Figure 5.2 the TEM data shows that the graphene oxide from Tour method had wrinkles, which resulted from microwave expansion of expandable graphite into expanded graphite. Graphene oxide was also analysed using XRD, as shown in Figure 5.3. The graphs shows that the had the characteristic peak of graphene oxide at 10° , which is agreement with literature [2]. The Tour's method graphene oxide had more broader peak at 10° when compared to the one obtained from modified Hummer's method. The data is in agreement with the TEM, where the GO from Tour's method was wrinkled and monolayered, as shown by the broad peak at 10° . The GO from the modified Hummer's method had a prominent sharp peak 10° indicating the structure to be more crystalline.

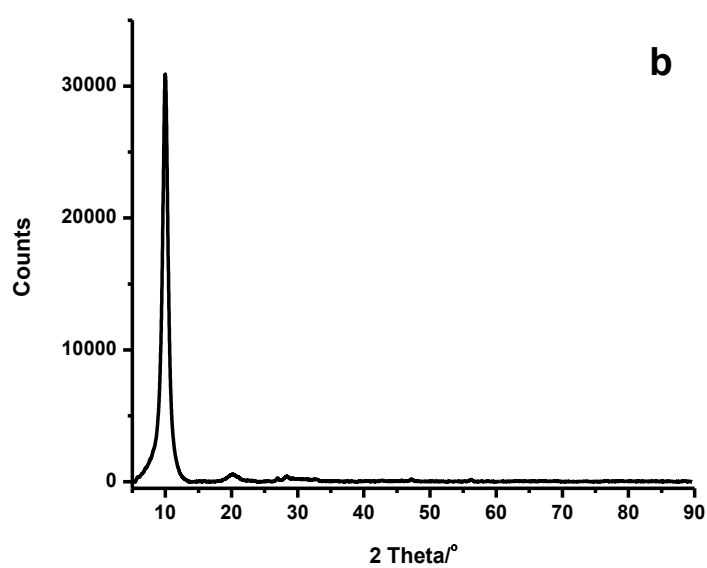
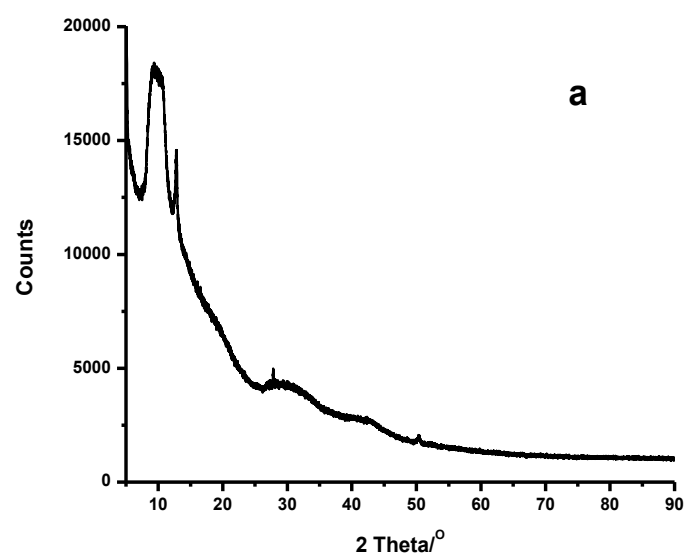


Figure 5.3: Graph showing the diffractogram of GO from (a) Tour's method and from (b) modified Hummer's method.

(b) Synthesis of reduced graphene oxide (rGO).

The synthesis of graphene from graphene was carried out from the reduction of graphene oxide obtained from the Tour's method. The reduced graphene oxide was observed as the black formation of graphene particulates in the solution. The reduced graphene oxide was characterized using infra-red spectroscopy. The most observable difference in the FTIR spectrum is that there is a reduction in the characteristic peaks in the region of 3221 cm^{-1} for the O-H stretching vibration and at 1750 cm^{-1} . These peaks correspond to the stretching modes of O-H 3200 cm^{-1} groups from phenol and carboxylic acid while carbonyl stretching mode at 1651 cm^{-1} which indicate the reduction of graphene oxide [3], as shown in Figure 5.4.

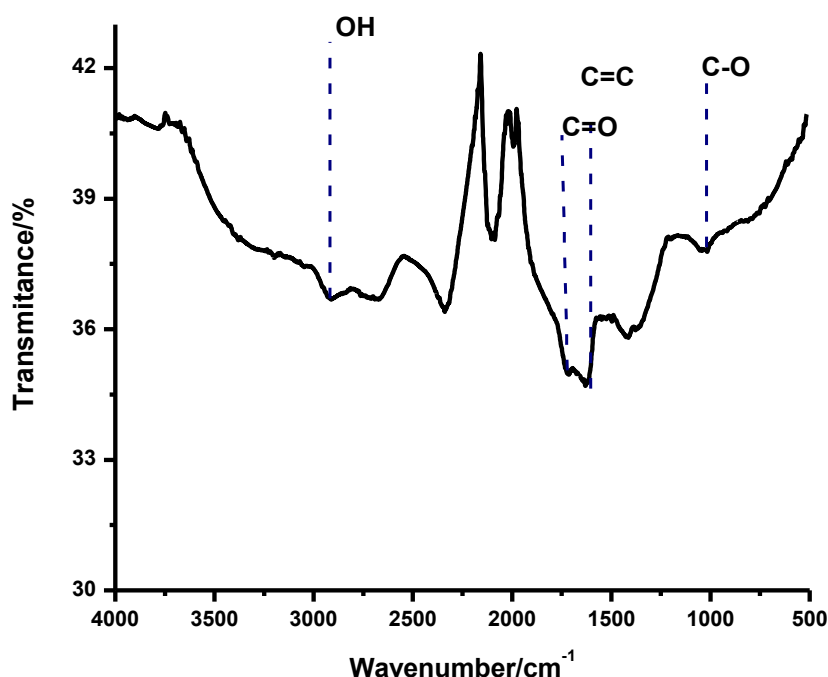


Figure 5.4: Infra-red spectrum of reduced graphene oxide.

The other method used to complement the FTIR results was Elemental Analysis, which used to compare to graphene oxide to reduced graphene oxide. The results

of the Elemental Analysis results are summarized in Table 5.1. The carbon content in the GO sample was 56%, which was increased to 84 % in rGO, which was due to the loss in oxygen content.

Table 5.1: Results of Elemental analysis results for GO and rGO

Sample	Carbon/ %	Oxygen / %	Nitrogen/ %	Hydrogen / %
GO	56.24	32.64	-	11.12
rGO	83.62	12.18	2.06	2.14

The other imaging techniques that were used, were TEM and SEM. The results are shown in Figure 5.5. The TEM shows the wrinkles in the structure of the reduced graphene oxide, which was expected. The SEM showed the 3D image of the reduced graphene oxide also showed that the rGO had crises and folds. The reduction method used extensive ultrasonic treatment which would have upset the morphology of the reduced graphene oxide [4].

Raman spectroscopy results are shown in Figure 5.6. The reduced graphene oxide has been reported to have a prominent D-band at 1380 cm^{-1} [5]. The D band is used to evaluate the defects in the graphene lattice, which usually results from sp^3 hybridization found in the graphene lattice [4 - 6]. The G-band is a measure of the amount of sp^2 carbons in the lattice. Pristine graphene will have a prominent G-band [5]. The intensity ratio (I_D/I_G) is used to determine where there are defects in the lattice. When the ratio is less than one, it is an indication that there are no defects in the graphene lattice, and when the ratio is greater than one there are defects and disorder in the graphene lattice [5]. The data obtained showed that the I_D/I_G ratio is greater than one, which was observed in the TEM image from the wrinkles of the graphene lattice in the rGO sample. The 2D band is used to measure the thickness of the graphene layers. The multilayered graphene will have strong $\pi - \pi^*$ interaction, between layers which results in a broad shaped 2D band in the spectrum [2 - 6].

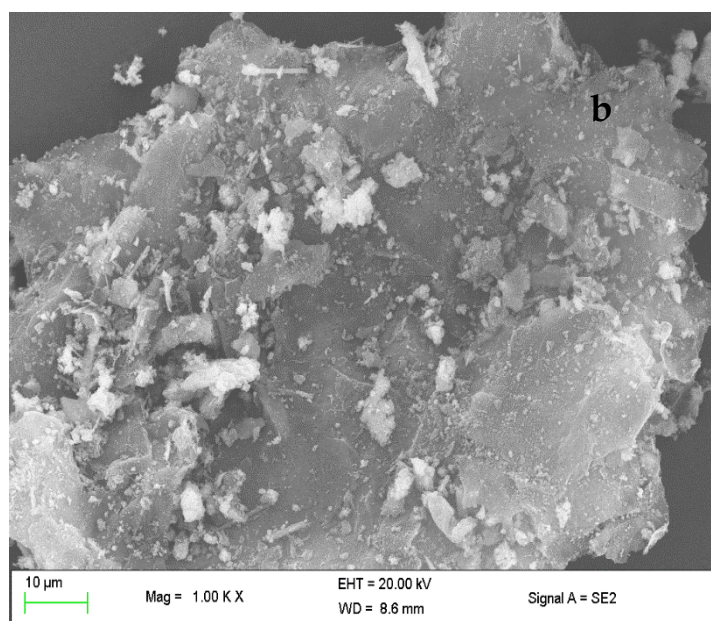
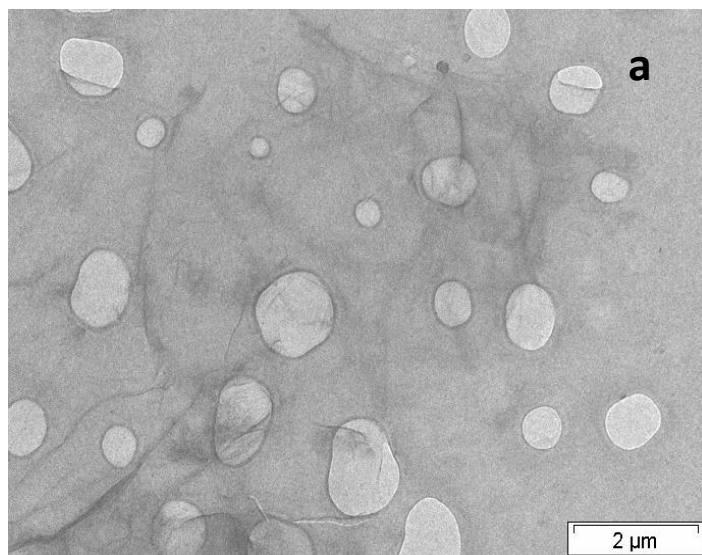


Figure 5.5: Photomicrograph of reduced Graphene oxide (Tour's method) (a) TEM image and (b) SEM.

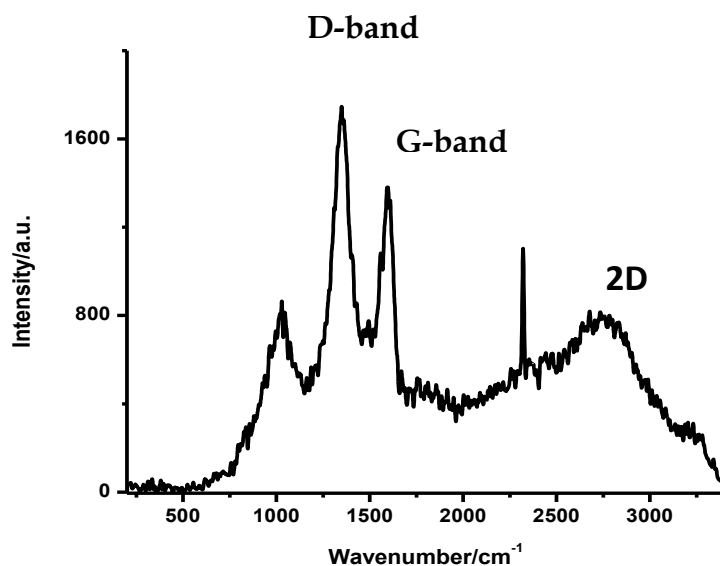


Figure 5.6: Raman spectrum of reduced graphene oxide (from the reduction of graphene oxide from Tour's method).

Thermal Analysis characterization methods used were TGA and DSC, as shown in Figure 5.7. The TGA results show that the degradation of rGO has a multistep degradation pattern. The first degradation from 0°C to 200 °C is associated with the loss of water from the samples. The degradation at 360 °C to 680 °C is associated with the labile oxygenated carbon compounds and the graphene matrix [12 -16]. The DSC curve shows heat absorbed for the moisture loss and in the degradation occurring in the region of 360 °C to 680 °C.

The diffractogram in Figure 5.8 shows that the characteristic peak of graphene is at 26° [4]. The other visible peak was at 10°, which corresponds to the graphene oxide peaks as seen in Figure 5.3. The peak is severely diminished when compared to the graphene peak, which further confirms that the graphene oxide had been reduced to reduced graphene oxide.

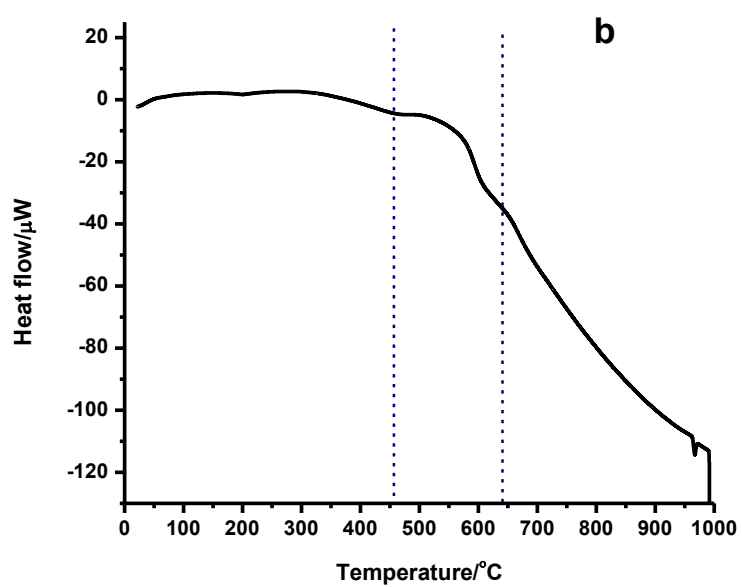
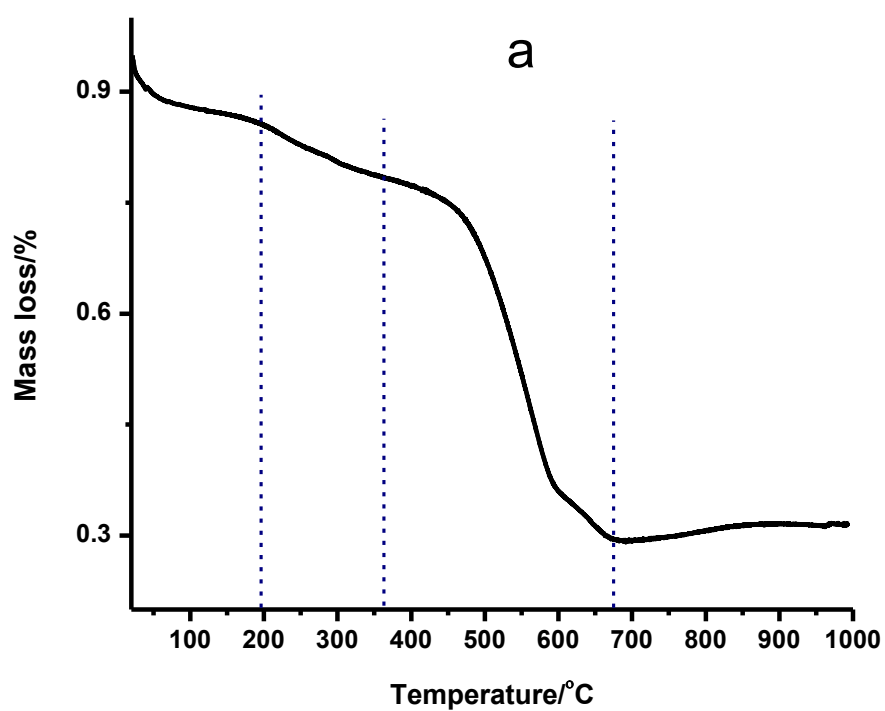


Figure 5.7: Thermal analysis spectra of reduced graphene oxide showing (a) TGA and (b) DSC data.

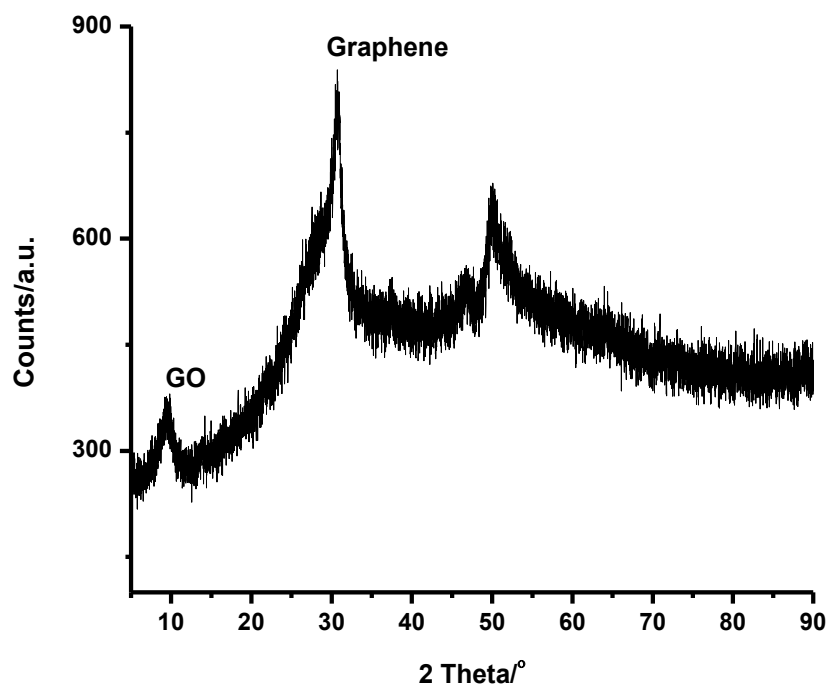


Figure 5.8: XRD spectrum of reduced graphene oxide.

5.1.2. Synthesis of boron doped graphene and nitrogen doped graphene.

The boron doping followed a modified method, which omitted the freeze-drying step [5,6]. The doping was successful, using a thick slurry of graphene oxide and boric acid. The same method was adopted for the synthesis of nitrogen doped graphene replacing boric acid with hydrazine hydrate. The infra-red spectra confirmed the formation of the target samples. The spectrum showed characteristic peaks for nitrogen and boron doped graphene. The nitrogen doped graphene had the peaks C=N and C=C occurring at 2345 and 2115 cm^{-1} , respectively [7-9] as shown in Figure 5.9. The absence of the carbonyl peak at $\sim 1700 \text{ cm}^{-1}$ confirmed the conversion of graphene oxide to nitrogen doped graphene. For the boron doped sample, the IR spectrum shows the characteristic peaks at 1120 cm^{-1} B-C and at 3192 cm^{-1} for B-OH [7-9] as can be seen in Figure 5.9. The evidence is further observed in Figure 5.10 which is TEM data with STEM. The figure shows the sample of the TEM, STEM and EDX

data of the samples. The STEM data Figure 5.10 a, b and c, show the mapping of the sample for carbon and nitrogen on the sample. TEM images of N-rGO is shown in (a) which has some wrinkles in the graphene matrix and in (b) which was subsequently used in the STEM mapping. The STEM mapping is shown for carbon in yellow can be seen on the image labelled (c) and red for the nitrogen atoms labelled (d). The EDX of the N-rGO is shown in Figure 5.11. The EDX was used to estimate the amount of nitrogen in the sample which was found to be about 6 %. The EDX and STEM was used for qualitative purposes, it confirmed the doping took place and were successful in creating N-rGO sample. The same was done for B-rGO, TEM image of B-rGO is shown in Figure 5.12 (a) which has some wrinkles in the graphene matrix and in (b) which was subsequently used in the STEM mapping. The STEM mapping is shown for carbon in yellow can be seen on the image labelled (c) and red for the boron atoms labelled (d). The EDX of the B-rGO is shown in Figure 5.13. The EDX was used to estimate the amount of boron in the sample which was found to be about 6 %. The EDX and STEM was used for qualitative purposes, it confirmed the doping took place and were successful in creating B-rGO sample. The EDX data is summarized in Table 5.2.

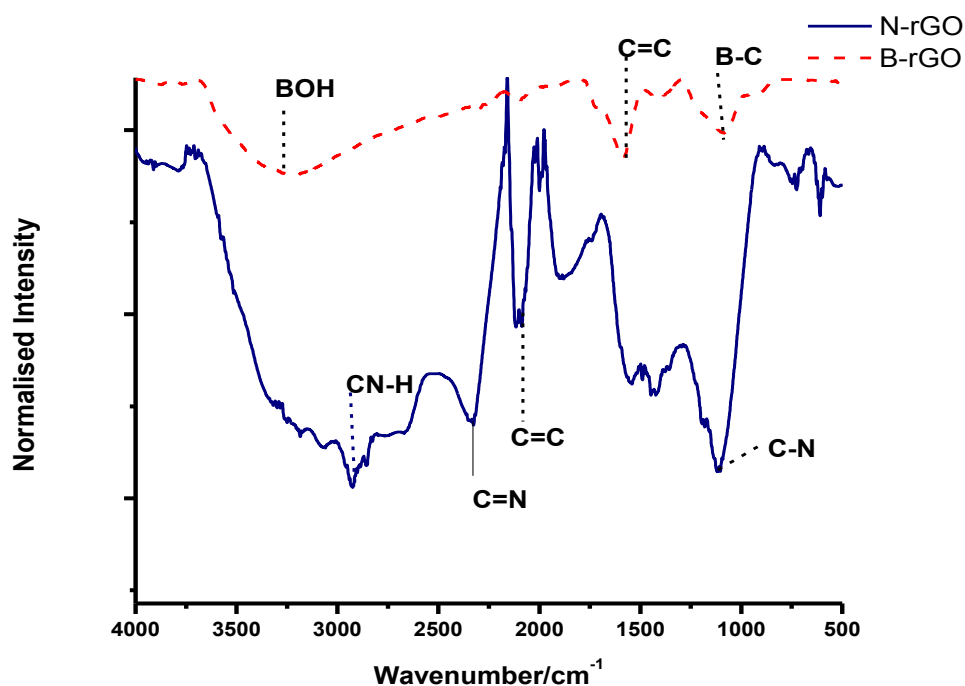


Figure 5.9: Infra-red spectrum of samples B-rGO and N-rGO.

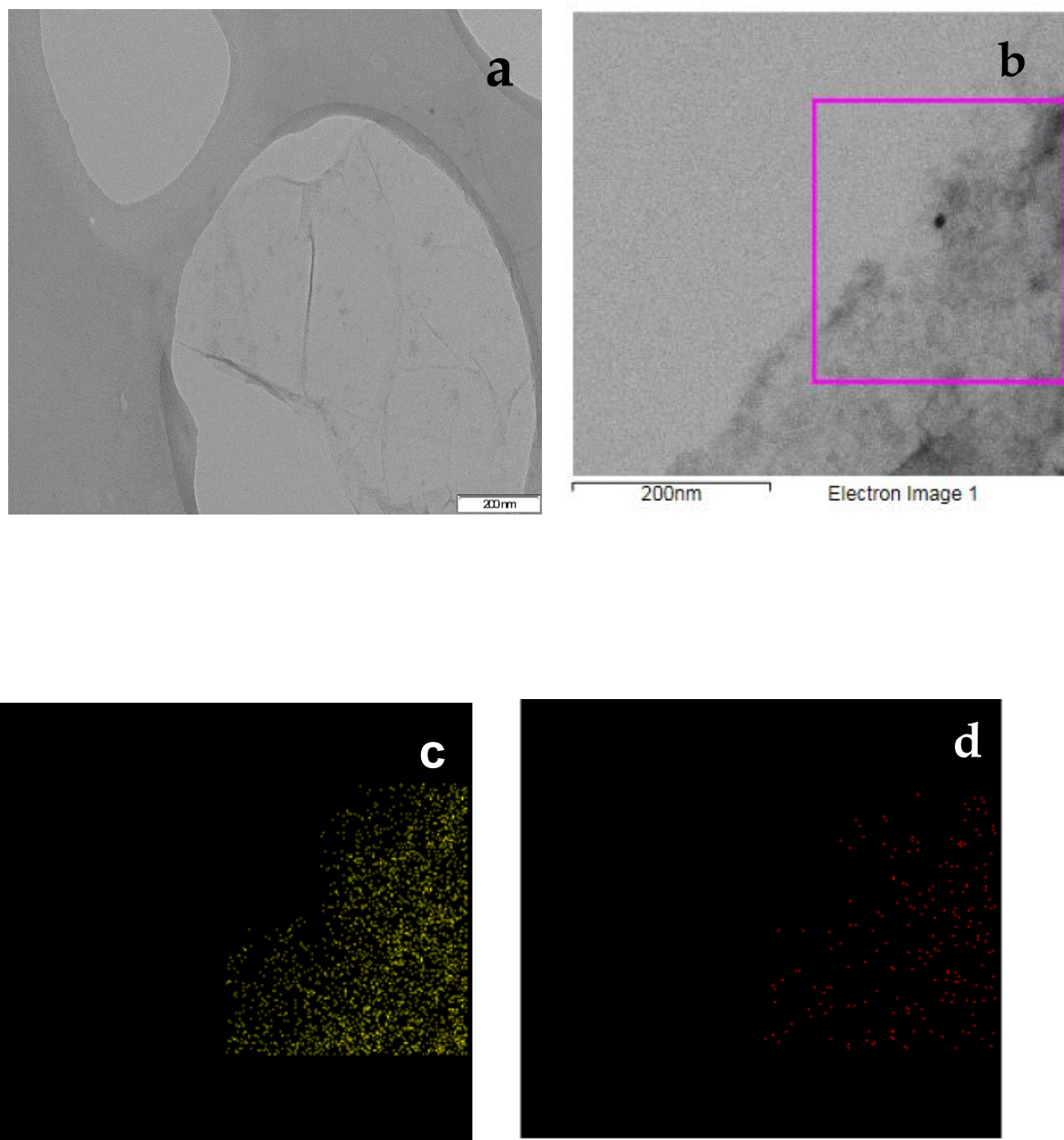


Figure 5.10: TEM image of (a) N-rGO, (b) STEM image of N-rGO, (c) STEM carbon mapping for N-rGO, (d) STEM nitrogen mapping.

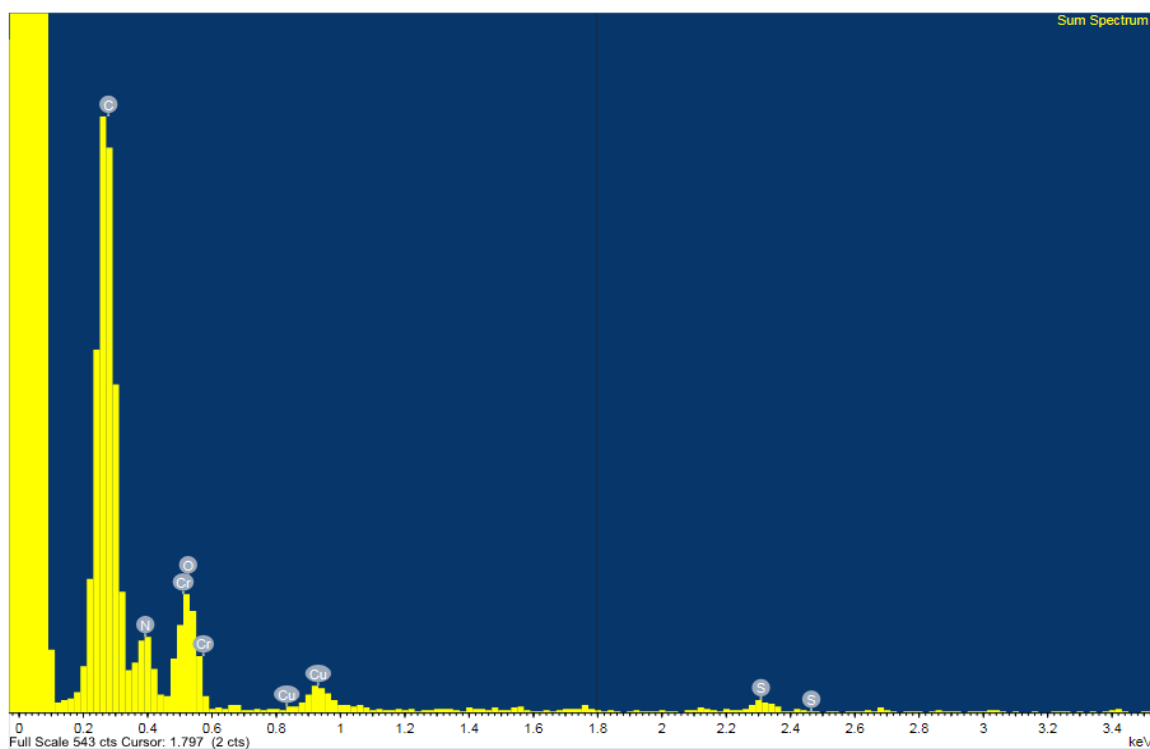


Figure 5.11: EDX of N-rGO, showing existence of carbon, nitrogen and oxygen in the sample.

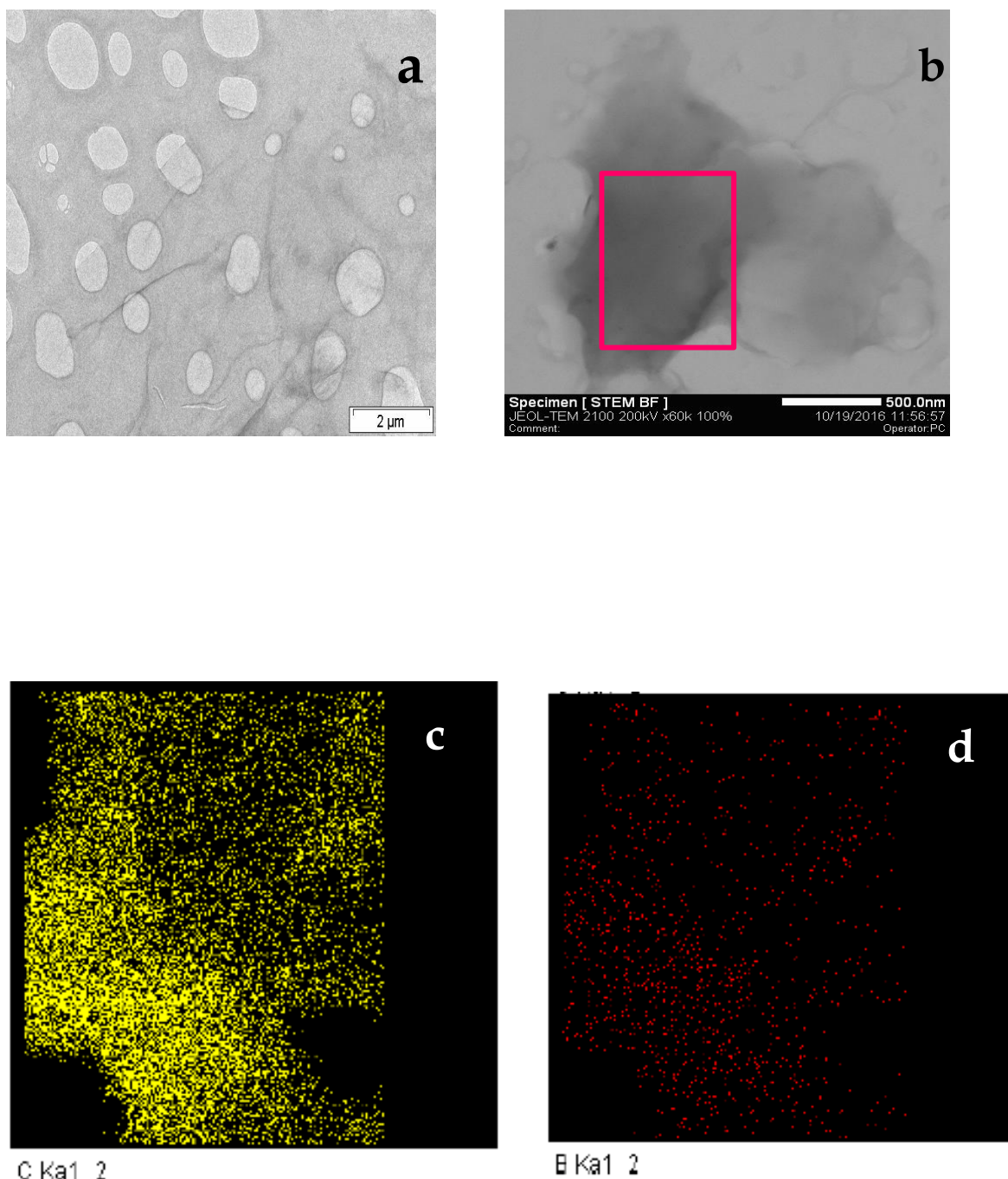


Figure 5.12: TEM image of (a) B-rGO, (b) STEM image of B-rGO, (c) STEM carbon mapping for B-rGO, (d) STEM boron mapping for B-rGO.

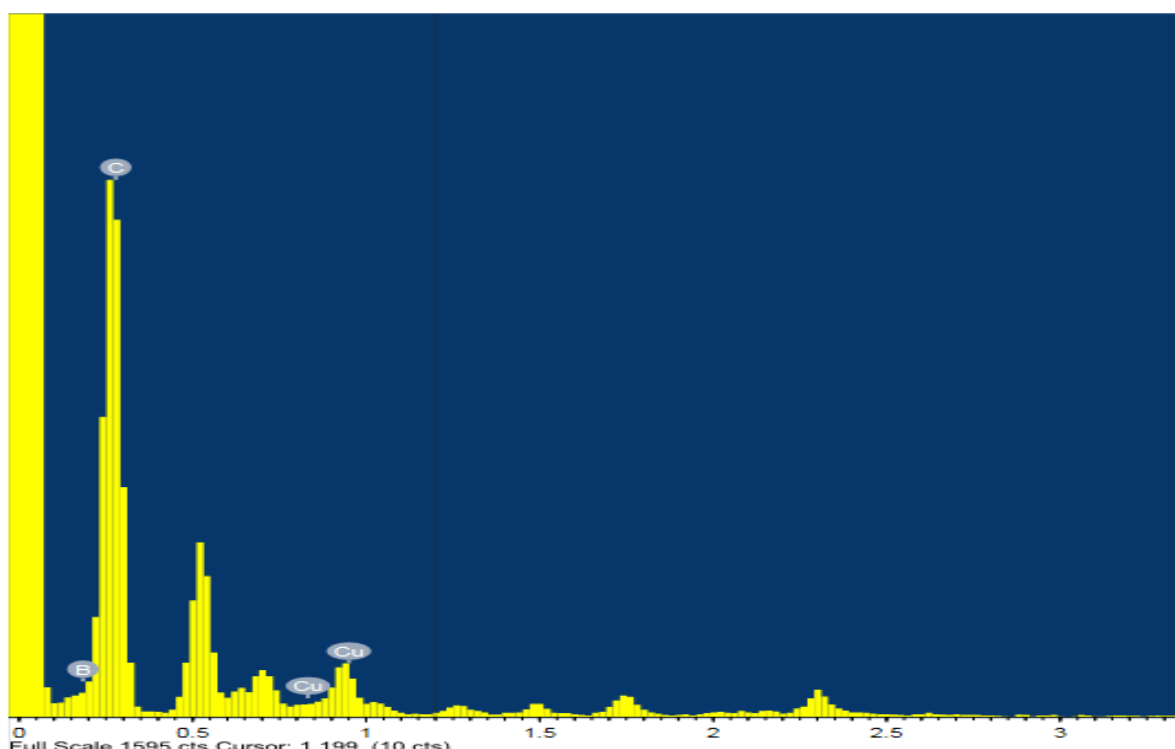


Figure 5.13: EDX of B-rGO showing existence of carbon, boron and oxygen in the sample.

Table 5.2: Summarized data from EDX of boron and nitrogen doped graphene

Sample	Carbon/ %	Oxygen / %	Nitrogen/ %	Boron/ %
N-rGO	89.3	5.3	6.4	-
B-rGO	84.2	10.2	-	6.6

EDX is not an accurate method to determine the amounts of nitrogen in the doped reduced graphene oxide. Therefore, the samples were also analyzed using elemental analysis. Nitrogen doped reduced graphene oxide was found to be 8 % nitrogen. The data from elemental analysis is summarized in Table 5.3. The results from the elemental are more than EDX for the determination of elemental of rGO samples. The more reliable method is XPS in the determination of amount of nitrogen and boron in the doped samples.

Table 5.3: Table of elemental analysis for B-rGO and N-rGO.

Sample	Carbon/ %	Nitrogen/ %	Hydrogen/ %	Oxygen/ %
B-rGO	78.12	0.37	1.77	10.74
N-rGO	77.81	8.12	1.92	12.08

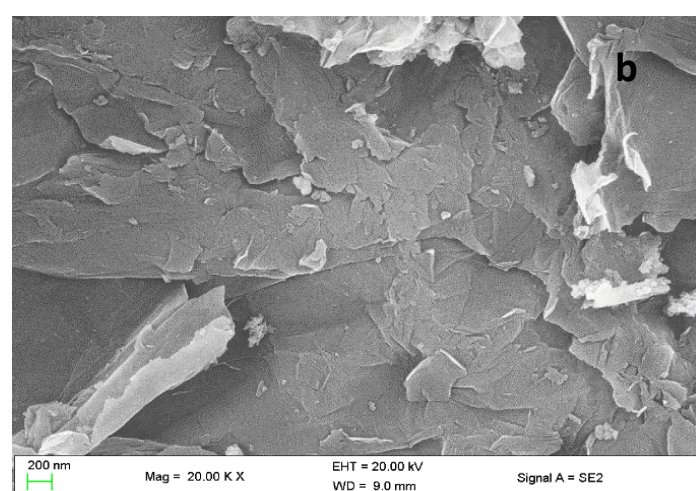
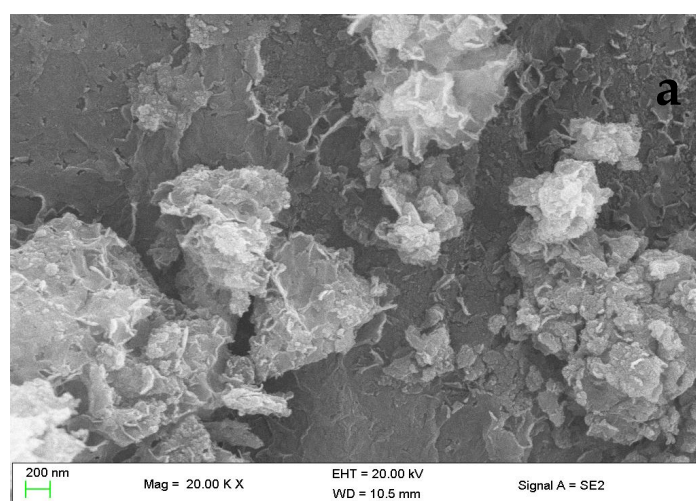


Figure 5.14: SEM images of (a) N-rGO and (b) B-rGO.

A more accurate method for doping determination would have been XPS, which was not available at the time of sample analysis. Thus the amount of boron in the sample B-rGO can be only be speculated to be 9 % from the elemental analysis data. Other methods were however used as an indication that doping took place. The elemental analysis data is more reliable than the EDX, which is more of a qualitative analysis. The other short coming of the EDX is that the analysis is done on the line or region where the X-ray beam is bombarding the sample. This means the analysis data is only region specific which means that the scientific merit to qualify the analysis as a quantitative tools.

Thermal characteristics were measured by TGA and DSC, which are shown in Figure 5.15. Both samples showed the loss of water at 110 °C, which corresponded to a mass loss of 5 %. The nitrogen doped reduced graphene oxide (a) showed a single smooth degradation, indicating that the sample is crystalline like. The sharp peak of the N-rGO on the DSC shows that there is a large endothermic reaction at 550 °C, which corresponds to the decomposition of nitrogen and carbon bonds. For the boron doped reduced graphene oxide sample the endothermic reaction occurs at 600 °C, showing that the nitrogen doped sample is slightly more thermally stable than the boron doped sample. The samples are more stable the reduced graphene oxide, shown in Figure 5.15, which decomposes around 450 °C [8]. The DSC data also confirms that N-rGO is more thermally stable than B-rGO which is shown by the spectra that more energy was needed to decompose the N-rGO sample.

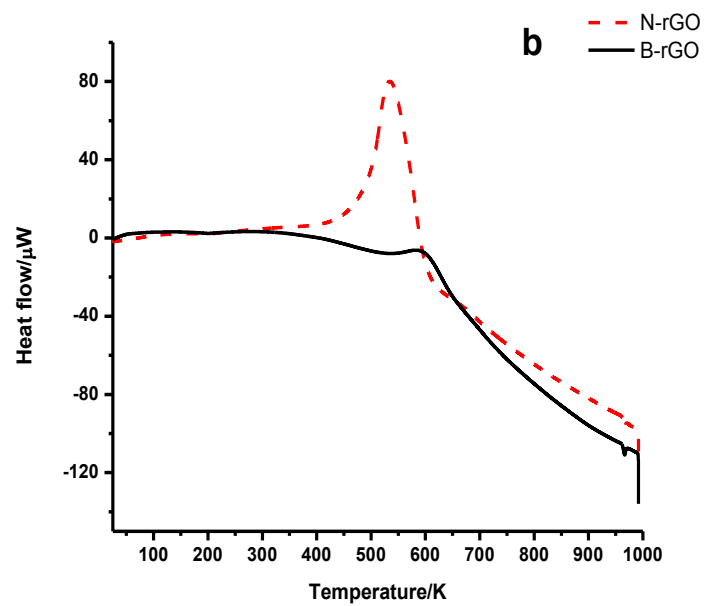
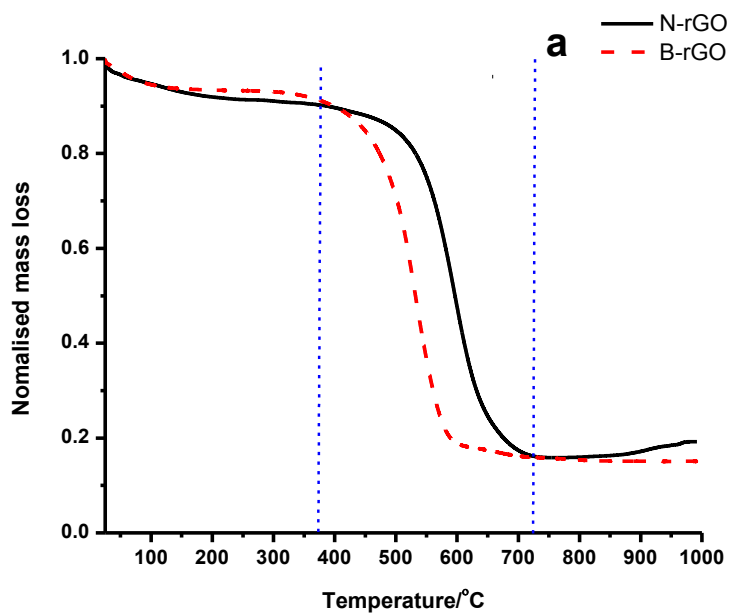


Figure 5.15: Thermograms of doped reduced graphene oxide TG (a) and DSC (b).

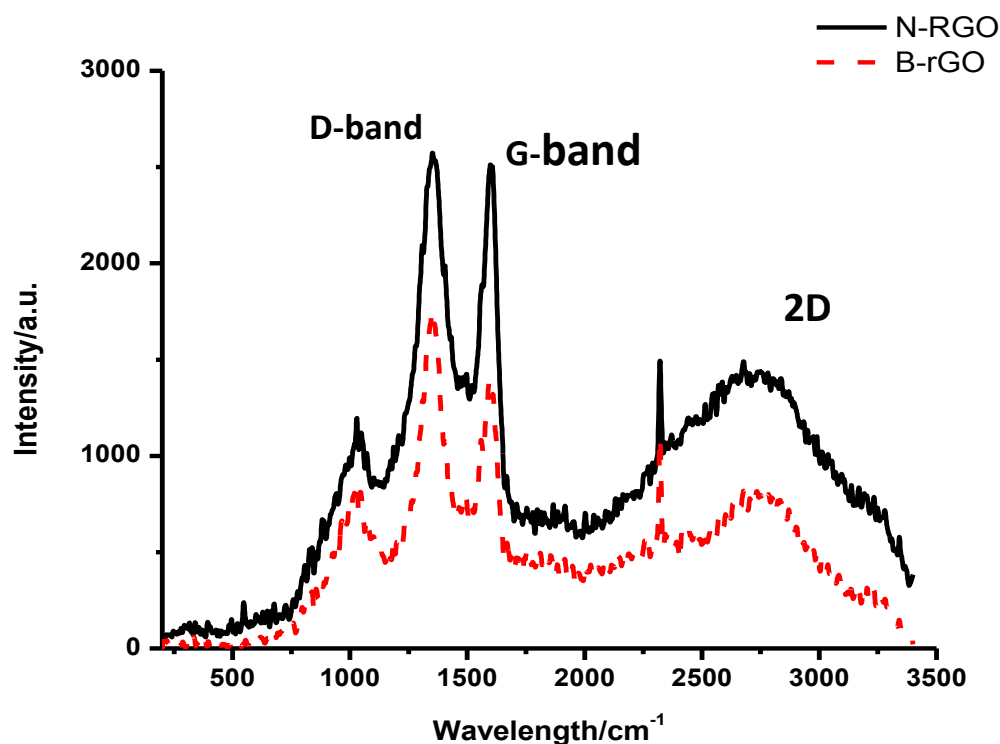


Figure 5.16: Raman spectra of doped reduced graphene.

Raman spectroscopy was also employed to analyze the doped sample and shown in Figure 5.16. Nitrogen doped reduced graphene oxide has D-bands and G-bands, which are close in intensity. The ratios of I_D/I_G in both the spectra were greater than 1, indicating defects and disorder in the graphene structure, which is common in graphene material obtained by the chemical reduction method [5]. The shape of the 2D peak is broad and wide, which is indication that the B-rGO and N-rGO are multilayered. TEM and SEM the nitrogen doped reduced graphene had less wrinkles and folds when compared to the boron doped reduced graphene oxide. The data from Raman spectroscopy is summarized in Table 5.3. The data shows that the samples are multilayered and have a larger degree of folding in the graphene matrix.

5.4: Table of Raman spectroscopy data, D-bands, B-bands and I_D/I_G ratio.

Sample	D band/ cm^{-1}	G band/ cm^{-1}	2D/ cm^{-1}	I_D/I_G
B-rGO	1382	1580	2780	1.22
N-rGO	1360	1600	2680	1.12

The XRD spectra of rGO, B-rGO and N-rGO are shown in Figure 5.17. The spectra had a prominent sharp peak at $\sim 26^\circ$ which is the indication of the formation of reduced graphene oxide. For both B-rGO and N-rGO the spectra shows sharps peaks indicating the sample are more crystalline than amorphous.

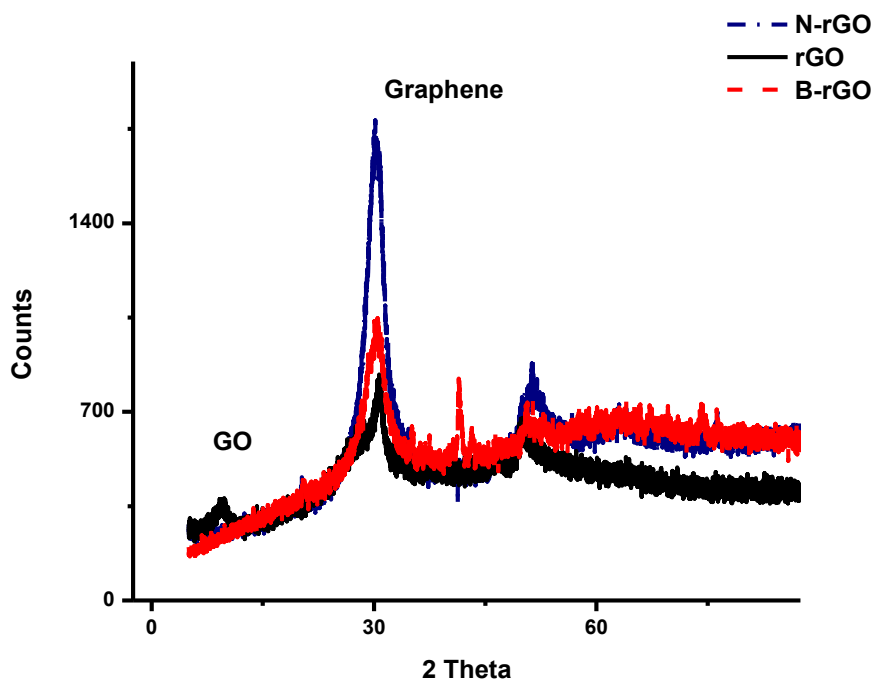


Figure 5.17: XRD spectra for rGO, N-rGO and B-rGO.

5.1.3. Synthesis of Reduced Graphene Oxide nanoparticle composite

The synthesis of composites was adapted from the synthesis of cobalt nanoparticles [11], that is a co-precipitation method, where the graphene oxide is mixed in with the metal salt and reduced together yielding graphene composites. The samples that were synthesized were: cobalt, nickel, and cobalt ferrite nanoparticles graphene composites. The infra-red spectra (Figure 5.18), shows that Ni-rGO and Co-rGO had O-H stretch at $\sim 3250\text{ cm}^{-1}$ and C=O at $\sim 1650\text{ cm}^{-1}$ from stabilizing agent. The stabilizing agents in composing citric acid and poly acrylic acid as stabilizing agent for nanoparticles. The stabilizing agents have OH and C=O functional groups which are seen in the FTIR spectra of the nanocomposites.

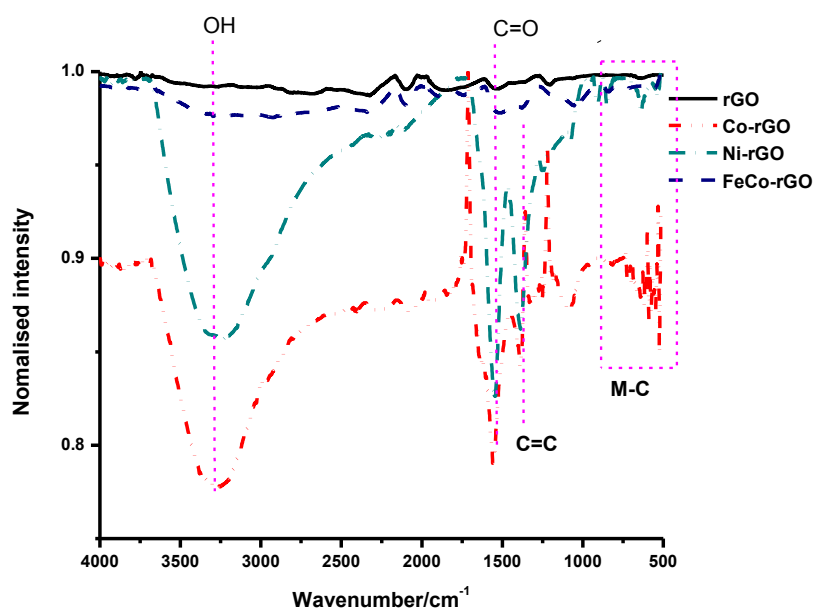


Figure 5.18: Infra-red spectra of rGO, Co-rGO, Ni-rGO and FeCo-rGO.

The samples that had magnetic nanoparticles were taken further in the characterization process. The TEM data in Figure 5.19, shows that the reaction was successful, as metal nanoparticles are observed on the surface of the graphene sheet.

The selected area electron diffraction (SAED) is shown in Figure 5.20 (a) to (c). SAED was done for the Co-rGO, Ni-rGO and FeCo-rGO samples. The spectra have spots which show that the samples were mono crystalline samples [8]. The nanoparticles are colloidal in shape which is due to the manner in which they were produced.

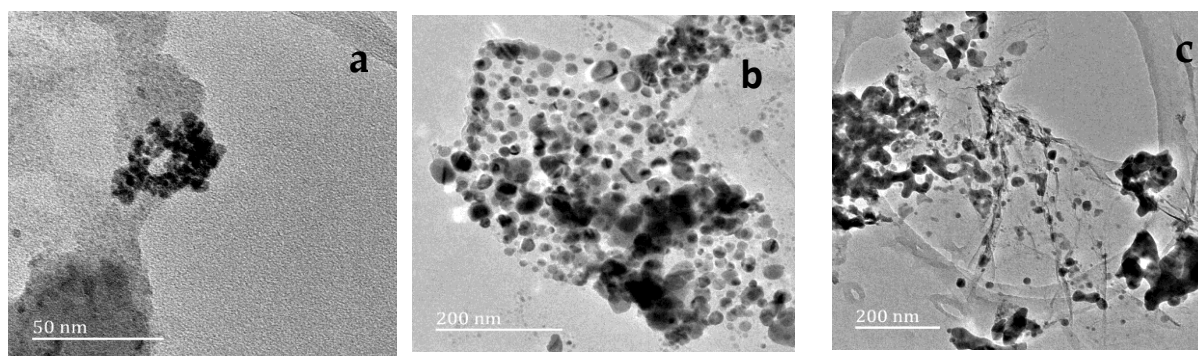


Figure 5.19: TEM images of (a) Co-rGO, (b) Ni-rGO and (c) FeCo-rGO.

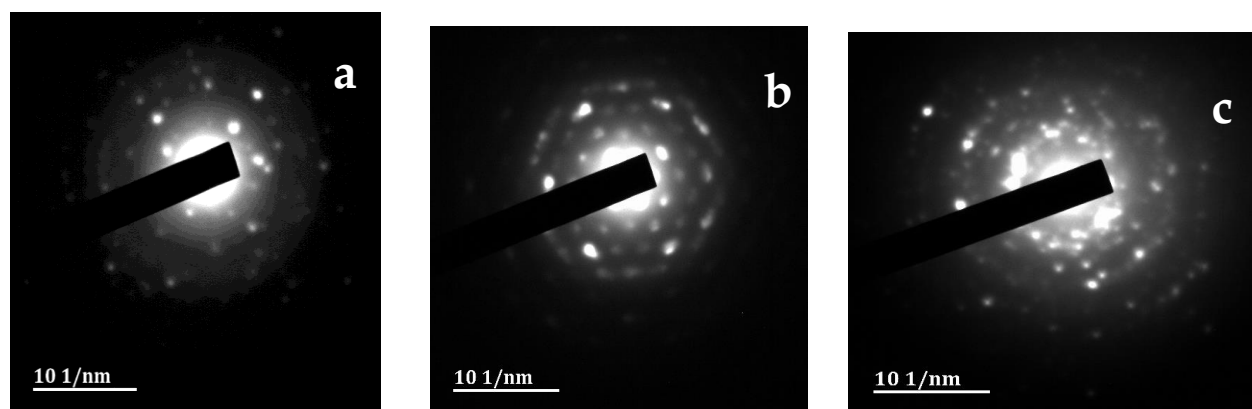


Figure 5.20: (a) SAED pattern of Ni-rGO, (b) SAED pattern of Co-rGO and (c) SAED pattern of FeCo-rGO.

XRD diffractograms of the composites are shown in Figure 5.21. The composite specimens were compared to the rGO spectrum, which had prominent peak at 26° and 49° [9]. All the composite specimens had peaks at 26° from reduced graphene oxide. Ni-rGO had the diffraction peaks at 26° , 45° , 55° and 80° . The peaks at 26° corresponds to the graphene, while peaks at 45° , 55° and 80° correspond to nickel nanoparticles [9,10]. The FeCo-rGO specimen had peak at 26° , 50° and 72° . The peaks at 50° and 72° were due to the ferrite [11]. Co-rGO had a peak at 26° which is due graphene, 47° due to cobalt nanoparticles which is reported [12] and 76° which is unreported.

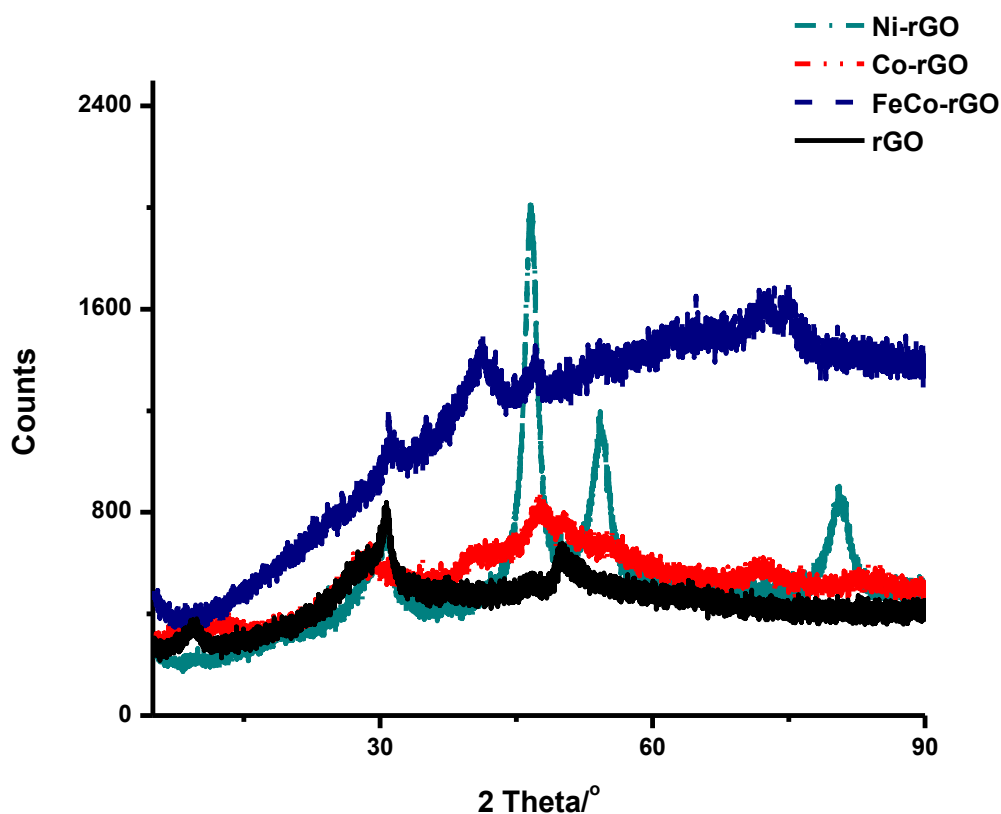


Figure 5.21: XRD spectra of rGO, Co-rGO, Ni-rGO and FeCo-rGO.

The thermal characteristics of the specimens were analyzed using TGA and DSC. The thermograms, shown in Figure 5.22, show the degradation patterns from room temperature to 1000°C . TGA thermograms (Figure 5.22a) shows samples had

'multistep' degradation patterns. The rGO, Co-rGO and Ni-rGO specimens had three predominant mass loss degradations. The rGO specimen had the following mass loss pattern: from room temperature to 150 °C there was a mass loss of 10 % due to water loss (absorbed moisture) and gasses, from 200 °C to 400 °C there was mass loss of 15 %, which was due to the destruction of loosely bound oxygen containing compounds. In the region, 400 °C to 670 °C, there was a mass loss of 45 %, which was due to the destruction of graphene nanosheets [13, 14]. Co-rGO specimen had the following degradation patterns: from room temperature to 100 °C there was a mass loss of 20 %, which due moisture loss. In the region, 150°C to 300°C, there was a mass loss of 10 %, which was the degradation of loosely bound oxygen containing compounds. The 10% mass loss was due to the degradation of graphene nanosheets, between 300 °C to 800 °C.

Ni-rGO had the following mass loss degradation pattern: the first was from room temperature to 100 °C, with a mass loss of 25 % due to water loss. The second degradation was a mass loss of 25%, from 200 °C to 320 °C which was due to the destruction of loosely bound oxygen containing compounds and a mass loss of 25 % from 330 °C to 750 °C was due to the degradation of graphene nanosheets. FeCo-rGO had a 3 step degradation pattern from room temperature to 100°C there was a mass loss of 12 %, which was moisture loss. In the region, 120 °C to 450°C, there was a mass loss of 20 % due to the degradation of loosely bound oxygen containing compounds. In the region, 450 °C to 750°C, there was a mass loss of 25 % due to the destruction graphene nanosheets [13 - 15].

In Figure 5.21b the DSC data shows the endothermic and exothermic processes of the specimens. The Ni-rGO specimen had a pronounced degradation peak at 450 °C which was due to degradation of graphene nanosheets [16]. The rGO specimen also showed a slight bump at 580 °C, which also correspond to the destruction of graphene nanosheets. Co-rGO and CoFe-rGO specimens had slightly observable peaks. The DSC had a broad peak for the endothermic reaction, and it had correlated with the

derivative mass loss showing 5 steps where the decomposition occurred. This showed that the composites were not thermally stable.

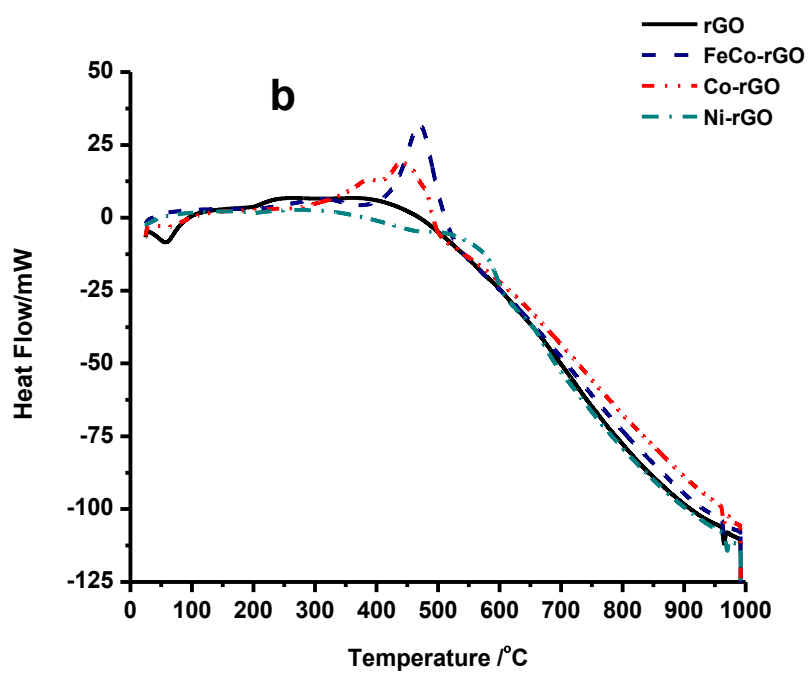
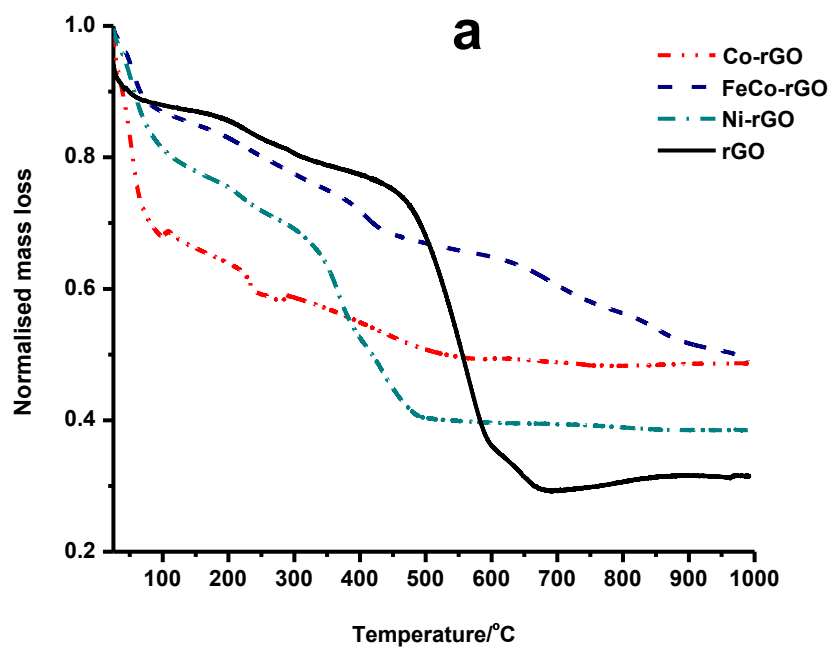


Figure 5.22: Thermal analysis spectra of graphene composites (a) TGA and (b) DSC.

Raman spectroscopy was also employed to analyze the composite sample. It shows the role of the different bands play in the analysis of the morphology of the doped reduced graphene oxide. The Co-rGO and FeCo-rGO have D-bands and G-bands, which are close in intensity. The nanoparticles prevent $\pi - \pi^*$ interactions between the graphene layers. The spectra are plotted in Figure 5.22 and summarized in Table 5.5. The D/G was greater than 1 indicating that the samples had defects in graphene matrix. The 2D peak is prominent and broad indicating a multilayered graphene samples.

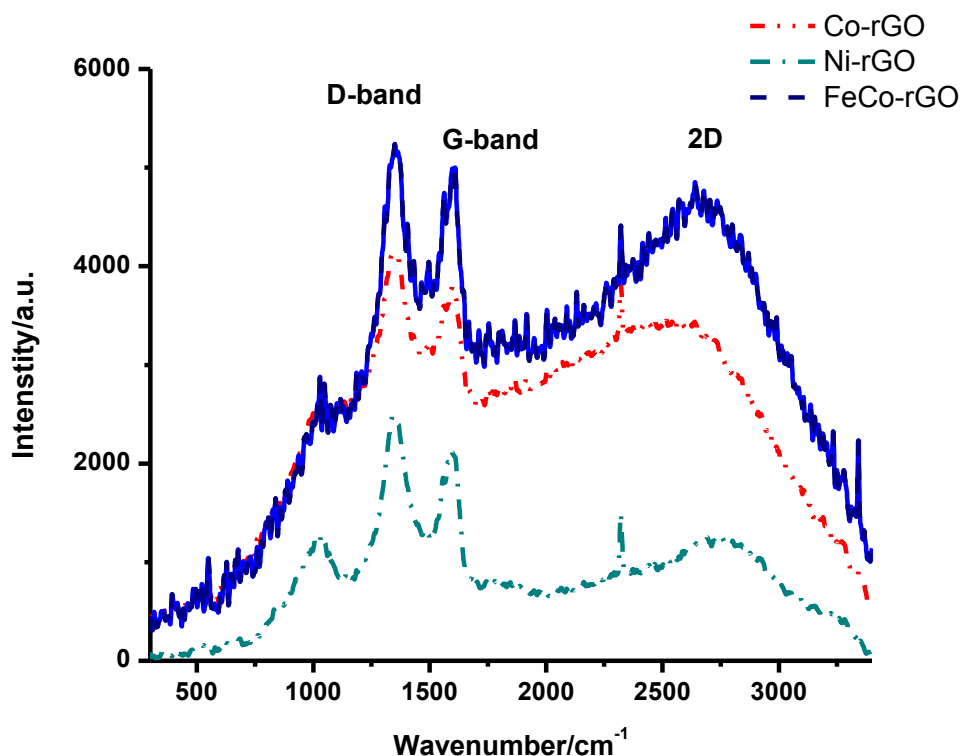


Figure 5.23: Raman spectra of metal nanoparticles reduced graphene oxide composite.

Table 5.5: Table of Raman spectroscopy data, D-bands, B-bands and I_D/I_G ratio

sample	D band/ cm^{-1}	G band/ cm^{-1}	2D/ cm^{-1}	I_D/I_G
Co-rGO	1376	1580	2720	1.22
Ni-rGO	1360	1600	2660	1.32
FeCo-rGO	1368	1590	2640	1.13

5.2. Characterisation of nanoparticles.

The prepared nanoparticles were synthesized for comparison with the graphene nanoparticles composites. The nanoparticles were characterized using TEM and the images are shown in Figure 5.24. The TEM images shows that the nanoparticles are small and colloidal in shape. The Co-NP and Ni-NP are agglomerated. The particle size distributions of the nanoparticles were estimated using image J Software and are shown in Figure 5.25. The particle sizes are widely distributed in all the prepared nanoparticles. The particle size distribution was determined to be between 1.32 nm to 3.25 nm and the average particle size was 1.89 with a standard deviation of 0.531. Ni-rGO had a particle size distribution between 2.23 nm to 18.5 nm and the average particle size was 12.23 nm with a standard deviation of 5.45. CoFeO-NP had the biggest particles and the shapes varied from spheres to rods. The particle size distribution was between 10.4 nm to 42.6 nm and the average particle size was 12.23 nm, with the standard deviation of 10.23. The shapes of the Ni-NP and Co-NP were uniform. The XRD results of the nanoparticles are shown in Figure 5.25 and Figure 5.26. The XRD was used to estimate the particle size of the nanoparticles using the Scherrer equation [23]. The average particle sizes were calculated to be 49.6 nm for

CoFeO-NP and the lattice constant was calculated, using $a = d\sqrt{(h^2 + k^2 + l^2)}$ [22], as $a = 8.39 \text{ \AA}$ which is in agreement with reported values for cobalt ferrite compounds [23]. The average particle size for Co-NP determined from XRD diffraction pattern was calculated to be 5.28 nm, which was an overestimation of the average. It was significantly different from the 2.5 nm which was determined using TEM image and image J software. The image J software also used to determine the average particle size which were determined to be 2.7 nm for Co-NP, 9 nm for Ni-NP and 26.5 nm for FeCoO-NP.

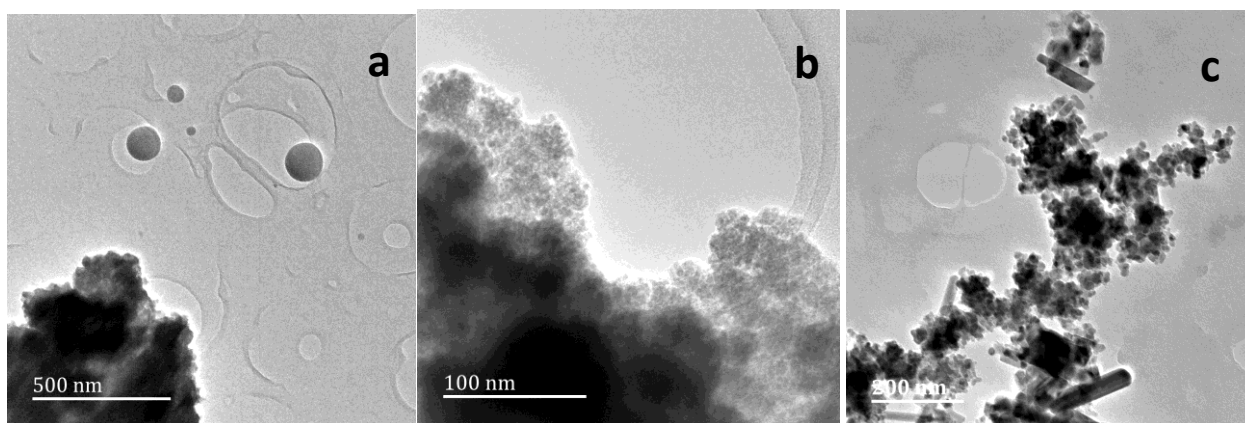


Figure 5.24: TEM images of prepared nanoparticles (a) Co-NP, (b) Ni-NP and (c) CoFeO-NP.

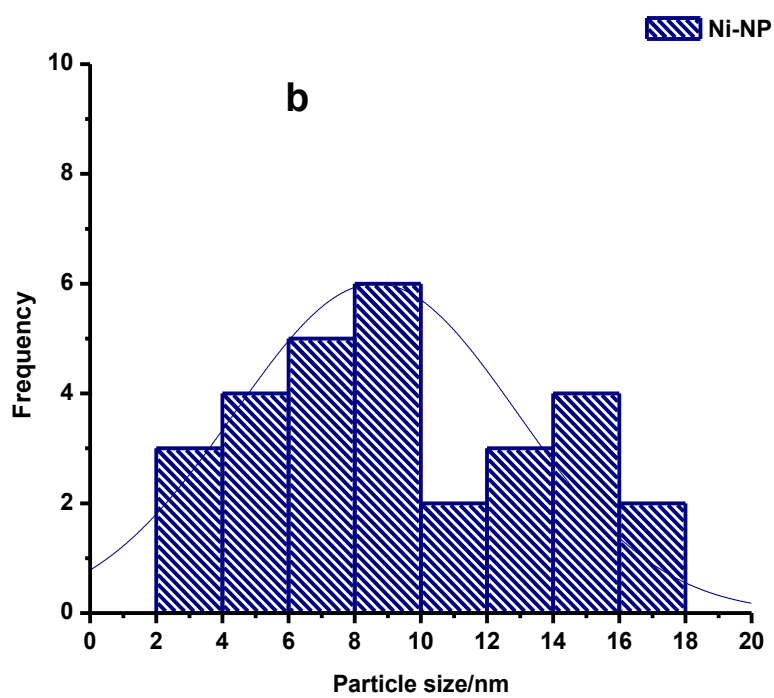
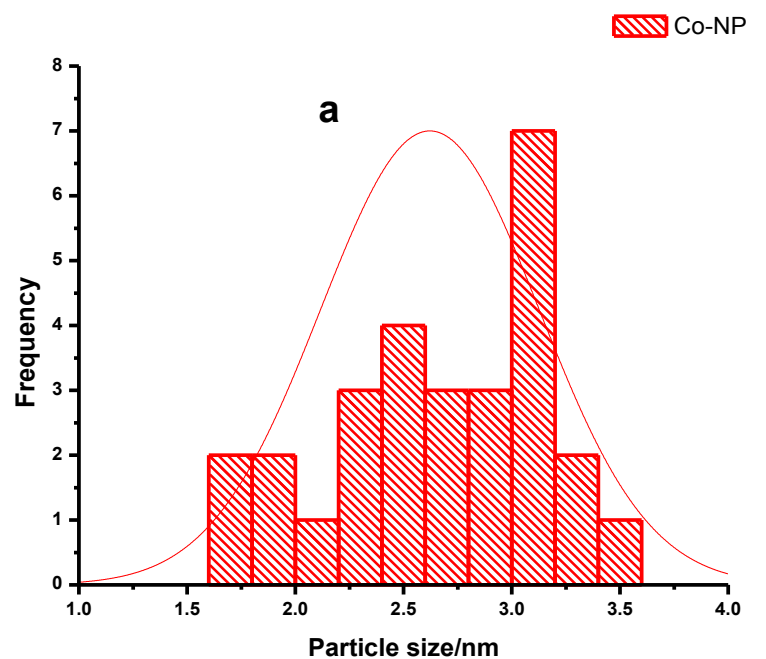


Figure 5.25: Particle size distribution of nanoparticles (a) Co-NP and (b) Ni-NP.

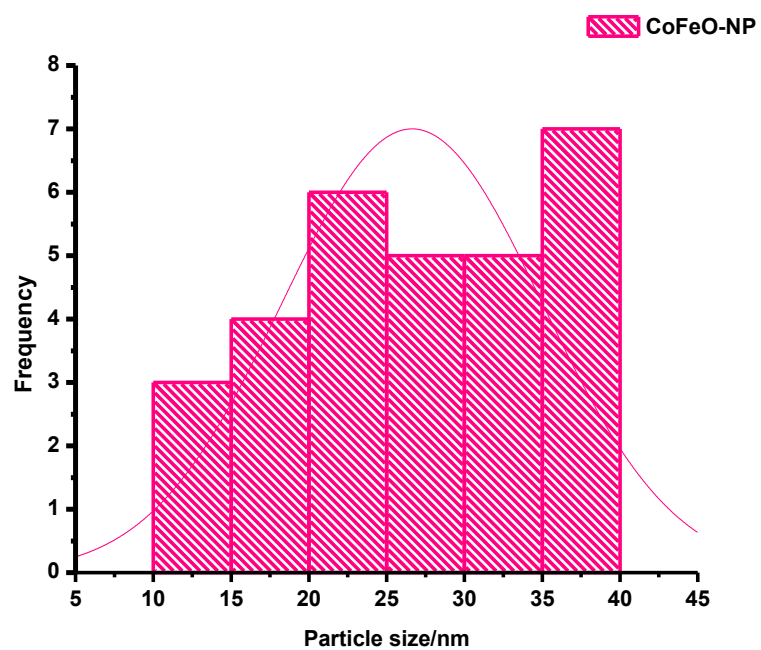


Figure 5.26: Particle size distribution of nanoparticles (CoFeO-NP).

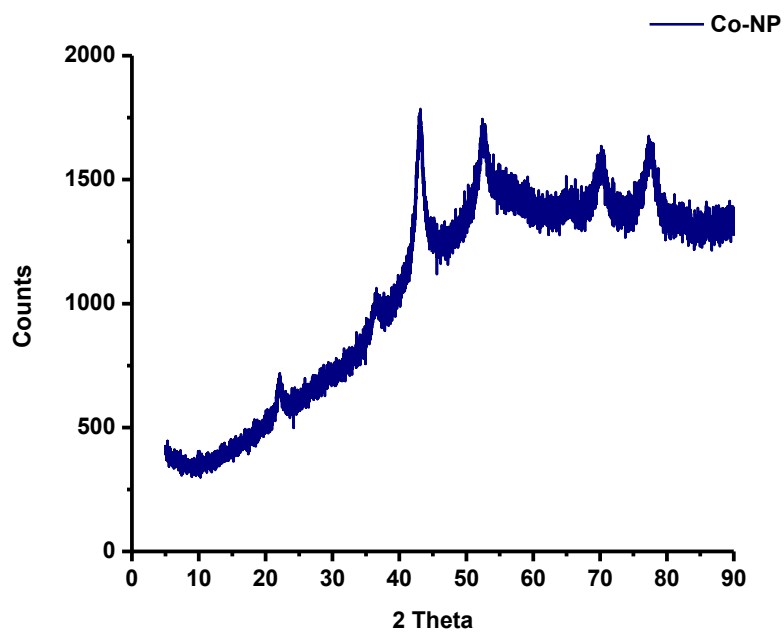


Figure 5.27: XRD diffractogram of Co-NP.

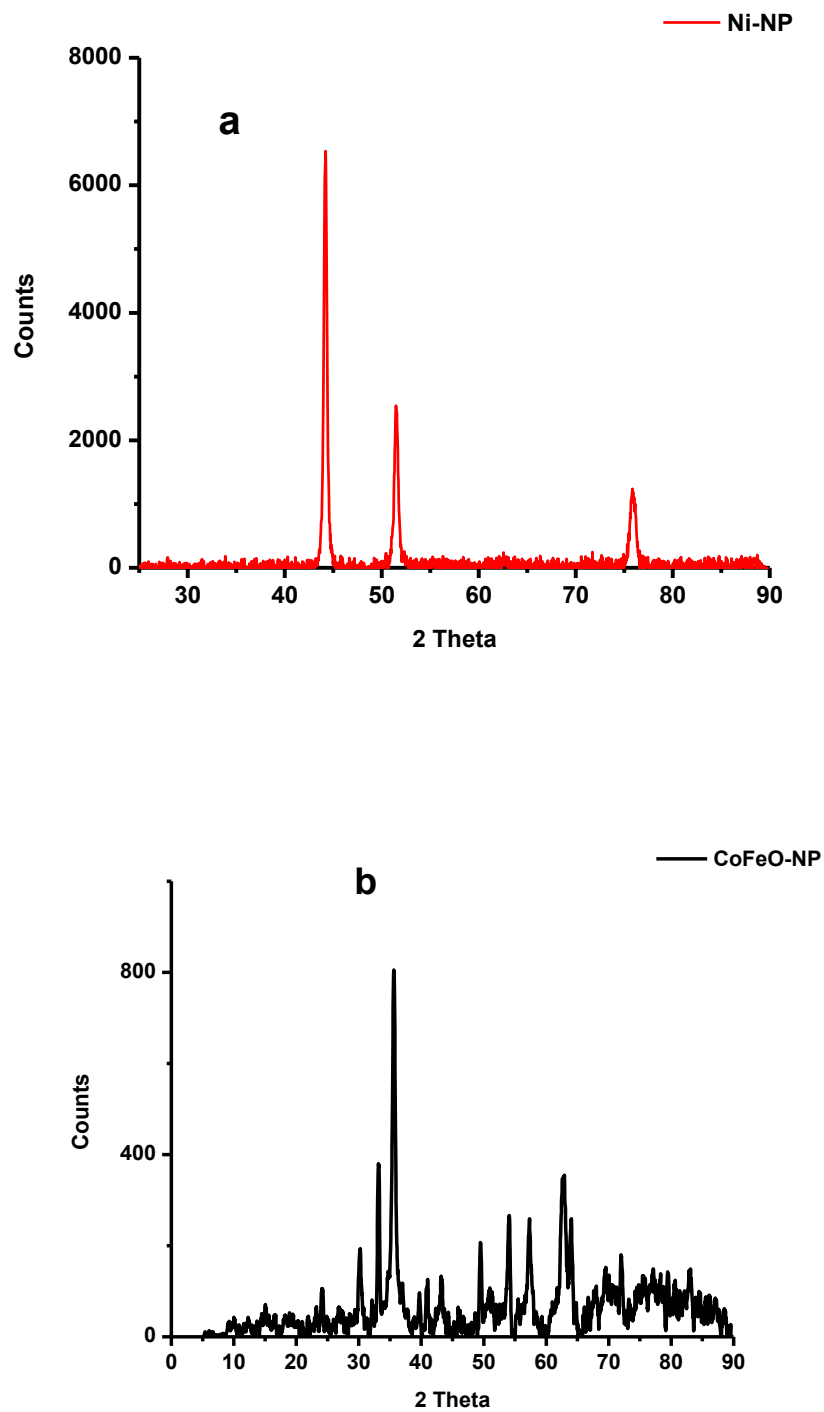


Figure 5.28: XRD diffractogram of (a) Ni-NP and (b) CoFeO-NP

5.3. Magnetisation results.

The magnetization data were recorded on a Vibrating Sample Magnetometer (VSM) and summarized in Table 5.5. The hysteresis loops were recorded at room temperature. The results from the hysteresis loop graphs show that the saturation magnetization (M_s), coercivity (H_c) and remanence magnetization. The graphs, for x and y, are plotted in Figure 5.27. The graphene exhibits a magnetization curve similar to that in literature [16]. It has been theorized that the zigzag pattern on the armchair model of the graphene introduces localized metallicity on the graphene, indicating that graphene has magnetic properties [17, 18]. The data obtained from the VSM results show that the reduced graphene oxide had magnetization of 1.39 emu g^{-1} . The boron doping showed a slight increase in the magnetization compared to the ordinary reduced graphene oxide. The boron has the same atomic radius as carbon atoms, and it can be easily assimilated in the graphene matrix. The effect of the doping is that the boron forms five membered ring which in turn introduces dangling bonds graphene [19]. The dangling bonds introduce high spin population of electrons which increases the magnetic moments of the material. The doped reduced graphene oxide was found to be superparamagnetic (Figure 5.27) and the results were summarized in Table 5.5. Graphene by itself has been reported, from theoretical calculations, to have long range ferromagnetic ordering resulting from point defects [20]. Doping graphene has been shown to introduce paramagnetic properties, due to the dopants neutralizing the point defects that induce ferromagnetism in graphene [21]. In this study, we observed that doping with boron introduced weak superparamagnetic properties to graphene.

Nitrogen doped graphene has been reported to have magnetic properties. It has been reported that in nitrogen doped graphene the magnetization of graphene was affected by the temperature at which the samples were synthesized [17]. The nitrogen doped reduced graphene displayed superparamagnetic response. However, they had higher values of magnetization compared to reduced graphene oxide.

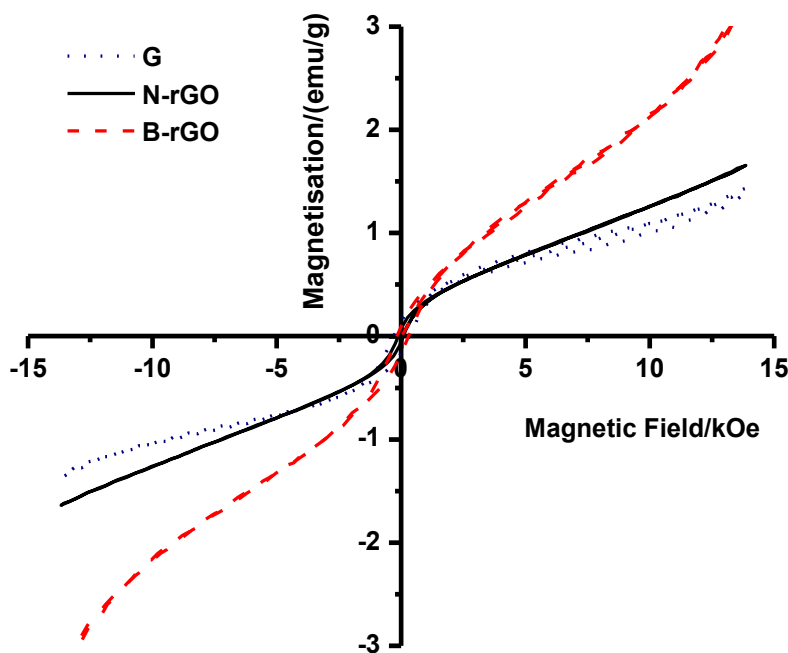


Figure 5.29: Magnetic hysteresis loops of rGO, B-rGO and N-rGO.

The other prepared samples were decorated with magnetic nanoparticles. The data was recorded in Table 5.5. The composite Co-rGO, Ni-rGO and FeCo-rGO are mixture of graphene and superparamagnetic nanoparticles, as explained in Chapter 4 and

shown by Figure 5.30. The nanoparticles are superparamagnetic [22 - 24] as shown in Figure 5.31. The cobalt nanoparticle shown in Figure 5.28 shows typical behavior of superparamagnetic species as the particles are easily attracted to the weak magnet. The prepared composites as shown in Table 5.4, contained nanoparticles which are superparamagnetic. This impacted on the overall magnetic properties.

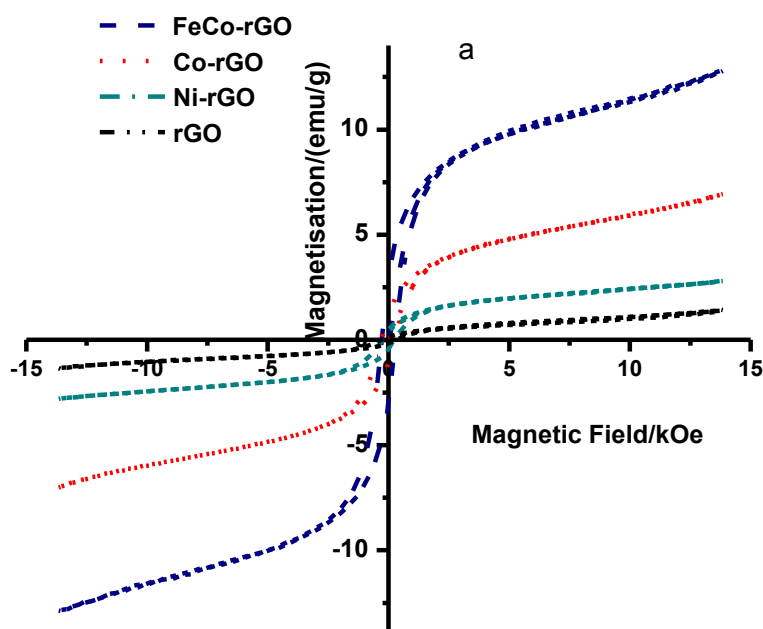


Figure 5.30: Typical magnetic hysteresis loops of samples (a) graphene-nanoparticle hybrids.

The samples Co-rGO, FeCo-rGO and Ni-rGO were still superparamagnetic as confirmed from the VSM data shown in Figure 5.31, and summarized in Table 5.6. The samples had small coercivity, which was confirmed that the samples were soft

magnets. The data shows the trend that the cobalt ferrite nanoparticles had the highest magnetization when compared to other nanoparticles, and the FeCo-rGO had the highest saturation magnetization when compared to other composites. The data showed that when magnetic nanoparticles are anchored to graphene, the nanocomposite has magnetic profile of the nanoparticles and the magnetization is reduced. The nanoparticles were all superparamagnetic as seen from the VSM data. The cobalt ferrite nanoparticles had a slightly larger coercivity, which was expected, since it is reported in literature that ferrite nanoparticles are hard magnetic materials [23]. The composites were found to have to be a mono-crystalline as determined by the SAED spectrum. This structure coupled with the mono dispersity of the nanoparticles on the graphene. This means that the samples can be used in the removal of Cr(VI) in water. The nanoparticles have active sites to adsorb the Cr(VI) ions and with the composites being magnetic. This allows the samples to removed the Cr (VI) and maybe regenerated. This work is detailed in Chapter 6 as an application of the nanocomposites.



Figure 5.31: Photograph showing easily magnetized Co-rGO.

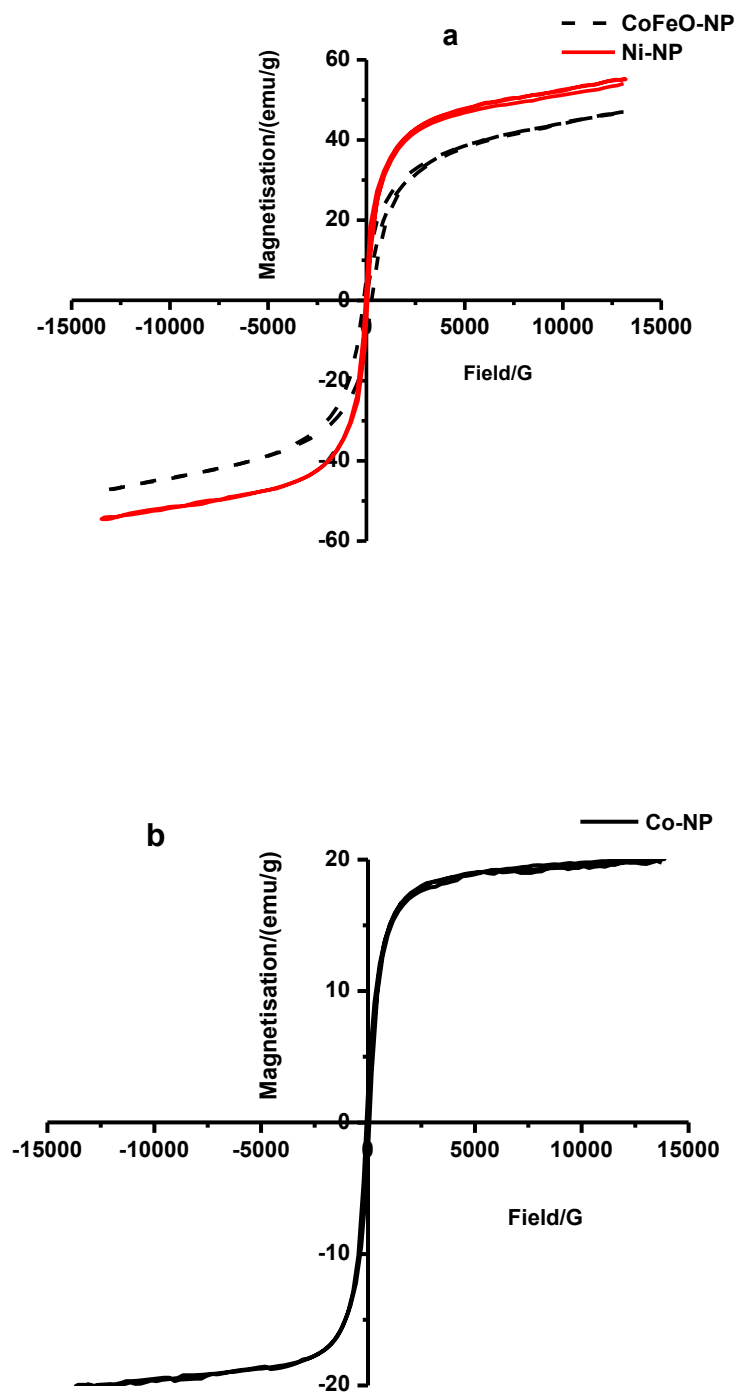


Figure 5.32: Typical magnetic hysteresis loops of samples (a) cobalt ferrite and nickel nanoparticles, (b) cobalt nanoparticles.

Table 5.6: Table of magnetization data for the all the prepared samples.

Sample	Magnetisation/ (emu.g ⁻¹)	Coercivity/T	Remanence magnetization/(emu.g ⁻¹)
rGO	1.34	0.29	1.36
B-rGO	3.32	0.21	3.34
N-rGO	1.61	0.13	1.59
FeCo-rGO	12.54	0.24	12.52
Ni-rGO	3.64	0.26	3.54
Co-rGO	6.82	0.27	6.95
Ni-NP	54.93	0.016	55.25
Co-NP	20.51	0.067	20.45
CoFeO-NP	47.23	0.19	47.08

5.4. Conductivity

The conductivity of samples was measured using the 4-wire measurement technique. The samples were pressed into pellets, each was weighed (0.1 g) and pressed at 4000 psi. The samples were tested under vacuum, where the resistivity was measured from 50 K to 300 K. The data is given in Figure 5.31 and summarized in Table 5.7. The graphene sample had the least change in the resistivity while all the other samples the resistivity decreased with increasing temperature. At room temperature the graphene had a resistivity of $0.819 \times 10^{-3} \Omega \cdot m$, which is slightly higher than reported in literature [27], which in turn has a lower conductivity than reported in literature [26]. The B-rGO sample had the highest conductivity and the lowest resistivity as the

doping of the graphene had improved the conductivity of graphene. The N-rGO also had a conductivity higher than that of graphene. The doping of the reduced graphene oxide has improved the conductivity.

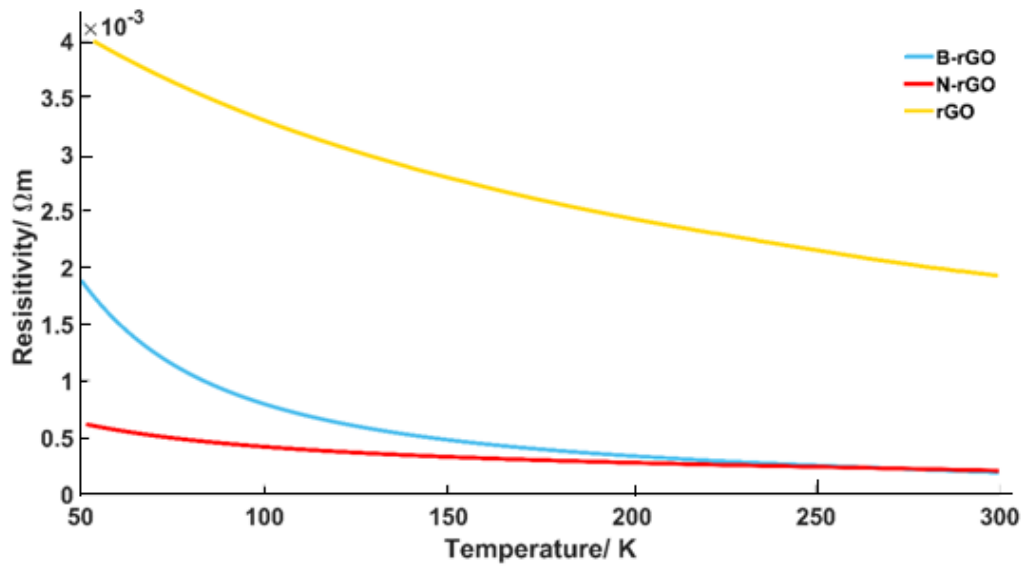


Figure 5.33: Graph of resistivity vs temperature for rGO, N-rGO and B-rGO.

In Figure 5.33 the doped rGO shows a 'freeze-out' response from 50 K to 250 K, where dopant charge carriers leave dopant atoms and become mobile charge carriers.

Table 5.7: Table of resistivity and conductivity for the prepared samples

Sample	Conductivity*/ $S.m^{-1}$	Resistivity/ $m\Omega m$
rGO	532.19	1.879
B-rGO	7245.38	0.138
N-rGO	5376.34	0.186
FeCo-rGO	25477.77	0.03925
Ni-rGO	62695.82	0.01595
Co-rGO	15650	0.06389

The samples anchored with nanoparticles had the highest conductivity. The Ni-rGO sample had the highest conductivity at 6267 $S.m^{-1}$ which was a surprise, since it was close to the reported value 8333 $S.m^{-1}$ [27-28]. The conductivity after the anchoring of nanoparticles improved by a factor of 43 for Ni-rGO and 17 for FeCo-rGO. All the samples that were tested had logarithmic curves in the resistivity vs temperature graphs (Figure 5.33 and Figure 5.34), which shows that the samples are semiconductors. The obtained data showed experimentally that doping and anchoring of metal nanoparticles improved the conductivity of reduced graphene oxide.

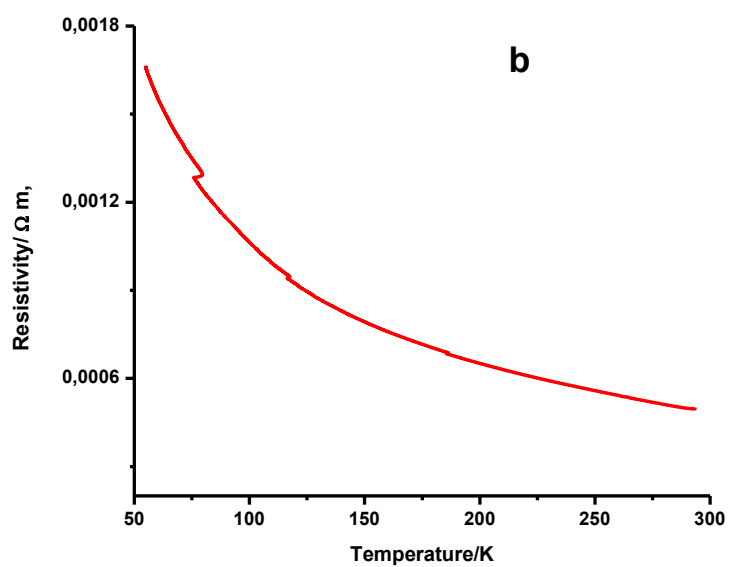
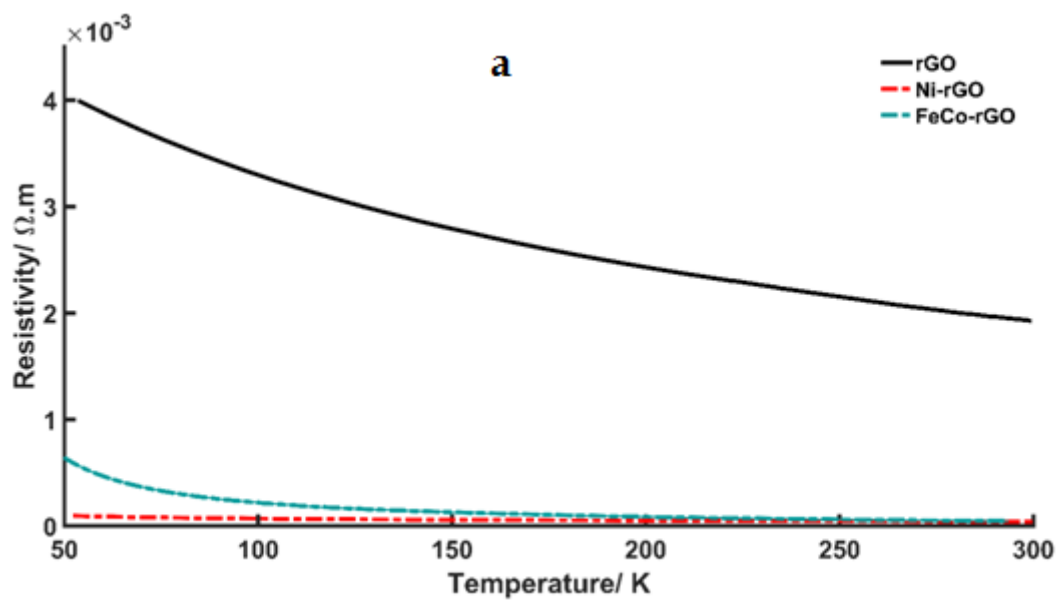


Figure 5.34: Graph of resistivity vs temperature for (a) rGO, Ni-rGO and FeCo-rGO and (b) Co-rGO

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Chapter 6: Removal of Cr(IV) from Aqueous Media

Chapter 6: Removal of Cr(IV) from aqueous media.

This chapter serves as a summary of applications of the prepared samples. The focus will be on the magnetic nanoparticle reduced graphene oxide composites. The availability of equipment allowed for the application in water treatment for the removal of heavy metal ions. The method is a relatively simple process, whereby the composite is separated from the solution with the aid of a magnet and the filtrate is collect for analysis. The high surface area in reduced graphene and nanoparticles imparts the application as sorbent material, as this chapter explores.

6.1 Removal of Cr (IV) from aqueous media using Co-rGO.

6.1.1. Introduction

Chromium is an element that is widely used in several different industrial applications such as metallurgy, electroplating, pigments and wood preservation [1-3]. Trivalent chromium (Cr (III)) ions are a micronutrient in biological systems, which play a pivotal role in glucose levels normalization, metabolism of lipids and steroid regulation [3]. Cr (VI) is a largely toxic carcinogen. Being in the hexavalent state it serves as a strong oxidizing agent to return to the trivalent state. In living cells hexavalent chromium forms free radicals in the form of reactive oxygen species, which damages DNA and oxidative stress in cellular activities [4]. Hexavalent chromium is introduced to water systems, by human industrial activities. This is catastrophic in environmental systems as it kills flora and fauna. Most plants do not have a proper and specific transport system for chromium. It interferes with the carrier channels for essential micronutrients which in turn alters germination processes, photosynthesis and other metabolic pathways [4]. Cr (VI) is highly toxic to humans and has adverse effects on human health. Cr (VI) is a hindrance to human health, because it blocks metalloenzymes systems, which carry out metabolic functions including

mitochondrial function [5]. Other effects of Cr (VI) is that it poisons the liver and kidneys through ingestion of contaminated water or food [5]. Cr(VI) is also a carcinogenic agent which alters the DNA transcription process [6]. The Environmental Protection Agency (EPA) of the United States has recognized Cr(VI) compounds as a top priority toxin. Thus, there is need for an economical method of remediation in order to remove Cr (VI) from fresh water.

Most reported methods of remediation of Cr(VI) include ion exchange, coagulation, precipitation, adsorption and membrane filtration [7–13]. Adsorption has been categorized as an economical method when compared to the other methods. One of the contenders for the adsorption is activated carbon but it has some problems such as fouling. The discovery of carbon nanotubes and graphene has allowed for the expansion of adsorption of Cr(VI) technologies. These materials have been reported to have high surface area, which in turn has a large number of active sites for the adsorption of Cr (VI). Graphene is obtained from the reduction of graphene oxide which is a single graphite oxide sheet [14]. Graphene oxide contains oxygenated functional groups such as hydroxyl, epoxide, carbonyl and carboxyl groups. Graphene generally has slow adsorption kinetics of Cr(VI). Nanoparticles have been studied to remove Cr(VI) from aqueous solution. Nanoparticles have a high surface-to-volume ratio, which has been shown to have benefits of fast adsorption kinetics. Magnetic nanoparticles usually have a poor adsorption capacity for Cr(VI), because due to the agglomeration of the nanoparticles [15]. The combination of the nanoparticles with reduced graphene oxide improves the dispersion of the nanoparticles. The adsorption of Cr(VI) on reduced graphene oxide decorated with magnetic nanoparticles occurs via electrostatic interaction [16]. The nanoparticles Fe_2O_3 are ferromagnetic allows for the formed Fe_2O_3 reduced graphene oxide nanocomposite (Fe_2O_3 -rGO) to be easily removed using a hand held magnet. The ease of separation allows the nanocomposite to be reusable. Fe_2O_3 -rGO with the adsorbed Cr(VI) is ultra-sonicated in a solution of pH 9 to remove the adsorbed Cr(VI) from Fe_2O_3 -rGO [15]. In this study cobalt nanoparticles on reduced graphene oxide nanocomposite (Co-rGO) was used in the removal of Cr(VI) from aqueous solutions. Cobalt nanoparticles are superparamagnetic, and when conjugated with reduced

graphene oxide, the composite become a weak ferromagnetic substance. The composite can be easily attracted to a hand held magnet. It also has a high surface area, which can be applied in the adsorption of pollutants in aqueous media. The cobalt nanoparticles are well dispersed in the matrix of the reduced graphene oxide. This ensures a large number of active sites for adsorption of Cr(VI). This makes the Co-rGO an effective adsorbent for Cr(VI). The ferromagnetic nature of the Co-rGO allows the adsorbent material to easily separate from samples containing Cr(VI) ions. The Co-rGO was selected as a mono metallic and non-metal oxide nanoparticle graphene composite to be used in the removal of Cr(VI) ions. This was reported before on Ni-rGO composites, but it catalyzed the reduction of Cr(VI) to Cr(III). In this experiment the emphasis is on the removal of the Cr(VI). The Co-rGO is the first monometallic nanoparticle graphene that was used for removal of Cr (VI) from aqueous media. The Co-rGO was characterized using XRD, TEM, Raman and IR. The ability of Co-rGO as sorbent material for Cr(VI) was evaluated in basic media. The removal efficiency of the Co-rGO was evaluated and the kinetics of the adsorption was also evaluated.

6.1.2. Experimental

6.1.2.1. Adsorption experiments

The adsorption experiments were contained in a series of Erlenmeyer flasks containing a 50 mL solution of Cr (VI) ions. The adsorption tests were conducted in order to evaluate the uptake of the Cr(VI) ions by Co-rGO. Different parameters such as mass of adsorbent, initial concentration, pH, and contact time were evaluated. The Cr (VI) solutions were fashioned from a 1000 mg L⁻¹ standard solution. A working solution of 100 mg L⁻¹ was used to create samples ranging from 10 to 80 mg L⁻¹. The mass of the Co-rGO used as an adsorbent was varied from 3 mg to 25 mg to determine the optimal mass for the adsorption of Cr(VI). The pH of the Cr(VI) solutions ranged from 2 to 12, and were adjusted using 0.1 M HCl and 0.1 NaOH. The agitation time

was varied from 30 to 180 minutes. The temperature of Cr(VI) varied from 298 to 318 K. The Co-rGO was separated from the Cr(VI) solution with the aid of a rare-earth magnet. The supernatant was collected, and the remaining heavy metal ion was evaluated using ICP-OES. The removal efficiency (R , %) and the amounts of heavy metal ions adsorbed q (mg.g^{-1}) were determined according to the formula:

$$R = \frac{(C_0 - C_t)}{C_0} \times 100 \% , \quad (1)$$

$$q = \frac{(C_0 - C_e)V}{m} , \quad (2)$$

where R is the removal efficiency of the metals ions, C_0 (mg.L^{-1}) the initial concentration of metal ions, and C_t (mg.L^{-1}) is the concentration of metal ion at time (t), q (mg.g^{-1}) is the amount of metal ions adsorbed per unit amount of adsorbents, $V(\text{L})$ is the volume of adsorbates, and m (g) is the mass of the adsorbents [17,18].

6.1.2.2. Kinetics and Adsorption studies

The kinetics of the adsorption is calculated a using pseudo first-order rate equation (3) [17], second-order rate equation (4) [17] and Avrami equation (5) [18] which are shown below:

$$q_t = q_e (1 - e^{-k_1 t}) , \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} , \quad (4)$$

$$q_t = q_e [(1 - e^{-k_3 t})]^{n_A} , \quad (5)$$

where k_1 (min^{-1}) is the rate constant for the pseudo first-order rate equation, k_2 is the rate constant for pseudo second-order rate equation, k_3 is the Avrami rate constant

and n_A is the Avrami constant. q_e (mg.g⁻¹) and q_t (mg.g⁻¹) are the amounts of Cr (VI) adsorbed at equilibrium and at time (t), respectively.

The adsorption isotherms also relate the amount of the chromate ions adsorbed at equilibrium, as per weight of the adsorbent, q_e (mg.g⁻¹), to the adsorbate concentration also at equilibrium, C_e (mg.L⁻¹). The data was evaluated using three isotherms equations, which were Langmuir, Freundlich and Lui. The Langmuir model [18], Freundlich [19,20] and Liu model/equations, are given below.

Langmuir:

$$q_e = \frac{b q_m C_e}{1 + b C_e}, \quad (6)$$

where q_m (mg.g⁻¹) and b are Langmuir constants related to the adsorption capacity and the energy of the adsorption.

Freundlich:

$$q_e = K_F C_e^{1/n}, \quad (7)$$

where K_F , is the adsorption capacity and n is the adsorption intensity.

Lui:

$$q_e = \frac{q_m (K_L C_e)^{n_L}}{1 + (K_L C_e)^{n_L}}. \quad (8)$$

where K_L , is the adsorption capacity, C_e is equilibrium concentration and n_L is the dimensionless exponent of the Lui equation. The statistical evaluation of the data is obtained, using the determination coefficient R^2 and standard deviation SD .

6.1.3. Results and Discussion

6.1.3.1. Synthesis and Characterization.

The characterization of the Co-rGO, using FTIR, XRD, TEM and TGA has been discussed in chapter 5.

The Co-rGO surface area was determined using adsorption and desorption of nitrogen gas, using the BET model shown in Figure 6.1. The specific surface area was determined to be $92 \text{ m}^2.\text{g}^{-1}$. The Barret-Joyneer-Halenda (BJH) analysis was used to determine the pore volume of the Co-rGO. The pore volume was found to be $0.0284 \text{ cm}^3 \text{ g}^{-1}$ with a pore diameter of 4.5 nm .

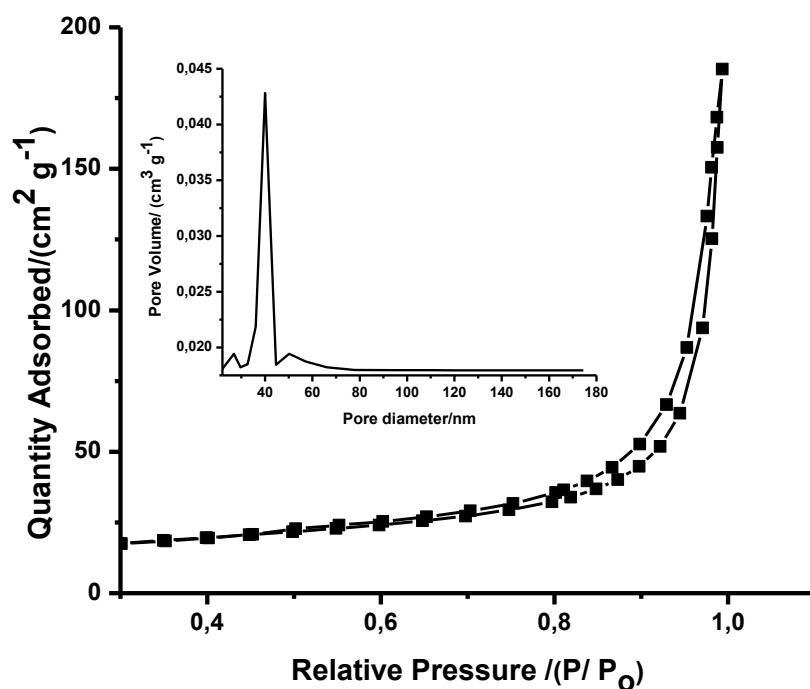


Figure 6.1: BET analysis of Co-rGO.

6.1.4.2. Removal of Cr (VI) in water.

The removal of the chromate ions in water is shown in Figure 6.2. The figure shows (a) Cr(VI) solution before removal, (b) Cr(VI) solution with Co-rGO before 3 hours had lapsed and (c) Cr(VI) solution with Co-rGO after 3 hours had lapsed. It was observed that the magnet attracted Co-rGO from the solution, as shown in Figure 6.2(c). The colour of the solution also changed from a dark yellow shown in Figure 6.2 (a) which showed the presence of Cr(VI) ions to a pale/faint yellow as observe in the Figure 6.2 (c), after the removal of Cr(VI) ions by the Co-rGO.

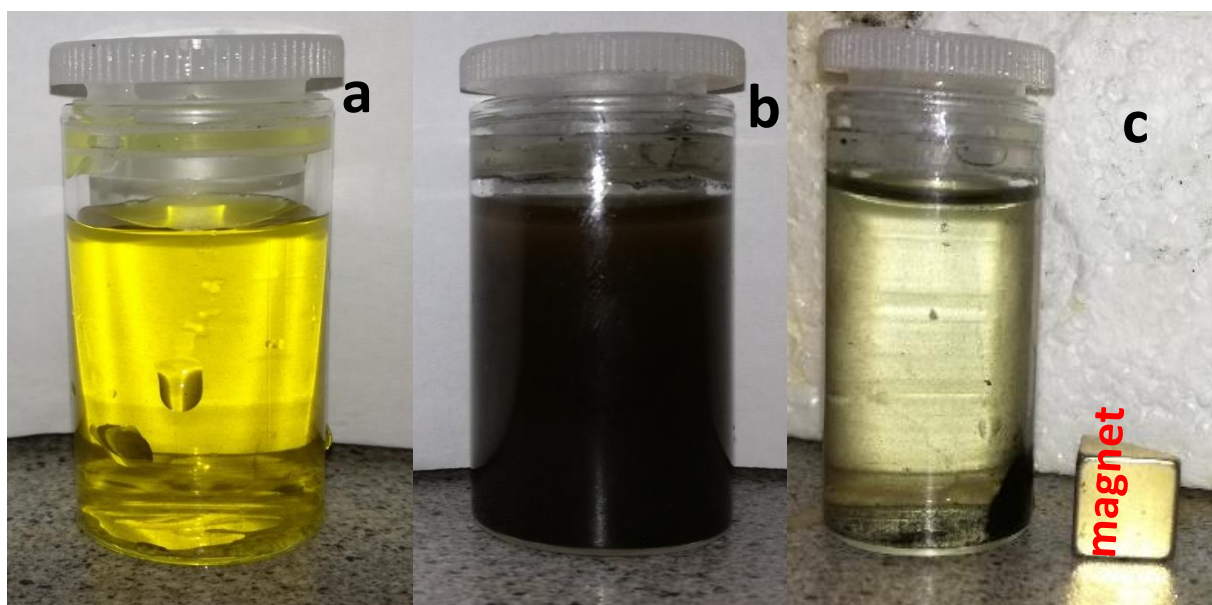
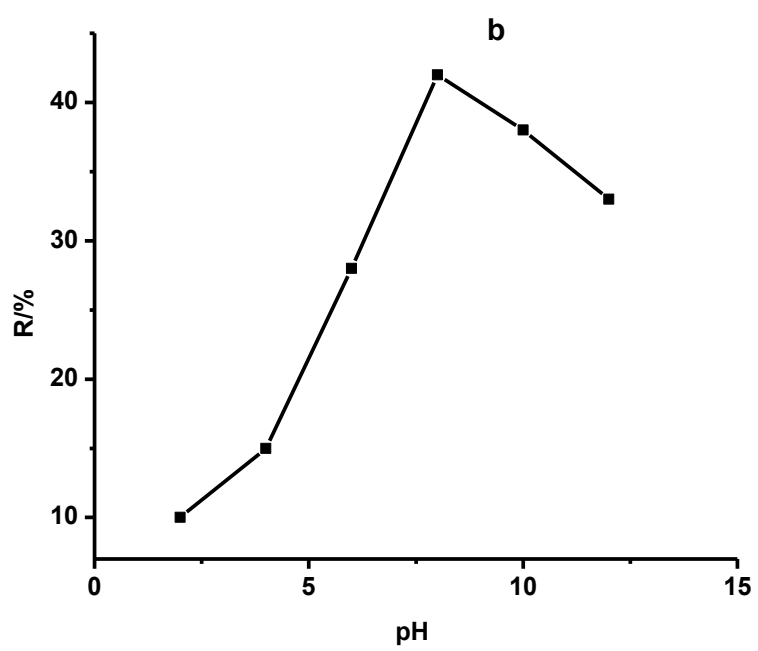
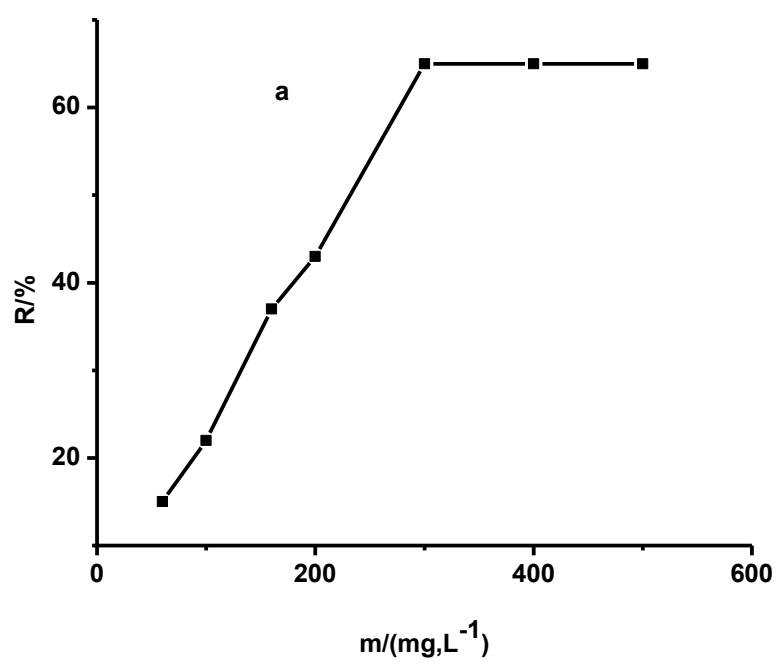


Figure 6.2: Picture showing removal of chromate ion in water using Co-rGO.

The effect of Co-rGO dosage on the removal efficiencies of Cr(VI) was evaluated and shown in Figure 6.3 (a). The concentration of Cr(VI) ions used in this study was 100 mg.L⁻¹. The temperature of the Cr(VI) solution was kept at 298 K and the agitation time was 3 hrs. The dosages of Co-rGO were 80, 100, 160, 200, 300 and 400 mg.L⁻¹, respectively, which adapted from reported method [10-12]. The results showed that

the adsorption efficiency of Co-rGO increased with increasing dosage of Co-rGO and it started to plateau at 65 % removal efficiency, as shown in the Figure 6.3 (a). The dosages of 80, 100, 160 and 200 mg L⁻¹ had removal efficiencies of 15, 23, 37 and 43%, respectively. The pH of the solution has been recognized as an important parameter in controlling the adsorption process [18]. The effect of pH on the removal efficiency of Cr(VI) was evaluated and the results are shown in Figure 6.3 (b). The pH of the Cr(VI) solution was in the range of 2 to 12. It was observed that at low pH the removal efficiency was low but the increase in pH saw a rise in the removal efficiency. At a pH of 8 the highest removal efficiency of 40% was achieved. Further increases in the pH beyond 8 saw a decrease in the adsorption efficiency. In basic media the Cr(VI) exists as CrO₄²⁻, which has an affinity for the Co-rGO which is positively charged [19, 21]. At pH greater 8 there is a high concentration of OH⁻ which competes for adsorption with Cr(VI) ions as reported previously [22, 23]. The graphene nanocomposites with metallic oxide nanoparticles remove Cr(VI) efficiently in lower pH because the metallic oxides have an affinity for H⁺ ions [23]. The effect of initial concentration of the Cr(VI) ions was evaluated. The obtained data is shown in Figure 6.3 (c). The data shows the initial 20 mg.L⁻¹ concentration of Cr(VI) with the highest removal efficiency. The removal efficiency decreased with increasing concentration of Cr(VI). This trend was expected because the increase in concentration tends to saturate active sites, which in turn lowered the removal efficiency [24]. The effect of contact time is shown in Figure 6.4 (d). The removal of the heavy metal Cr(VI) ions reached equilibrium at 90 min. The drop in the removal efficiency beyond 90 min was a trend, which was reported on. The heat from evolved the agitation for extended hinders the performance of the Co-rGO as adsorbent material [17-27]. The optimum conditions for adsorption studies were determined from Figure 6.3. It was found to be a contact time of 90 min, a pH of 8, concentration of 20 mg.L⁻¹ and a dosage of 300 mg.L⁻¹.



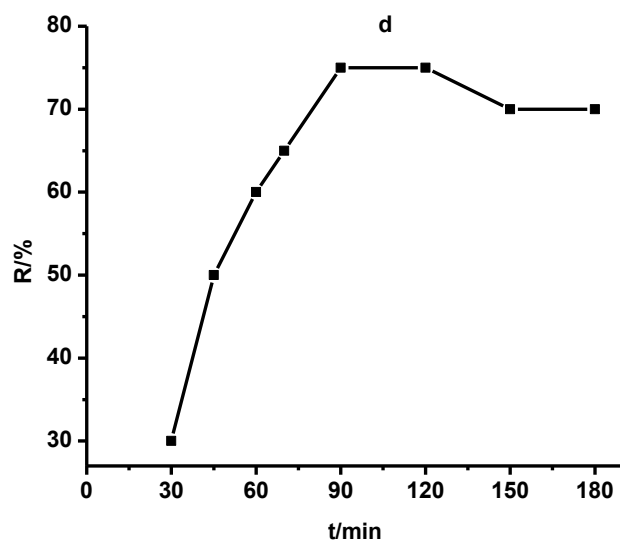
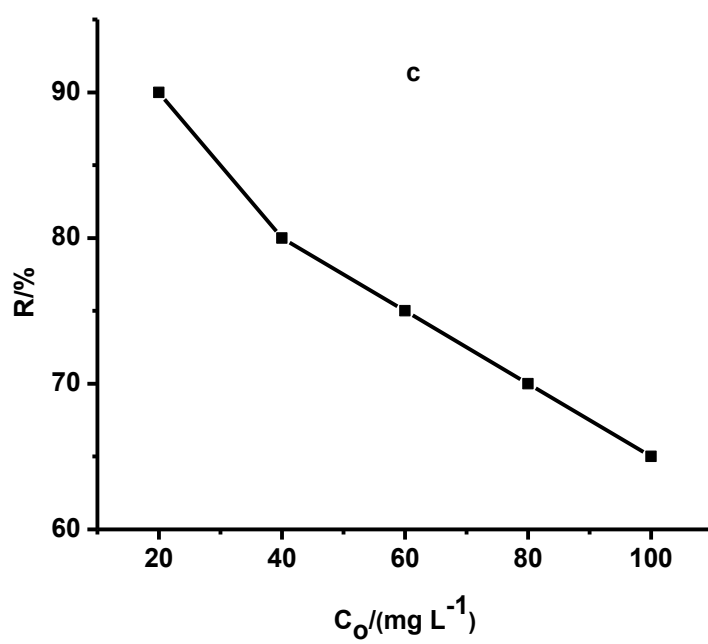


Figure 6.3: Effect of initial parameters such (a) dosage, (b) pH, (c) concentration and (d) contact time on removal efficiency of Cr(VI).

The point zero charge was determined according to a reported method [25]. The potential was measured as a function of the changing pH and is shown in Figure 6.4. The results explain that the surface charge above a pH of 7.35 is positive. The operating pH of Co-rGO in this experiment was 8, which was positively charged and will attract the negatively charged CrO_4^{2-} ions. Figure 6.5 shows the proposed mechanism of how the Co-rGO adsorbs the CrO_4^{2-} through positively charged cobalt nanoparticles.

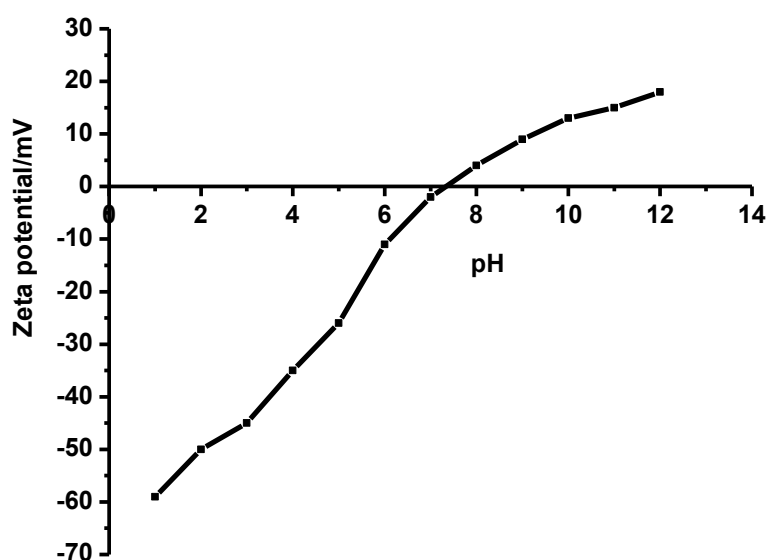


Figure 6.4: Point zero charge of Co-rGO.

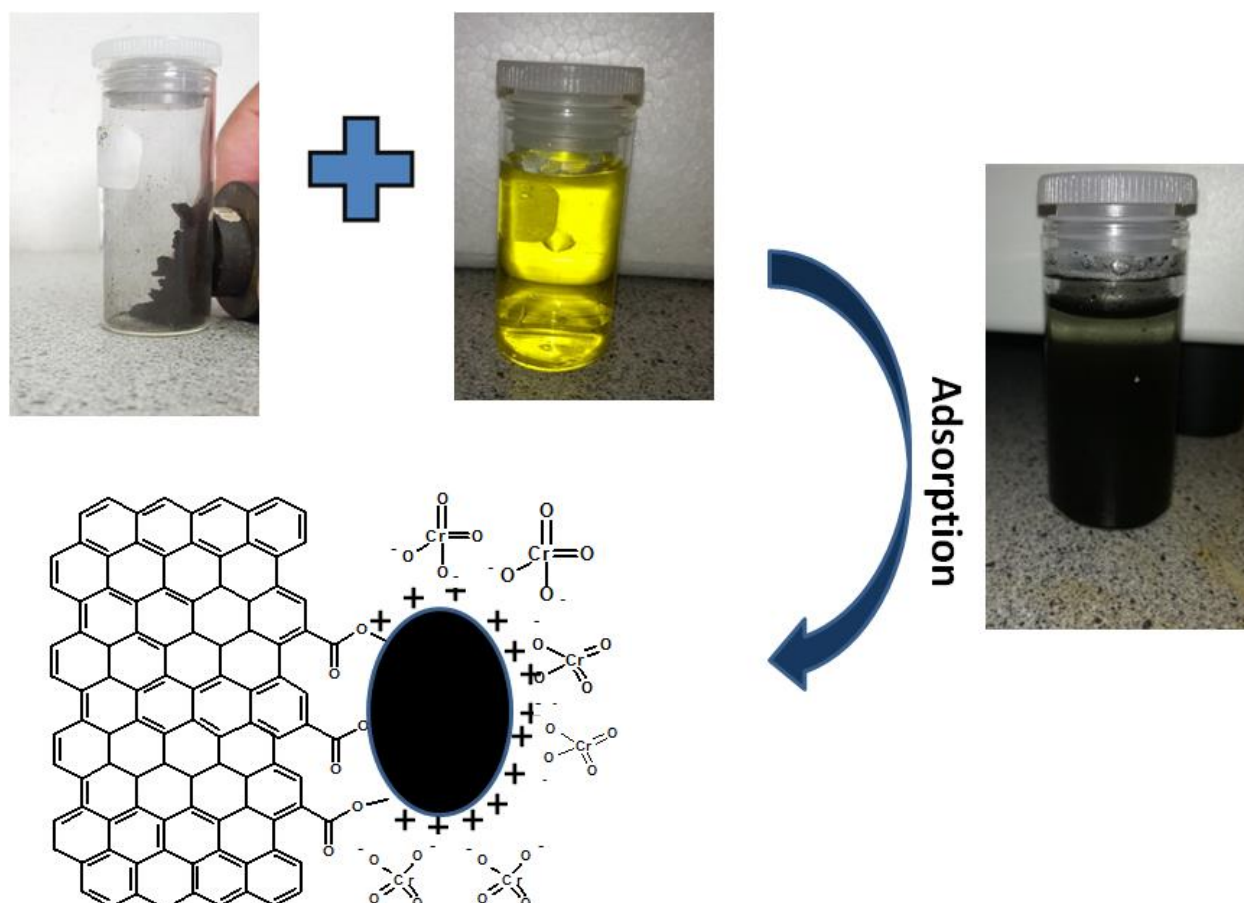


Figure 6.5: Proposed scheme of the adsorption Cr(VI) ions on Co-rGO.

6.1.4.3. Adsorption studies

6.1.4.3.1. Adsorption kinetics

The adsorption parameters and the kinetics of the adsorption process are important parameters to evaluate. This is important in dealing with waste water purification. The parameters which were determined in the above section were used in this study. The parameters were a concentration of 20 mg.L^{-1} , pH of 8 and a contact time of 90 min. The adsorption kinetics were evaluated with the pseudo first-order, pseudo

second-order kinetic models and Avrami fraction kinetic model [26, 17]. The fitting of the raw data to the kinetic models is shown in Figure 6.6.

The data was summarized in Table 6.2. Figure 6.7 shows the plot of the raw data and the fitting of the raw data to the rate equations. The smooth plots were obtained by using the equation to obtain the different parameters. From the plot it is observed that the adsorption of Cr(VI) on Co-rGO follows a pseudo-second-order kinetics model. This was evaluated using the statistical R^2 values of the data. The correlation coefficient of the pseudo-second-order model was 0.992, which was closer to 1. R^2 was used to evaluate how the model correlated to the obtained values. The pseudo second kinetic equation had the highest R^2 when compared to the other two models. It also had the lowest standard deviation value of 4.33, which concluded that the adsorption kinetics followed the pseudo second order kinetic equation. The Avrami fractional order kinetic model and the pseudo first order kinetic model had R^2 values of 0.981 and 0.945 respectively. The pseudo first order kinetic model had the highest standard deviation of about 20.7. The value for q_e 92.3 mg.g⁻¹ was determined using the graph.

Table 6.2: Table of constants and correlation coefficient.

Pseudo-first-order				Pseudo-second-order				Avrami fractional order			
$k_1/(\text{min}^{-1})$	$q_e/(\text{mg.g}^{-1})$	R^2	SD	$k_2/(\text{g.mg}^{-1}\text{min}^{-1})$	$q_e/(\text{mg.g}^{-1})$	R^2	SD	$k_1/(\text{min}^{-1})$	$q_e/(\text{mg.g}^{-1})$	R^2	SD
0.0319	89.9	0.945	20.7	0.0421	92.3	0.992	4.33	0.0347	90.6	0.981	7.89

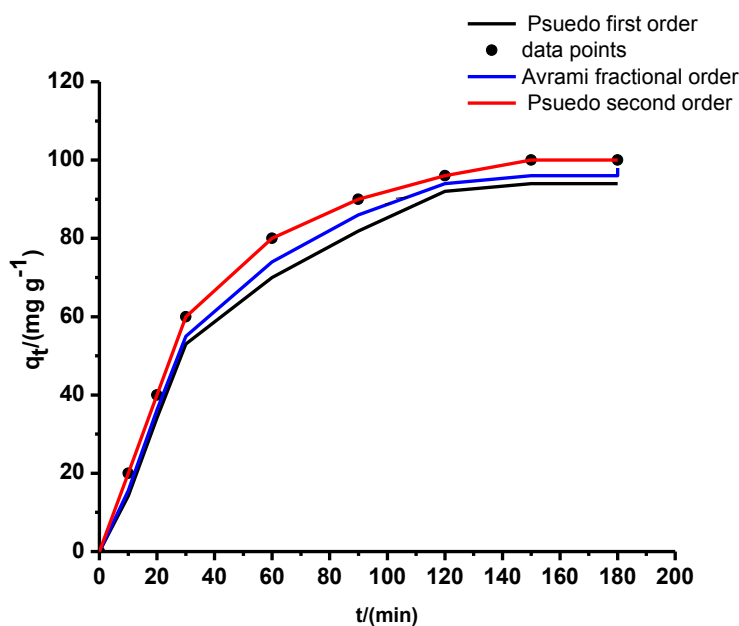


Figure 6.6: Adsorption kinetics curves of the Cr(VI) on the Co-rGO.

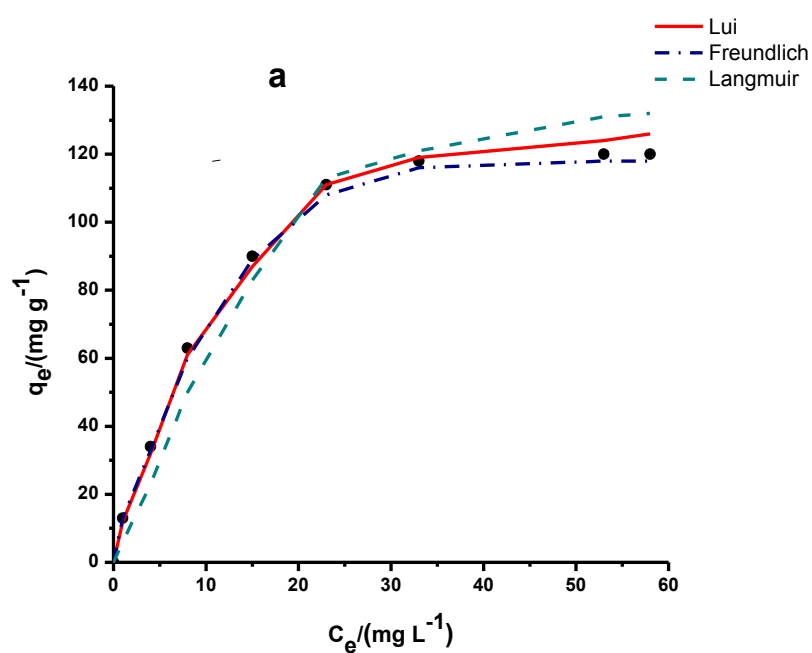
6.1.4.3.2. Adsorption isotherms and thermodynamics parameters.

The adsorption isotherm is used to determine the distribution of the chromate molecule within the solid phase when the adsorption process reaches equilibrium [25]. The adsorption isotherms also relate the amount of the chromate ions adsorbed at equilibrium, as per weight of the adsorbent, q_e (mg g⁻¹), to the adsorbate concentration also at equilibrium, C_e (mg L⁻¹). The models are plotted from the of q_e using the equation of the different adsorption models. The raw data is plotted along to model data point to evaluated which model the raw was in concordance with model data points. The extent of how well the experimental data fitted to the studies' models was evaluated using R^2 and SD values. Values of R^2 and SD which are closer to 1 denote that the data fitted the model better. It also affirms that there are no differences between the experimental and theoretical values. The raw data is plotted in Figure 6.7.

The data is summarized in Table 6.3. The Langmuir isotherm describes an adsorption process which is monolayered and has uniform distribution process between the adsorbed. This correlated to the adsorbed molecules to have no interaction with each other and the adsorption surfaces are of equivalent energies. However, it was determined that the R_L was less than 1 which meant that the adsorption process was unfavorable [26]. Q_m and adsorption capacities were obtained by calculating the mean value from the model equations. The Freundlich isotherm describes a monolayered to multilayered adsorption of heterogeneous surfaces. The adsorption is between the liquid and solid surfaces. The model assumes that there is interaction between the adsorbed molecules [27 - 37]. The nature of the adsorption can be verified by the value of n_F . If $n_F = 1$, the adsorption is chemical, when $n_F < 1$ the adsorption is unfavourable and $n_F > 1$ is favourable. The data fitted well to the Freundlich isotherm and the value n_F was 2.99 at 298 K. This affirms that the adsorption fitted well to the Freundlich isotherm and that the process is favourable. The correlation coefficient R^2 was 0.996. This was closer to 1 and standard deviation for the Freundlich fitting was the lowest and the data could be multilayered. There was a decrease in the adsorption capacity when the temperature increased, which was expected since it is well reported in literature [27 - 38]. The increase in the temperature corresponds to the decrease adsorption capacity of the Co-rGO. The comparison of obtained adsorption capacity compared to other carbon based materials is summarized in Table 6.3.

Table 6.3: Table of constants, adsorption isotherms parameters, and Qm.

T/ K	Langmuir					Fruendlich				Lui				
	q_m (mg.g ⁻¹)	B (L mg ⁻¹)	R_L	R^2	SD	K_F	n_F	R^2	SD	K_L (L.g ⁻¹)	Q_m (mg. g ⁻¹)	n_L	R^2	SD
298	113.3	0.689	0.456	0.989	3.29	17.1	2.99	0.996	0.632	0.119	119.5	1.21	0.969	5.77
308	106.2	0.519	0.325	0.948	5.51	12.3	2.22	0.989	0.741	0.418	108.4	1.15	0.926	2.97
318	82.3	0.332	0.192	0.922	3.62	10.3	2.05	0.945	0.845	0.621	88.8	1.13	0.882	3.87



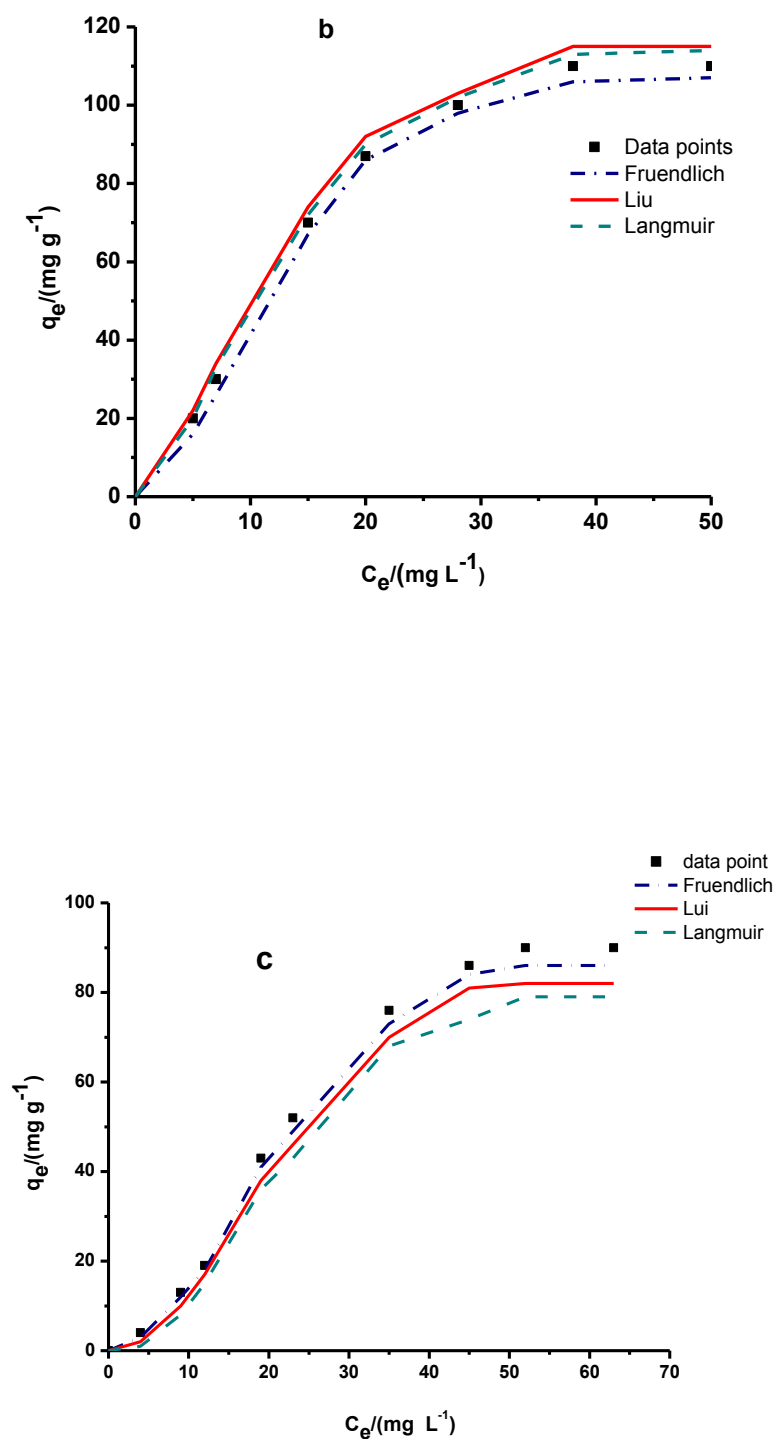


Figure 6.7: Adsorption isotherms (Langmuir, Freundlich and Liu) Cr(VI) on Co-rGO at different temperatures (a) 298 K, (b) 308 K and (c) 318 K. The plot shows the raw data and the fitting of the raw data to the adsorption isotherms.

Table 6.4: Maximum adsorption capacities for the adsorption of (VI) on carbon based materials.

Adsorbent	Adsorbate	Adsorption capacity/(mg g ⁻¹)	Conditions	References
Co ₃ O ₄ -rGO	Cr(VI)	208.8	298 K, pH =2	[22]
GSC	Cr(VI)	2859.4	298 K, pH = 1.5	[14]
ZVI-Fe ₃ O ₄ -rGO	Cr(VI)	101	298 K, pH= 8	[21]
rGO	Cr(VI)	98.2	298 K, pH= 2	[24]
MWCNT- Fe ₃ O ₄	Cr(VI)	65	298 K, pH= 3	[25]
Activated carbon	Cr(VI)	69	298 K, pH= 3	[26]
Magnetic rGO - loaded PEGDMA	Cr(VI)	119	298 K, pH= 3	[15]
Co-rGO	Cr(VI)	116.8	298 K, pH= 8	This work

The thermodynamic equilibrium constant can be determined using the following equations [21, 22]:

$$K_d = \frac{q_e}{C_e} , \quad (9)$$

$$\Delta G = -RT \ln K_d , \quad (10)$$

and

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} , \quad (11)$$

where R (8.314 J.mol⁻¹.K⁻¹) is the gas constant, T (K) is the absolute temperature, K_d is the thermodynamic equilibrium constant, ΔG (kJ.mol⁻¹) is the Gibbs free energy, and ΔH (kJ.mol⁻¹) is the enthalpy of the adsorption and ΔS (J.mol⁻¹.K⁻¹) is entropy. The

values of ΔH and ΔS are calculated by plotting the Van Hoff equation in the form of $\ln K_d$ vs $1/T$ and are shown in Figure 6.8. From Table 6.5, it was observed that the Gibbs energy values were negative, suggesting that the adsorption is spontaneous. The positive value of the entropy suggests there is a high disorder in the system and increased randomness. The interaction between the solution and solid is increased. The interface solid/solution had an increased uptake of Cr(VI) by the Co-rGO. Thus the Co-rGO has an affinity for Cr(VI) ions. The enthalpy of the sorption process was negative which affirms the process is exothermic [17, 18]. The magnitude of the enthalpy can be used to distinguish between chemisorptions and physisorption. For $\Delta H > 40 \text{ kJ mol}^{-1}$ the sorption process is chemisorptions, and for $\Delta H < 40 \text{ kJ mol}^{-1}$ the sorption process is physisorption. Thus the obtained value of $-14.2 \text{ kJ mol}^{-1}$ for ΔH indicates that the adsorption process was physisorption [17]. The exothermic nature of the adsorption process affirms the decrease in the adsorption capacity. The correlation coefficient was 0.996 which is a measure of how well the values concur with each other. The magnitude of the correlation coefficient suggests that the obtained values of ΔH and ΔS are reliable. The adsorption process occurs as a result of the electrostatic interaction between the positively charged cobalt nanoparticles and the negatively charged CrO_4^{2-} ions.

Table 6.5: Table of the thermodynamic parameters for the adsorption at different temperatures.

T/K	$\Delta G/ (\text{kJ mol}^{-1})$	$\Delta H/ (\text{kJ mol}^{-1})$	$\Delta S/ (\text{kJ mol}^{-1} \text{ K}^{-1})$
298	-1.72	-14.2	4.76
308	-1.95		
318	-2.21		

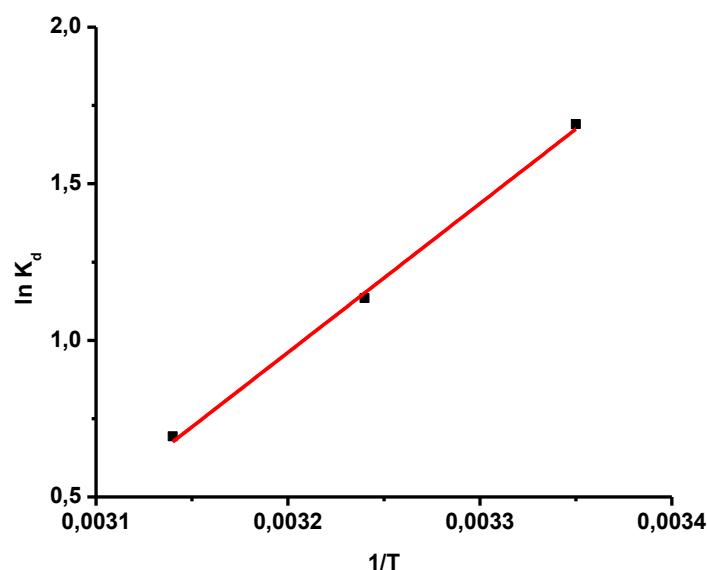


Figure 6.8: Van'Hoff plot for the adsorption of Cr(VI) on Co-rGO.

6.1.4.3.3. Regeneration and desorption.

The economical feasibility of the Co-rGO is the ability for the composite to be regenerated. The Cr(VI) was soaked in an ethanol solution with 10 % NaOH. The mixture was then ultrasonicated which loosened the electrostatic interaction between the Co-rGO and Cr(VI). Desorption was then achieved when CrO_4^{2-} was displaced by the OH^- . After soaking and ultrasonication the ethanol solution turned from a clear to a yellowish solution. The Co-rGO was separated from the solution using a held magnet. The Co-rGO was washed with water and acetone. The Co-rGO was then dried in a vacuum oven at 60° C. The concentration used for regeneration of Co-rGO was 20 mg L⁻¹. The adsorption-desorption cycles are shown in Figure 6.9. The first regeneration resulted in a drop in the removal efficiency from 90 % to 82 %. The removal efficiency did not change after the sixth cycle.

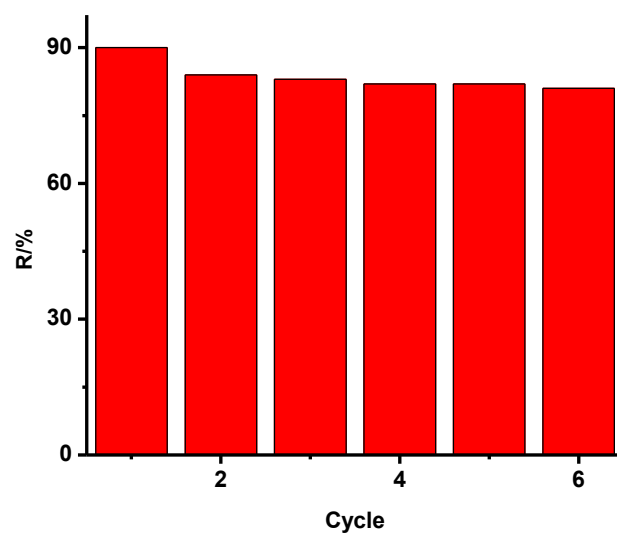


Figure 6.9: The removal efficiency of recycled Co-rGO.

6.2. Reduction of Cr (VI) to Cr (III) using Ni-rGO and CoFe-rGO.

6.2.1. Method.

The reduction experiment was contained in a series of Erlenmeyer flasks containing 50 mL solution of Cr (VI) ions. The reduction tests were conducted in order to evaluate the catalytic reduction of the toxic Cr (IV) ion to Cr(III) which is non toxic, by Ni-rGO and rGO. The CoFe-rGO and Ni-rGO was then separated from the solution with the aid of rare-earth magnet. The supernatant was collected, and the remaining heavy metal ions were evaluated using UV-Vis spectroscopy. The Cr (VI) solutions were fashioned from 1000 mg/L standard solution. A working standard solution of 100 mg/L was used to create samples of 100 mg/L. The pH of the solution was adjusted to 8 by adding drops of a concentrated of sodium hydroxide solution.

6.2.2. Results.

The other synthesized samples such as Ni-rGO and rGO, were also tested using a 100 ppm standard of Cr(VI). A mass of 30 mg of each sample was added to 50 mL of 100ppm standard and agitated for 3 hours. The solution was then analyzed using UV/Vis spectrophotometry as shown in Figure 6.16. The UV/Vis spectrum revealed that the sample of Ni-rGO and FeCo-rGO had reduced the Cr(VI) ions to Cr(III). This evident in appearance of the Cr(III) absorption peak at $\lambda_{\max}$ 398 nm. It has been observed in literature that the positively charged rGO function groups tend to facilitate the reduction of the Cr(VI) to Cr(III) [6]. Cr(VI) ions are in the form of HCrO_4^- , which is attracted to the positively charged centers of the rGO. It has been reported before in literature that Ni-rGO has the ability of reducing Cr(VI) to Cr(III) [43]. The Cr(III) ions are non-toxic to life and are a micronutrient.

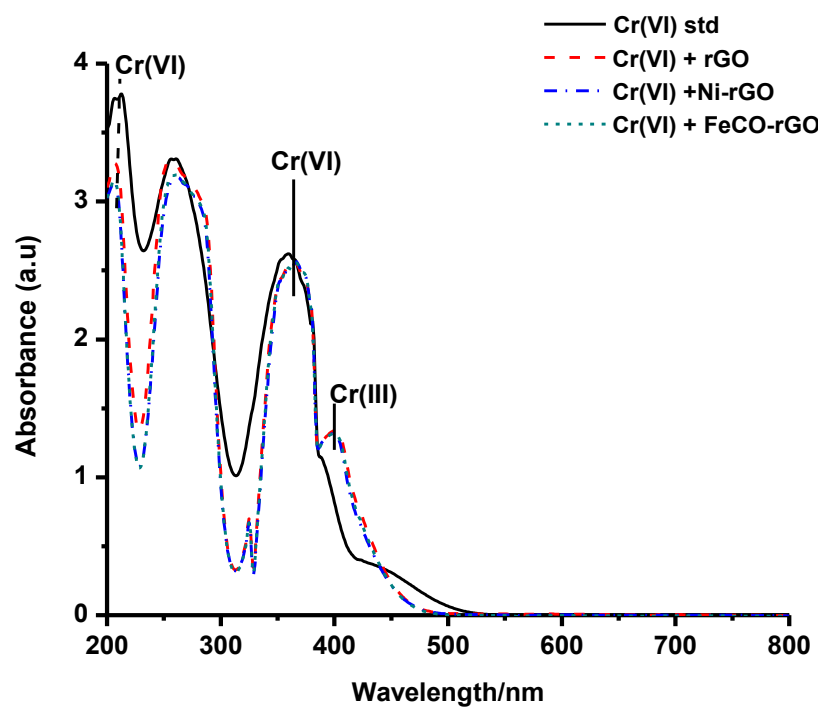


Figure 6.10: Plot of UV/Vis spectrum of 100 ppm Cr(VI) standard, Cr(VI) after adding Ni-rGO and, FeCo-rGO.

6.3. Conclusions

The study was to synthesize Co-rGO using a coprecipitation method, with graphene oxide and $\text{Co}(\text{acac})_2$ as starting materials. The Co-rGO was characterized and it was found that the cobalt nanoparticles were on the surface of the rGO. The Co-rGO was a monocrystalline material. The Co-rGO was subsequently used in the removal of Cr(VI) under basic medium. High concentrations of Cr(VI) saturate the active sites and decrease the removal efficiency of the Co-rGO. The adsorption processes follow pseudo-second-order kinetics. The best removal efficiency was at pH 8 that once exceed, hydroxide ions competed with Cr(VI) ions for active adsorption sites. The adsorption fitted well to the Freundlich adsorption mode, much better than to the the Langmuir and Liu isotherm models. The model suggested that the adsorption sites are heterogeneous. The adsorption process follows a monolayer to multilayer sorption with interaction between the adsorbed molecules. The adsorption process occurs due to the electrostatic interaction between the positively charge cobalt nanoparticles and the negatively charged CrO_4^{2-} ions. The adsorption capacity of the Co-rGO for Cr(VI) was 116 mg.g^{-1} , which was higher than some of magnetic nanoparticles-graphene composites. The magnitude of the ΔH was 14.2 kJ mol^{-1} , suggesting that the adsorption process and the adsorption capacity decrease with increases in temperature. Co-rGO, being a weak ferromagnetic material was easily removed from Cr(VI) solution. The Co-rGO can be regenerated using an ethanol solution treated with a 10 % NaOH solution. The Co-rGO was recycled 6 times and showed no significant change in the removal efficiency. Ni-rGO, rGO and FeCo-rGO were found to catalyze the reduction of Cr(VI) to Cr(III).

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Chapter 7: Conclusions and Recommendations.

Chapter 7: Conclusions and Recommendations

7.1. General Conclusions

The main aim of this thesis was to, in principle, demonstrate the use of rGO to purify water. Synthesis of GO and rGO was researched and a number of different documented methods were investigated. Both GO and rGO offered great surface area per gram in order to adsorb contaminants in the form of pollution. In order to collect the adsorbed contaminants a method of anchoring nano-magnetic particles to rGO ('scaffolding') was employed. This thesis has shown the novelty of synthesis where there is pretreatment step is introduced and the conductivity studies of prepared samples.

Chemical exfoliation uses the route of the formation of graphene oxide as an intermediate. In this work the intermediate was synthesized using expanded graphite which was irradiated using a microwave oven and less oxidants were thus used in the production. The formation of reduced graphene oxide was obtained from using sodium borohydride as a reducing agent. The experiment proved that graphene oxide and reduced graphene oxide can be obtained affordable starting materials. The synthesized graphene oxide was characterized with TEM, XRD and FTIR. The characteristic peaks for graphene oxide was obtained from XRD at 10° and 26° , an which is indication of the successful formation graphene oxide. This was complemented FTIR. The TEM analysis showed that the graphene oxide was wrinkled. The two main methods used in the oxidation was Tour's method and the modified Hummer's method. The two methods yielded two different types of graphene oxide. Tour's method yielded graphene which was more soluble and wrinkled.

The graphene oxide synthesized using Tour's method was used in subsequent reactions to produce reduced graphene oxide samples. The doped reduced graphene oxide was tested in the Material Science laboratory for resistivity vs temperature. The

doped samples were obtained from chemical vapour deposition. The dopants were boron and nitrogen, which were found to increase the conductivity of the reduced graphene oxide. The reduced graphene oxide was found to exhibit semiconductor behavior. The doped reduced graphene oxide was slightly more conductive as the dopants increased the number of charge carriers. The magnetic properties were also increased. The doped samples were found to be magnetic, as verified by VSM analysis.

The composites were obtained from decorating reduced graphene oxide with metallic nanoparticles. The nanoparticles were cobalt, nickel and cobalt ferrite. The composites were analysed with TEM, Raman, XRD, ICP-OES and VSM. The TEM showed that the nanoparticles were mono dispersed on the surface of graphene. The Raman spectroscopy showed that the composites were highly disordered and not pristine graphene sheets. It also showed that specimens were multilayered in nature. ICP-OES was used as qualitative and quantitative analysis of the composites. It was found that the cobalt was 10 % by weight in the Co-rGO composite, nickel was 15 % by weight in Ni-rGO, and on the FeCo-rGO cobalt was 7 % and iron 14 % by weight. The composites showed semiconductor behavior on resistivity vs temperature measurements. The composites were slightly more conductive than reduced graphene oxide. The VSM showed that the composite were soft magnetic materials. The XRD showed that the composites had peaks corresponding to nanoparticles and reduced graphene oxide.

The Co-rGO specimen was used in the removal of chromate ions in aqueous media. The study revealed that the Co-rGO sample was porous, and that the adsorption of the chromate ions followed pseudo second-order rate kinetics. The adsorption was tested with several adsorption isotherms such as Langmuir, Freundlich and Lui. Langmuir and Freundlich are mono-layered adsorption isotherms, and the results suggested that the data followed the Freundlich adsorption isotherms. This isotherm suggested that the adsorption sites were heterogenous and there was interaction between adsorbed chromate molecules. The nature of the adsorption was determined

to be physisorption and the adsorption occurred via electrostatic interaction between negatively charged chromate ions and positively charged Co-rGO.

7.2. Recommendations.

- i) The recommendation would be the different techniques that are used to synthesize graphene oxide such as different modified Hummer's method and such unzipping of CNT's.
- ii) The production of reduced graphene oxide obtained from different methods of producing graphene oxide.
- iii) The study of physical properties of the different sample of reduced graphene oxide.
- iv) The applications of N-rGO and B-rGO in supercapacitor applications. The effect of increased charge carriers from may be explored and exploited in the targeted application such as supercapacitors.
- v) The successful use of Co-rGO in the removal of Cr(VI) from water. The other samples were found to catalyze the reduction of Cr(VI) to Cr(III). There is a possibility of catalyzing toxic pollutants to less toxic compounds which can be easily removed
- vi) TEM analysis proved to be challenging since the superparamagnetic nature of the composite. This suggests that this composite can be used in antenna research as a reflector reflecting the electron beam used by the TEM instrument. The other composites which were magnetic such as Co-rGO, Ni-rGO and FeCo-rGO, can also be used in antennas, membrane electrode assemblies and photonics.

Chapter 8: Appendices

Chapter 8: Appendices

8.1. Patch Antenna Application

8.1.1. Introduction.

Graphene nanoparticles composite has been used in many technological application in recent year. Graphene cobalt-boron nanoparticles has been shown to promising candidates for anode for lithium ion batteries. The electrode has been shown to have a high reversible capacity [1]. The other promising application of graphene-based compounds is graphene aerosol decorated with iron cobalt oxide nanoparticles which is Li-ion batteries [2]. Composite graphene material has been shown to be useful as anode material for Lithium ion batteries, where the nanoparticles prevent graphene sheets restacking. The composite has superior lithium ion storage, specific capacity and cycle stability [2]. Magnetic nanoparticles such as iron, cobalt and nickel have large saturation magnetization and high Snoek's limit and compatible dielectric loss [3]. The combination of the magnetic nanoparticle with graphene is beneficial. The large surface area is combined with dielectric loss, magnetic loss component, increased interface polarization and electromagnetic loss ability. This implies graphene-based compounds have microwave absorbance antenna performance [3]. The combination of graphene and nickel nanoparticles showed enhanced performance as microwave absorbance than graphene and nickel nanoparticles individually due to the improvement of electromagnetic loss [3]. Reduced graphene oxide has promising properties in the microwave absorption properties. The reduced graphene oxide has a Fermi level with defects in the polarization relaxation and

electronic dipole relaxation. This favors light absorption and in turn graphene and graphene composites can exhibit microwave absorption properties.

8.2.2. Preparation of micro strip antenna and measurements

The length and width of the patch were determined using equations (1) and (2) [6], using copper model.

$$L = \frac{c}{2f_r\sqrt{\epsilon_r}} \quad (1)$$

$$w = \frac{c}{2f_r} \sqrt{\frac{2}{1+\epsilon_r}} \quad (2)$$

Where, L is the length of the patch, w is the width of the patch, f_r is the resonant frequency of the patch, ϵ_r is the extinction coefficient, c is the speed of light. The effective dielectric constant, at low frequencies is basically constant, at higher frequencies it began to increase given by:

$$\epsilon_{reff} = \frac{\epsilon_r+1}{2} + \frac{\epsilon_r-1}{2} \left[1 + 12 \frac{h}{w} \right]^{-\frac{1}{2}} \quad \frac{W}{h} > 1 \quad (3)$$

The extended length by the distance ΔL with respect to the effective dielectric constant and width-height ration given by:

$$\frac{\Delta L}{h} = 0.412 \frac{(\epsilon_{reff} + 0.3) \left(\frac{W}{h} + 0.264 \right)}{(\epsilon_{reff} - 0.258) \left(\frac{W}{h} + 0.8 \right)} \quad (4)$$

Where h is height of the substrate. The thickness of the substrate was determined to be 1.5 mm. After all the parameters were determined, a boundary of the patch in order to keep the dimension of the patch for dropcasting of the Ni-rGO slurry. The Ni-rGO was mixed with 50:50 solution of water and isopropanol forming a slurry. The slurry

was dropcasted in the patch boundary. The patch had a ground plain and the substrate used was a FR4 substrate. Figure 7.1 shows a (a) plain patch showing the boundary and (b) patch antenna with dropcasted Ni-rGO.

In order to determine the reflection coefficient, radiation pattern and the gain of the patch a simulation was done using CST microwave studio. The radiation pattern was also measured using Rohde & Schwarz ZVL Network Analyser 13.6 GHz. The simulations and measurements were done between 2 and 3 GHz. The dimensions of the patch are summarized in table 8.1.

Table 8.1: Table of parameters and value for the simulations of patch antenna

Parameters	Value	unit
Resonant Frequency, f_r	2.4	<i>GHz</i>
Dielectric constant of substrate, ϵ_r	4.4	-
Thickness of the substrate, h_s	1.5	<i>mm</i>
Copper thickness, h_t	0.035	<i>mm</i>
Patch length, L	28.95	<i>mm</i>
Patch width, W	28.95	<i>mm</i>
Ground plane length, L_g	57.9	<i>mm</i>
Ground Plane width, W_g	57.9	<i>mm</i>
Feedline length, F_i	9	<i>mm</i>
Feedline width, W_f	2.932	<i>mm</i>
Dielectric constant of Ni-rGO	65	-
Gap between feed and patch, G_{pf}	1	<i>mm</i>

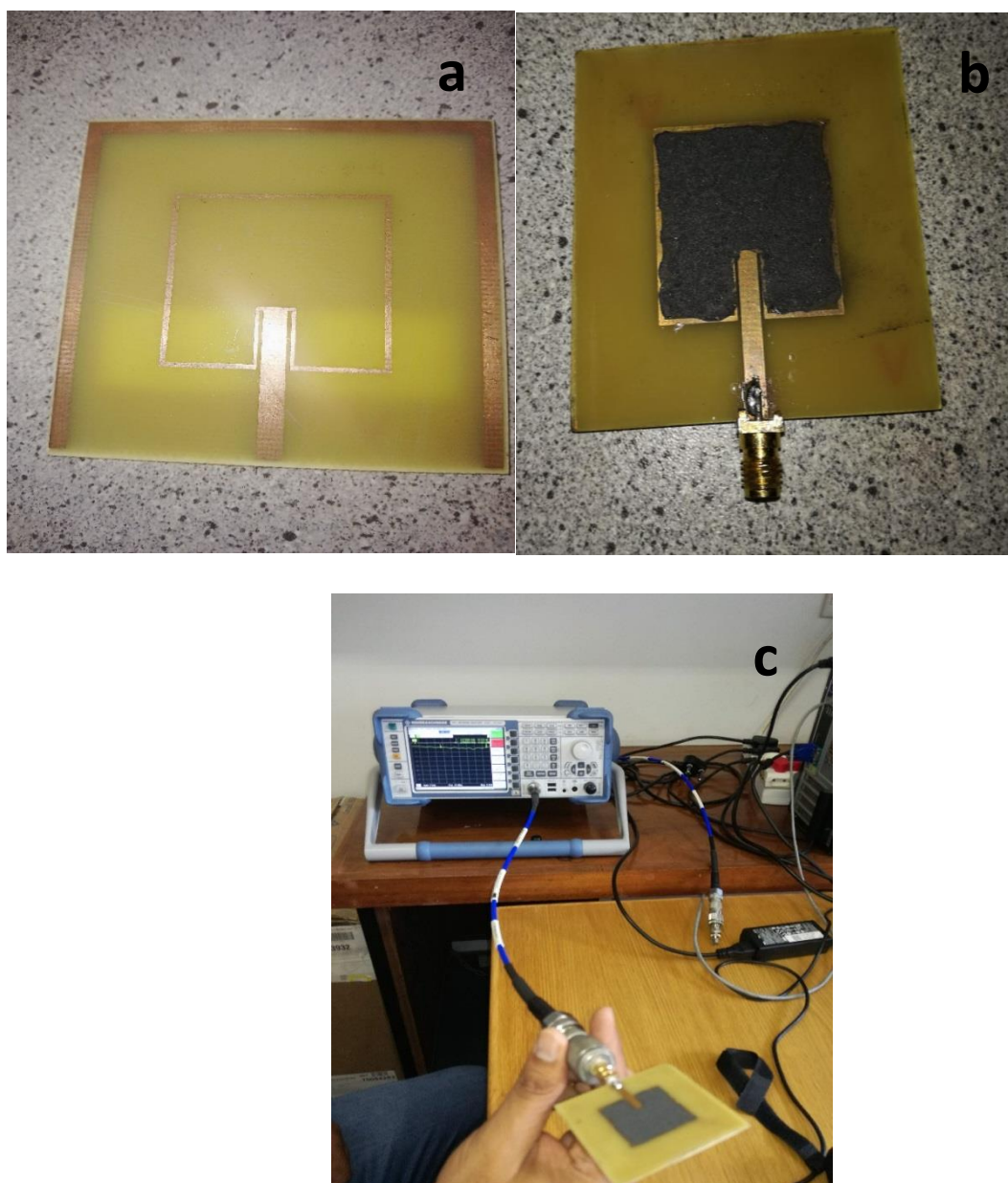


Figure 8.1: Picture showing patch used in the experiment (a) plain patch, (b) patch antenna with Ni-rGO drop casted and (c) measurement of patch using network analyzer.

8.3. Results and Discussion

The synthesis of reduced graphene oxide decorated with magnetic nanoparticles was successful, as seen by inspection of TEM images in Figure 7.2. TEM data shows the

prepared specimens Ni-rGO, were monodispersed in the graphene sheet. The selected electron area diffraction shown that Ni-rGO was monocrystalline and that the metal nanoparticles are on the graphene sample [7]. The conductivity of Ni-rGO was previously determined to be 62695.82 S/ m and the extinction coefficient (ϵ) was 4.82×10^6 L/g m [8]. The values were used in the simulation of the microwave absorption characteristics for Ni-rGO. The targeted measurement frequencies were between 2 to 3 GHz because of the wide applications of communication devices at 2.4 GHz [9].

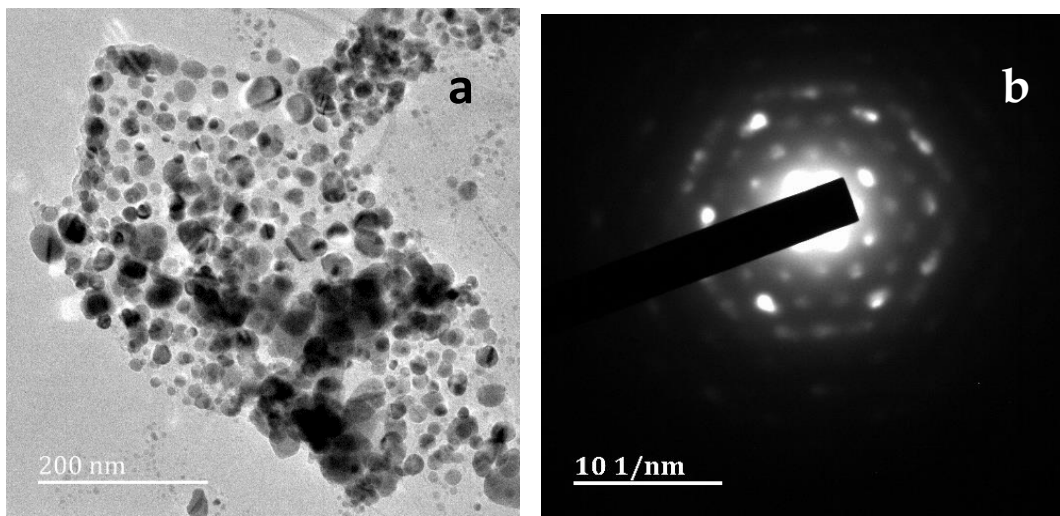


Figure 8.2: (a) TEM image of Ni-rGO and (b) selected area electron diffraction of Ni-rGO.

The proposed antenna design was carried out using CST Microwave Studio. The parameters that were investigated were return loss and radiation pattern as well the gain in dBi. The return loss is value which indicates the amount of the reflected and forward power of the patch which is given by S11 [9]. An acceptable operation of the antenna the S11 must be less than -10dB [10]. The bandwidth of the operation antenna is measured at the return loss of -10 dB [10]. Figure 3 shows the return loss parameter from the simulation and the measured results. The measured results with the simulated both had resonant frequencies less than -10 dB. This meant that NI-rGO can be used as a patch antenna. The simulated data has on one resonant frequency at 2.5

GHz at -13.5 dB. The measure data multiple resonant frequencies with the lowest return loss at 2.78 GHz with -14.35 dB. The measured result had a wide bandwidth from 2.28 to 2.97 GHz and the simulated data had a bandwidth of 2.46 to 2.54 GHz. The measured results show that the Ni-rGO can be used in WLAN, Bluetooth and wireless applications [11]. The other application for the patch antenna is WiMAX which operates between 2.4 GHz to 2.8 GHz which is known as the low band [12]. The other value important parameter is the voltage standing wave ratio (VSWR) which should be between 1 and 2 [13]. The simulated data is plotted in Figure 7.4; the obtained from the simulation is 1.73 which lies in the acceptable operation of the antenna. Value of the VSWR which is greater than 2 usually implies that the antenna is reflecting the power and transmission of the power is not achieved. Therefore the proposed antenna has the ability to transmit power.

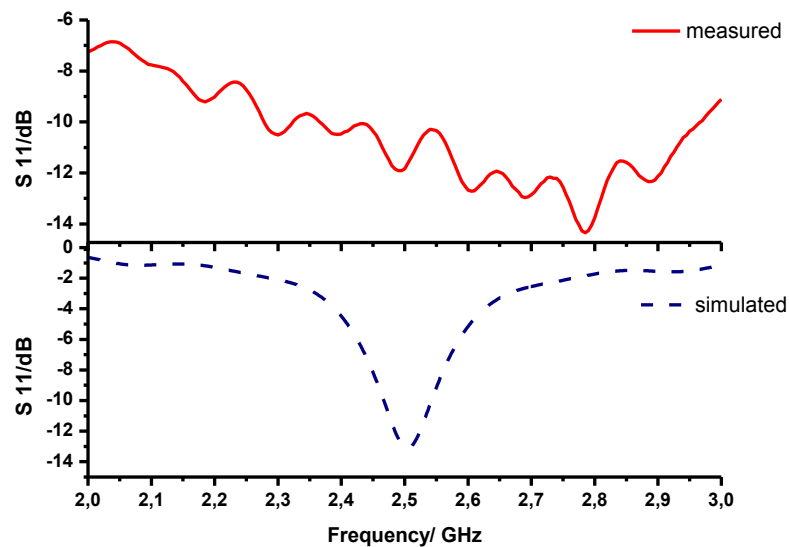


Figure 8.3: Measured and simulated reflection coefficient $[S1, 1]$ of the Ni-rGO patch antenna.

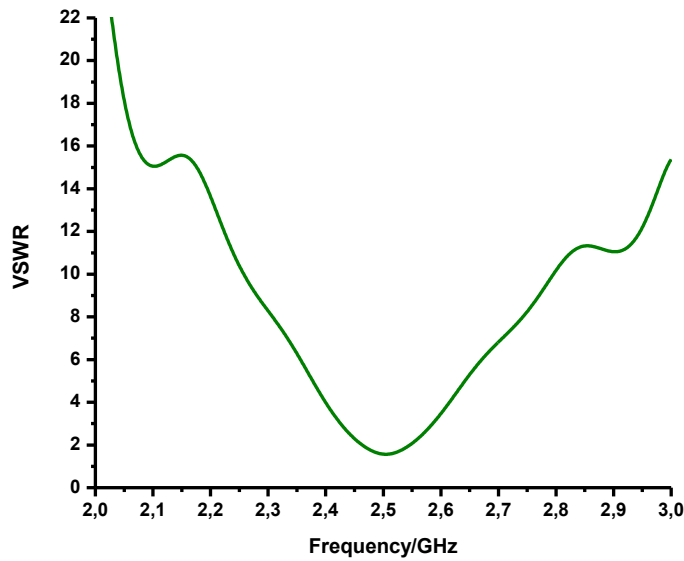


Figure 8.4: Simulated values Voltage Standing Wave Ratio of the Ni-rGO patch antenna.

The operation of the antenna can be improved by employing a defected ground structure (DGS). This method improves the radiation efficiency of the patch antenna by removing higher harmonics and impeding power loss [14]. It also lowers the resonant frequency of the antenna.

Figure 7.5, shows the simulated and measured results of the reflection coefficient. The simulated reflection coefficient result has shifted and as low as -31 dBi. The measured results multiple resonant frequencies at 2.45 and 2.56 GHz. The reflection coefficient was -14.56 and -15.12 dB, which was a marginable improvement to the normal ground state patch antenna. The measured result had a wide bandwidth from 2.28 to 2.97 GHz and the simulated data had a bandwidth of 2.46 to 2.54 GHz. The measured results show that the Ni-rGO can be used in WLAN, Bluetooth and wireless applications [11]. The other application for the patch antenna is WiMAX which operates between 2.4 GHz to 2.8 GHz which is known as the low band [12].

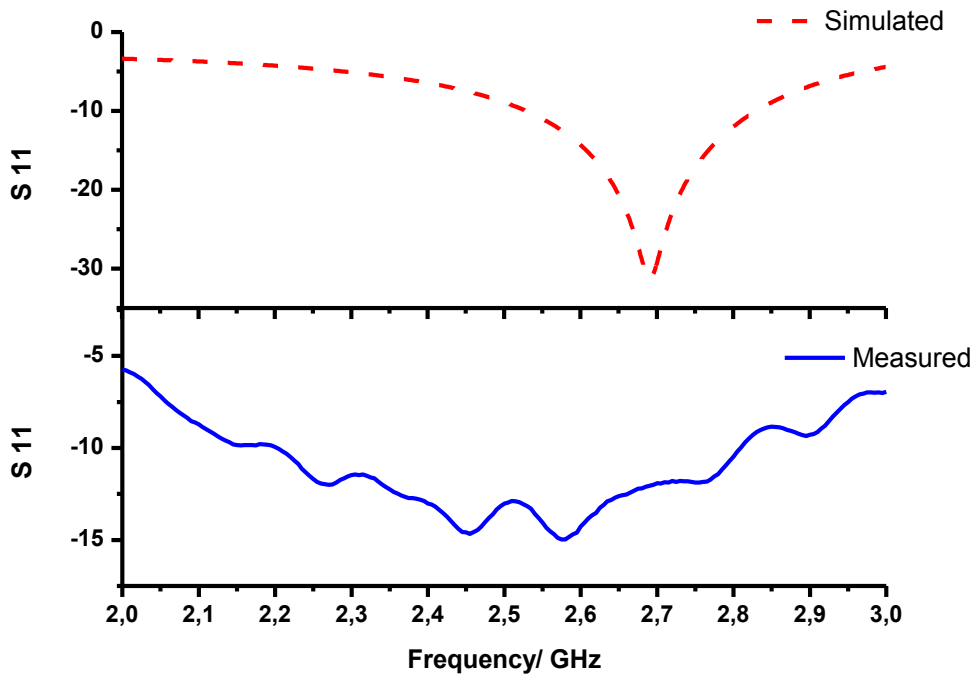


Figure 8.5: Measured and simulated reflection coefficient $[S_{11}, 1]$ of the Ni-rGO patch antenna with defected ground structure (DGS).

The simulated data is plotted in Figure 7.6; the obtained from the simulation is 1.2 which lie in the acceptable operation of the antenna. Value of the VSWR which is greater than 2 usually implies that the antenna is reflecting the power and transmission of the power is not achieved. Therefore, the proposed antenna has the ability to transmit power.

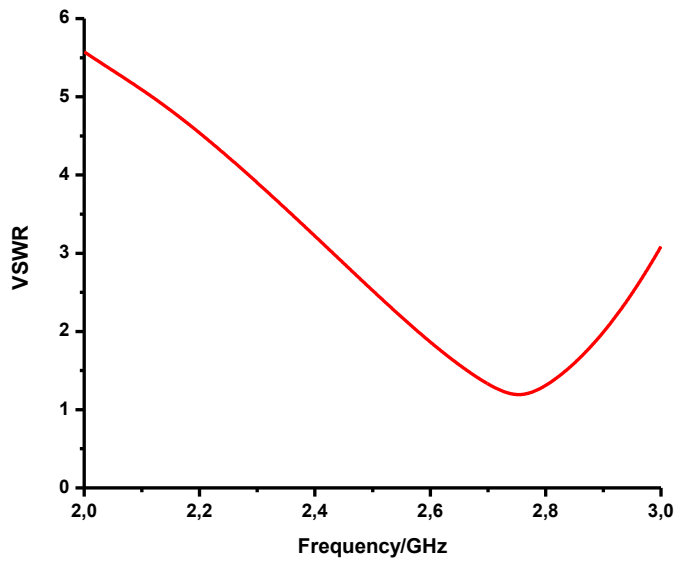


Figure 8.6: Simulated values Voltage Standing Wave Ratio of the Ni-rGO patch antenna with defected ground structure (DGS).

The radiation pattern is another important parameter the simulated results are shown in Figure 7.7. The patch without DGS is shown as 7.7 a where the main lobe has a directivity of 6.25 dBi with a gain of -1.18 dBi. The patch with DGS was different to patch without DGS. The directivity at the main lobe was 3.75 dBi and the gain was 2.6 dBi. The patch with DGS performed better when compared with the patch antenna without DGS. The patch antenna with DGS had positive gain and faced the opposite direction.

Table 8.2: Table of resonant frequency, bandwidth, directivity and gain for Ni-rGO patch antenna.

Sample	Resonant frequency/GHz		Bandwidth/GHz		Directivity/ dBi	Gain/dBi
	Measured	Simulated	Measured	Simulated		
Ni-rGO	2.79, 2.89	2.45	2.28 -2.92	2.45 – 2.55	-6.25	-1.18
Ni-rGO (DGS)	2.45,2.77	2.69	2.16 – 2.81	2.53 – 2.83	3.75	2.63

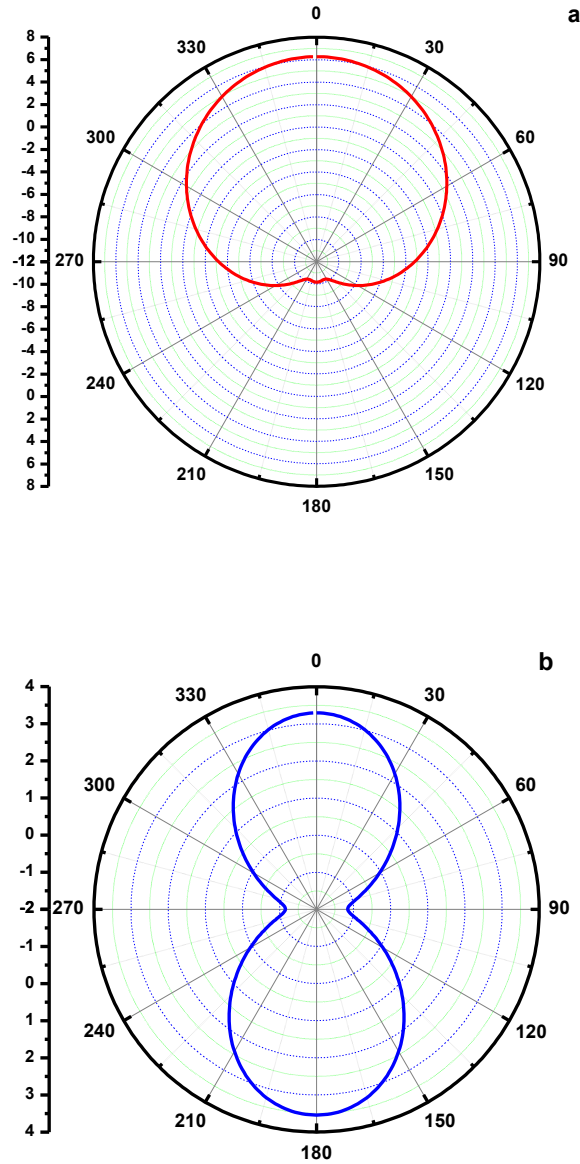


Figure 8.7: Simulated values radiation pattern of Ni-rGO patch antenna (a) without DGS and (b) with DGS.

Conclusion

The Ni-rGO was used in the patch antenna application. The results of the reflection coefficient were both from simulations and measured results. The patch antennas had reflection coefficient which were less than -10 dBi. The resonant frequencies of the

patch were between 2.2 to 2.9 GHz. The results shows the Ni-rGO can function as antenna with application in wireless communications such as Bluetooth, WiLAN and WiMAX. The patch with defected ground state structure was found to perform better than the antenna without DGS. The gain was found to be positive and had the lowest reflective coefficient.

Other Simulations

The other samples were prepared for the preparation of patch antennas. The samples were rGO, N-rGO, B-rGO, Co-rGO and FeCo-rGO. Their conductivities less than of conductivity of Ni-rGO. The ability of the prepared samples perform as patch antennas were simulated also. The simulation data is Figure 7.8 and summarized in Table 7.3. The samples that were found to have the potential to be used in patch antenna applications were B-rGO, Co-rGO and FeCo-rGO which have the reflection coefficients that surpass -10 dBi. Even though the gains were negative we can theorize that employing the ground state structure on the sample. The N-rGO samples had a reflection that did not reach -10 dBi and can be applied in patch antenna applications.

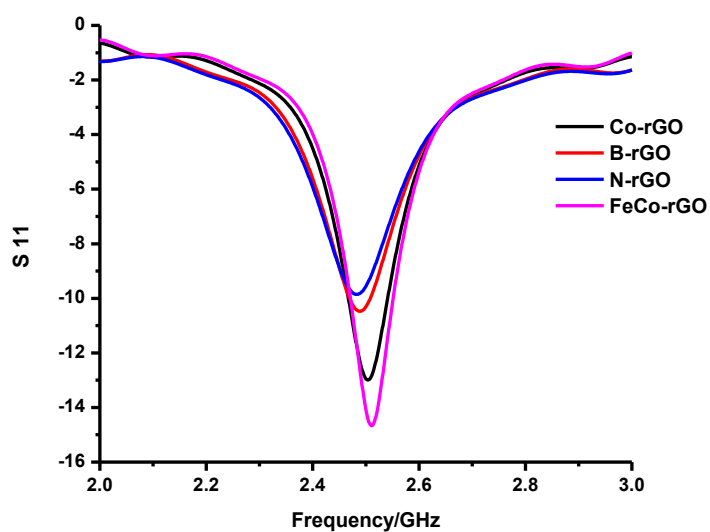


Figure 8.8: Simulated results of the reflection coefficient of Co-rGO, FeCo-rGO, B-rGO and N-rGO.

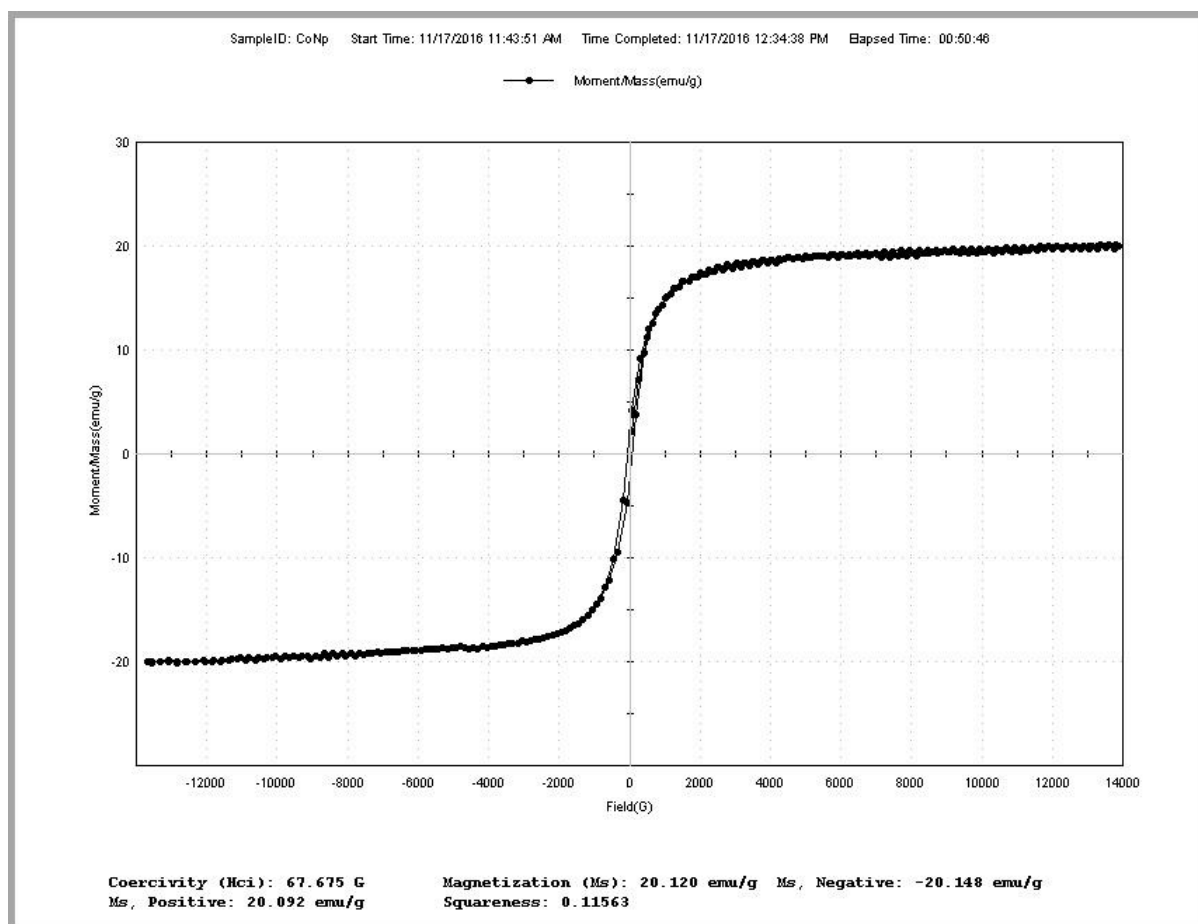
Table 8.3: Table of simulated data: resonant frequency, bandwidth, directivity and gain for Co-rGO, FeCo-rGO, N-rGO and B-rGO.

Sample	Bandwidth/GHz	Resonant frequency/GHz	Directivity/dBi	Gain/dBi
FeCo-rGO	0.82	2.505	-16.2	-1.44
Co-rGO	0.75	2.509	-16.4	-1.43
N-rGO	-	-	-	-
B-rGO	0.051	2.45	-16.5	-2.33

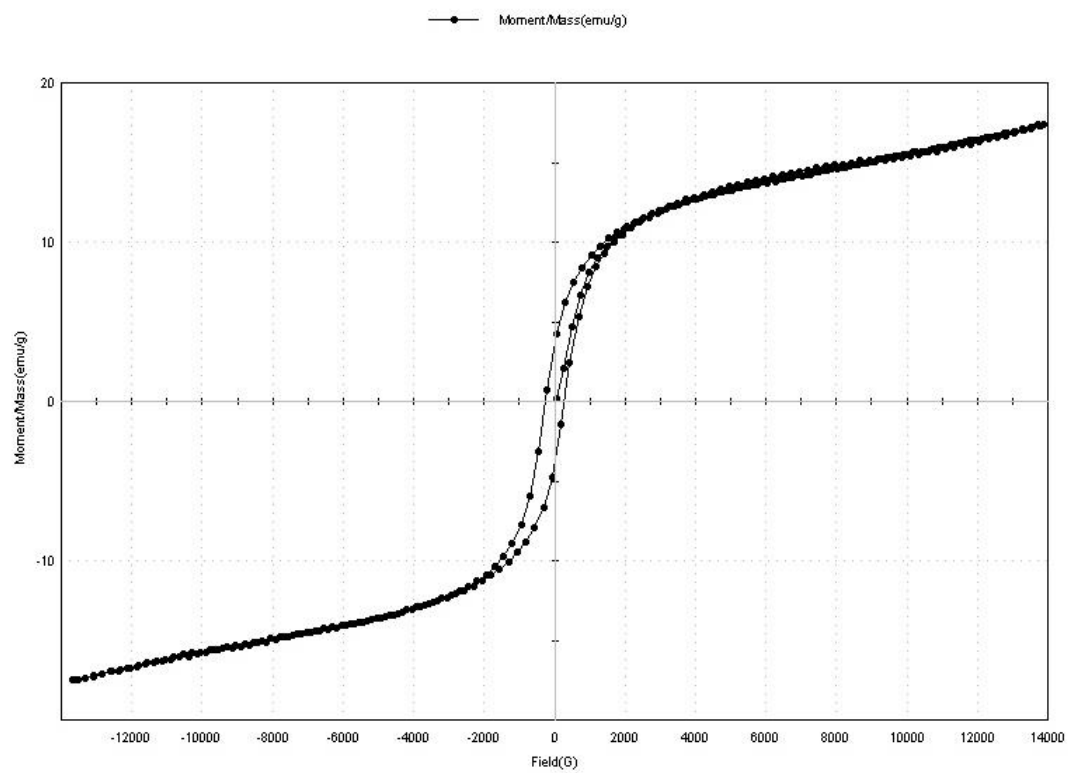
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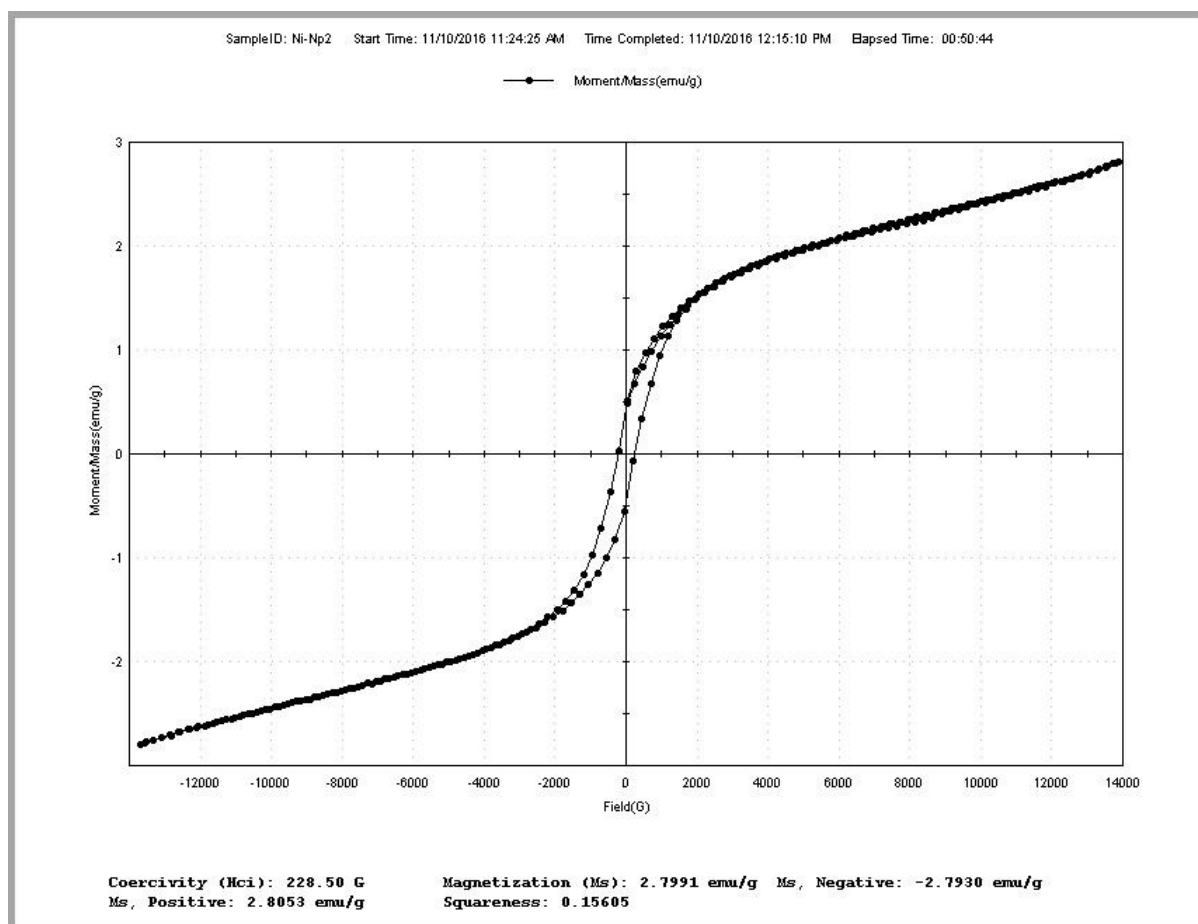
Hysteris loop of Co-NP



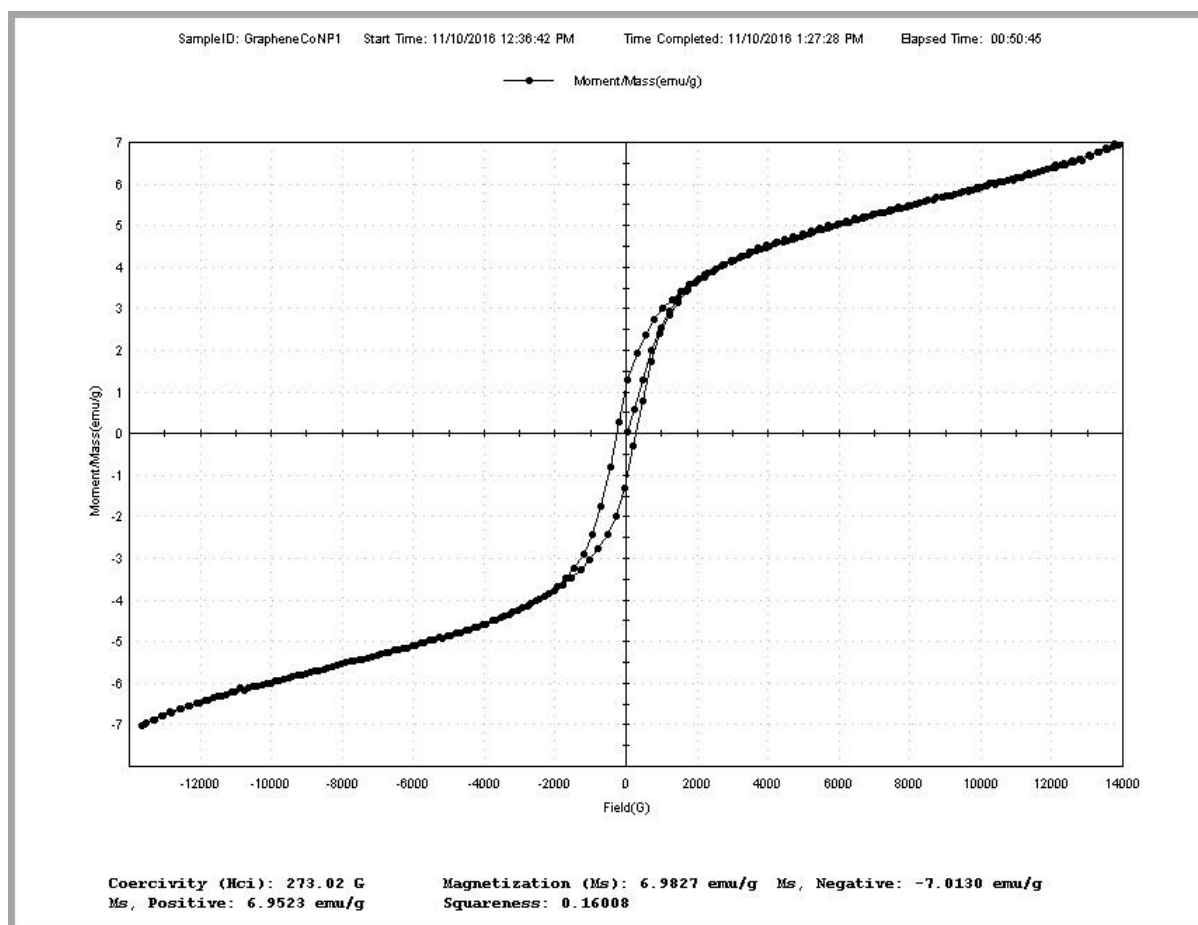
Coercivity (H_{ci}): 262.55 G
 M_s , Positive: 17.392 emu/g

Magnetization (M_s): 17.450 emu/g M_s , Negative: -17.509 emu/g
Squareness: 0.21368

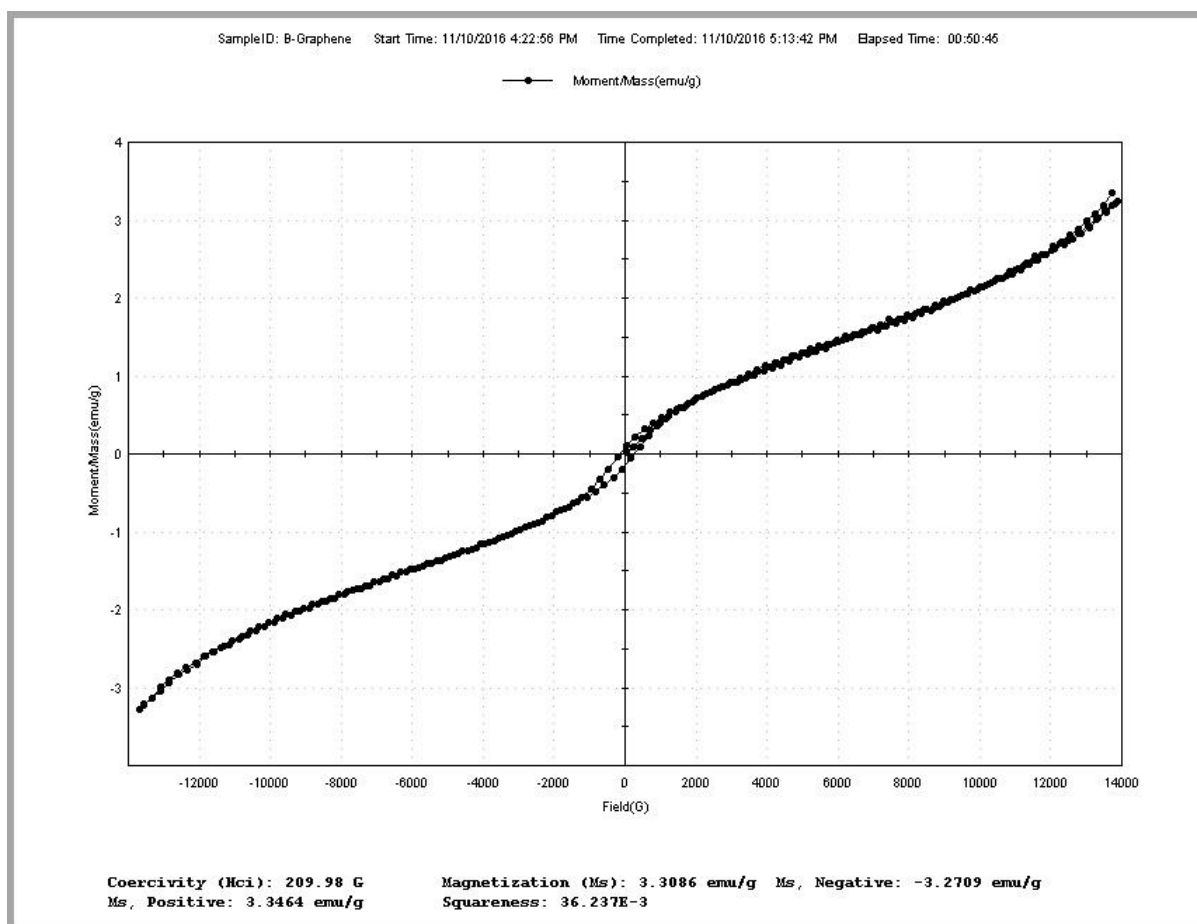
Hysteris loop of FeCo-rGO



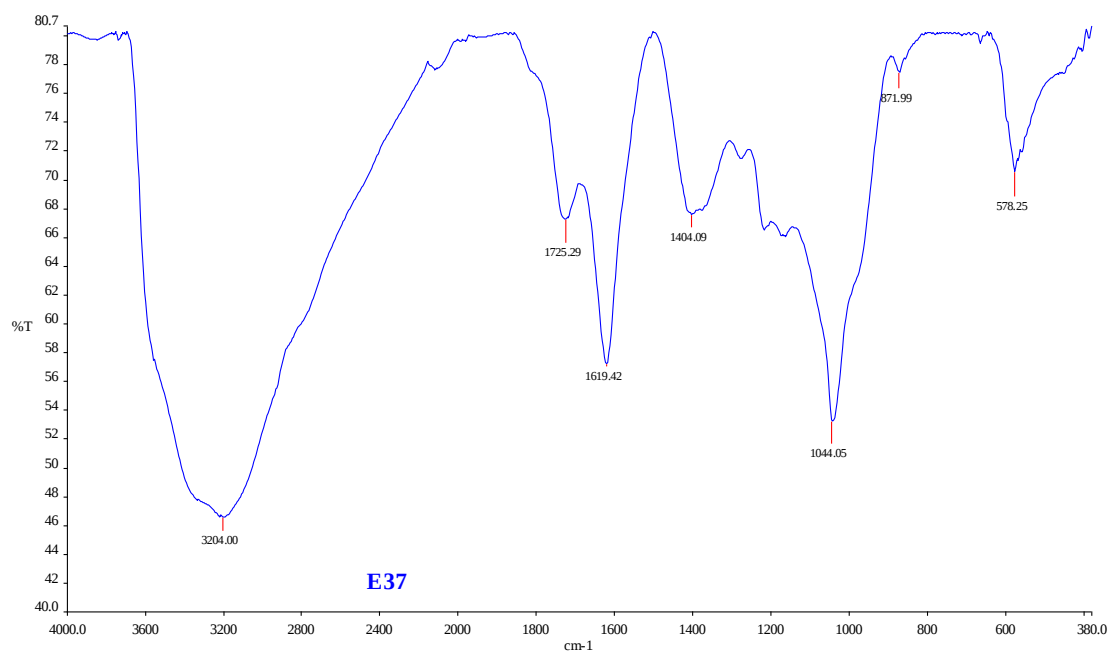
Hysteresis loop of Ni-rGO



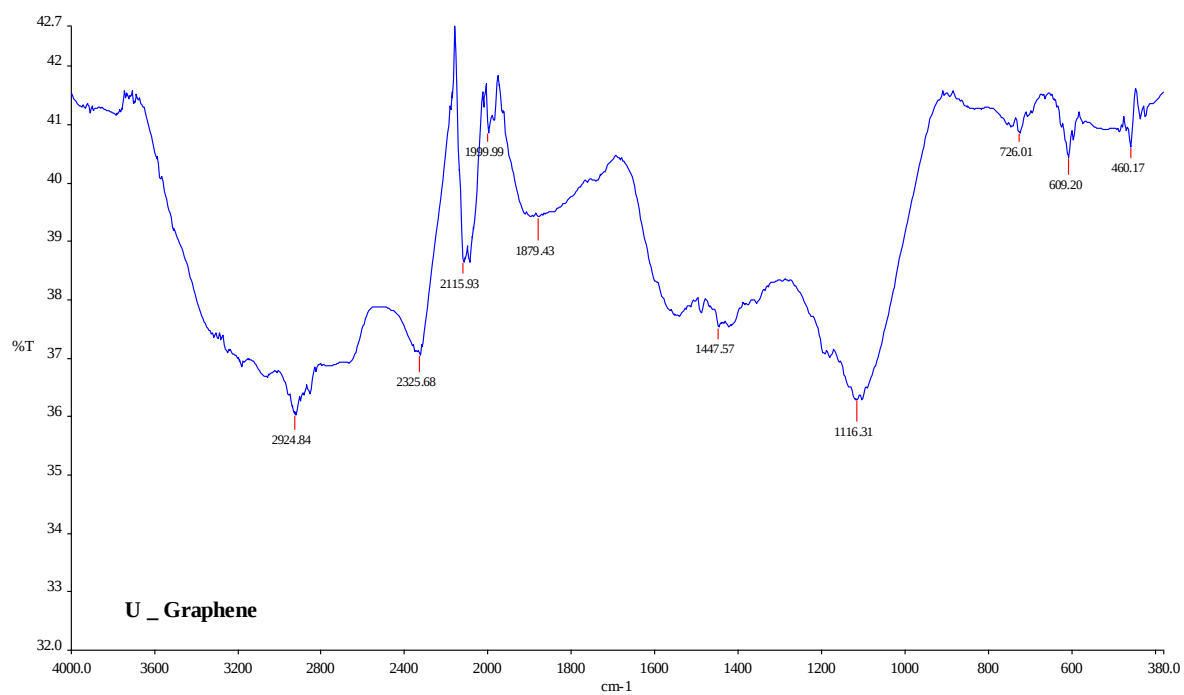
Hysteris loop of Co-rGO



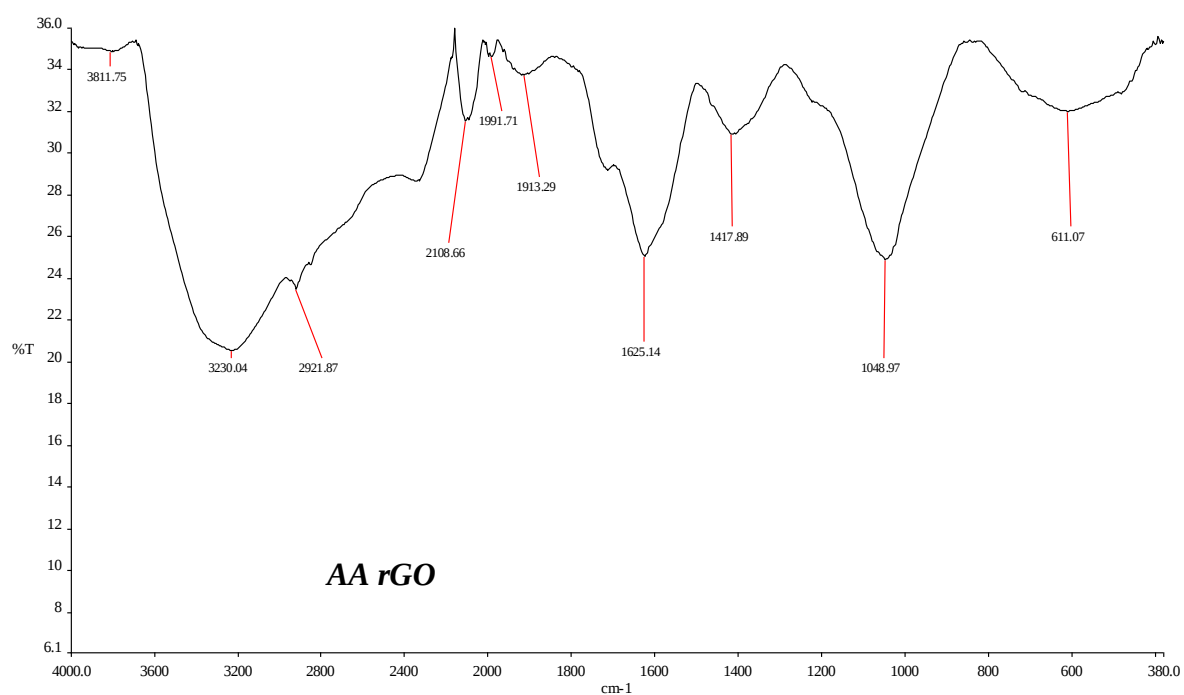
Hysteris loop of B-rGO



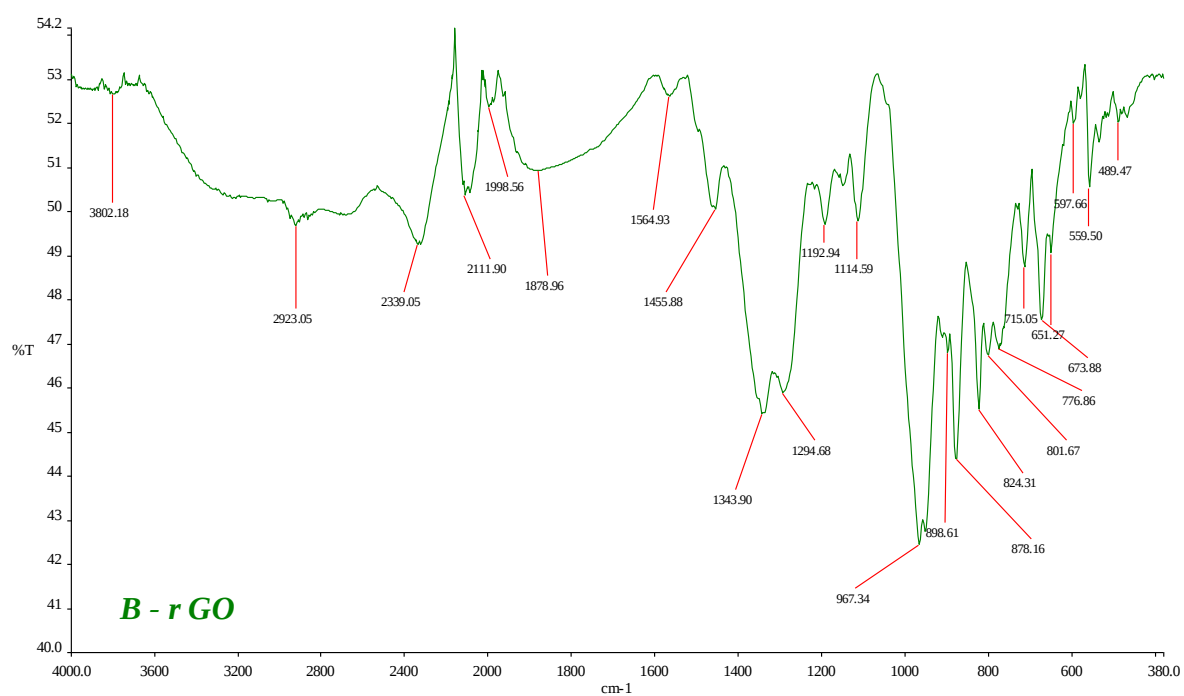
FTIR Spectrum of GO



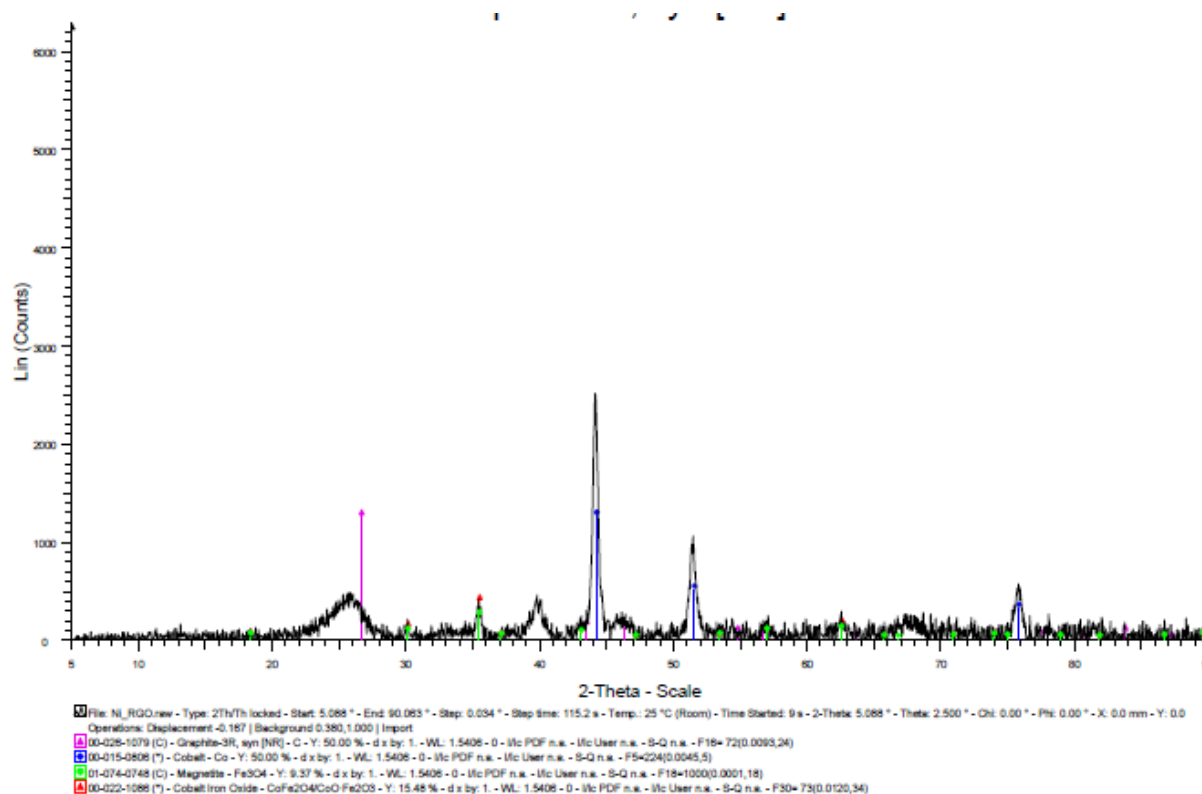
FTIR Spectrum of N-rGO



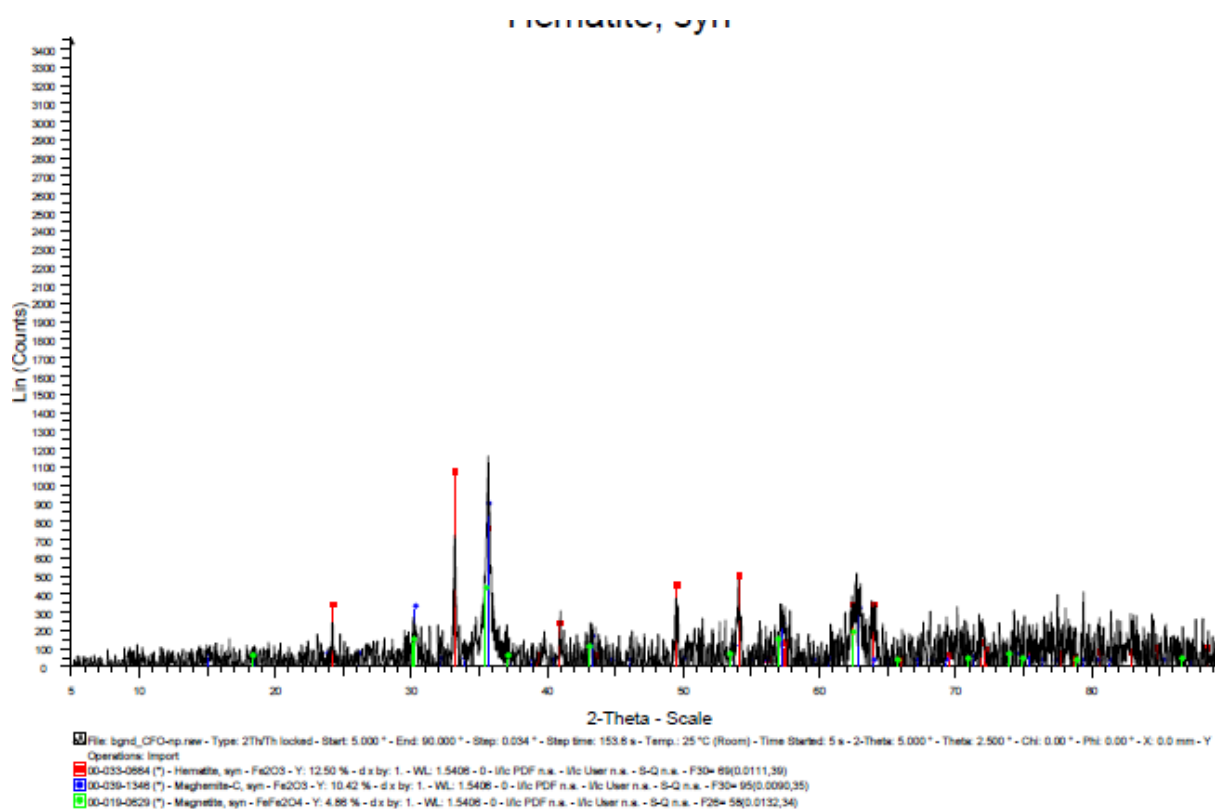
FTIR Spectrum of rGO



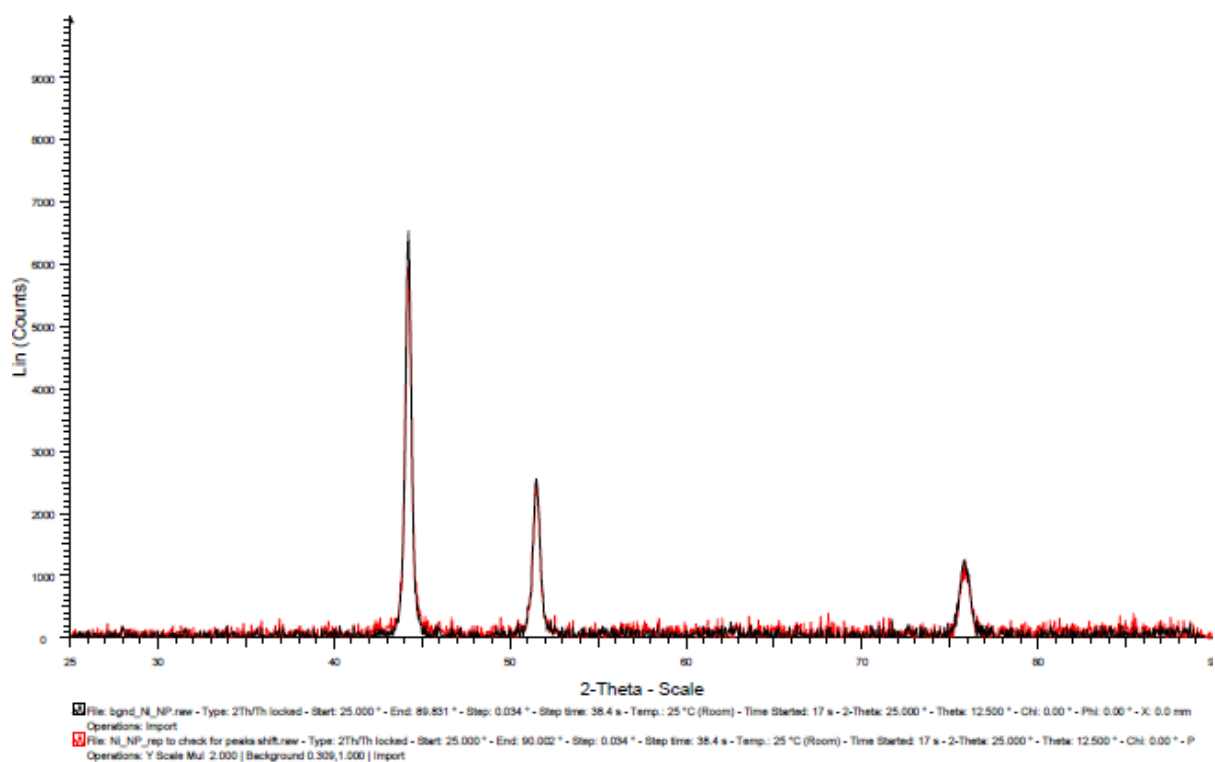
FTIR Spectrum of B-rGO



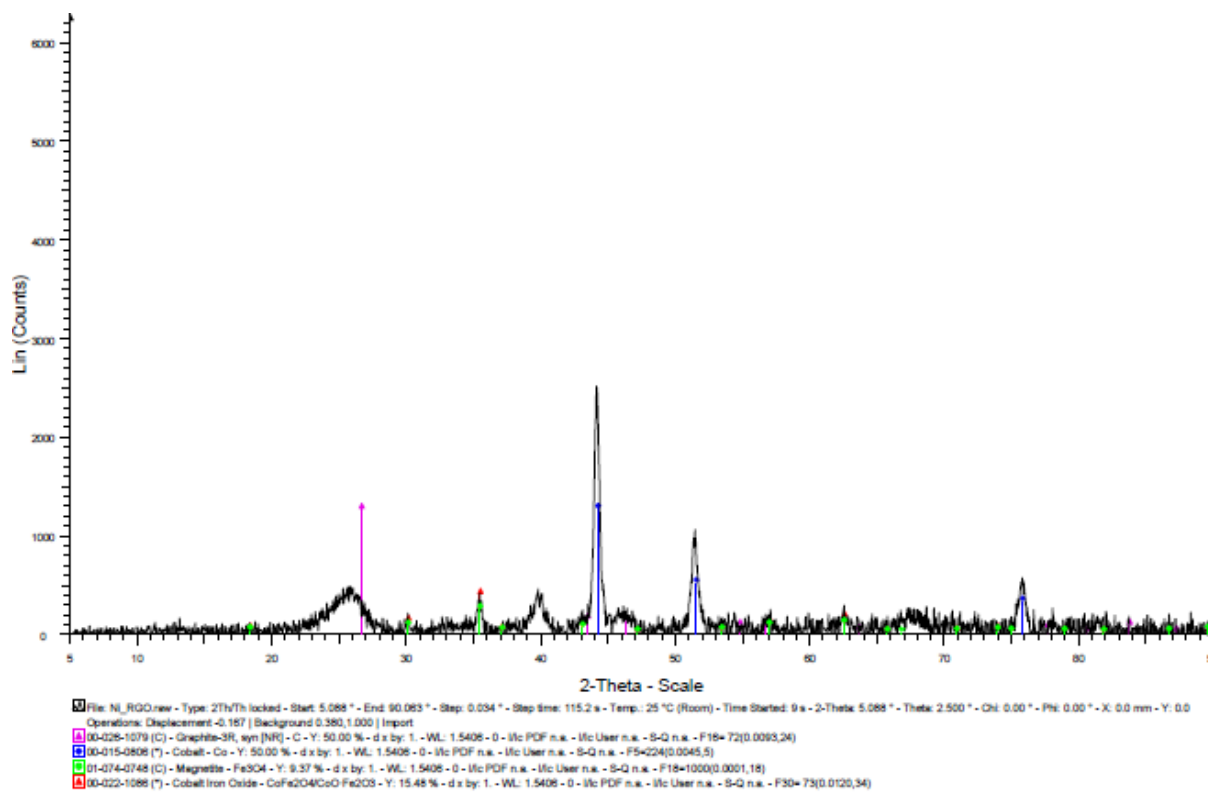
XRD of FeCo-rGO



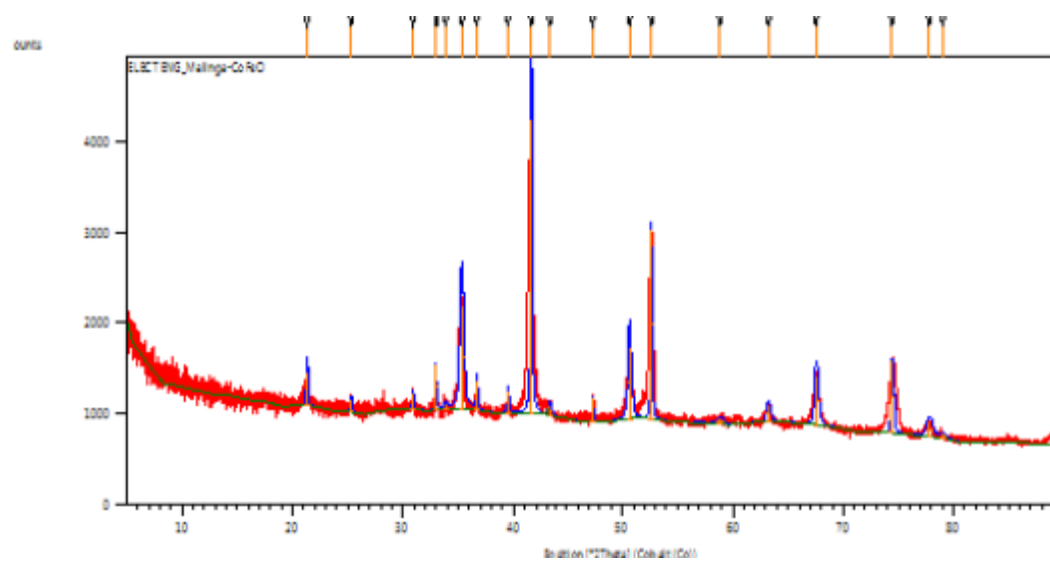
XRD of FeCoO-NP



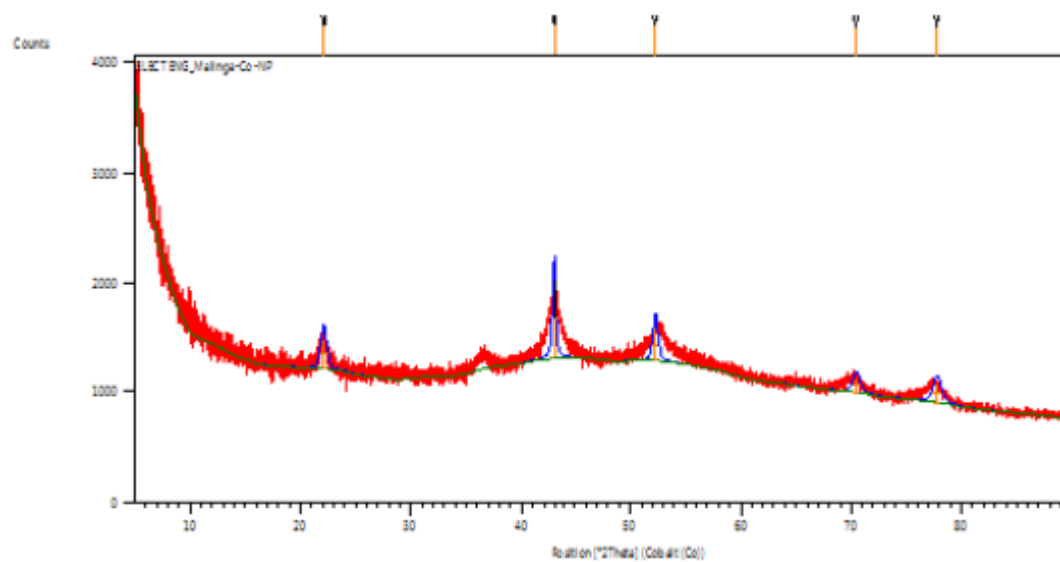
XRD of Ni-NP



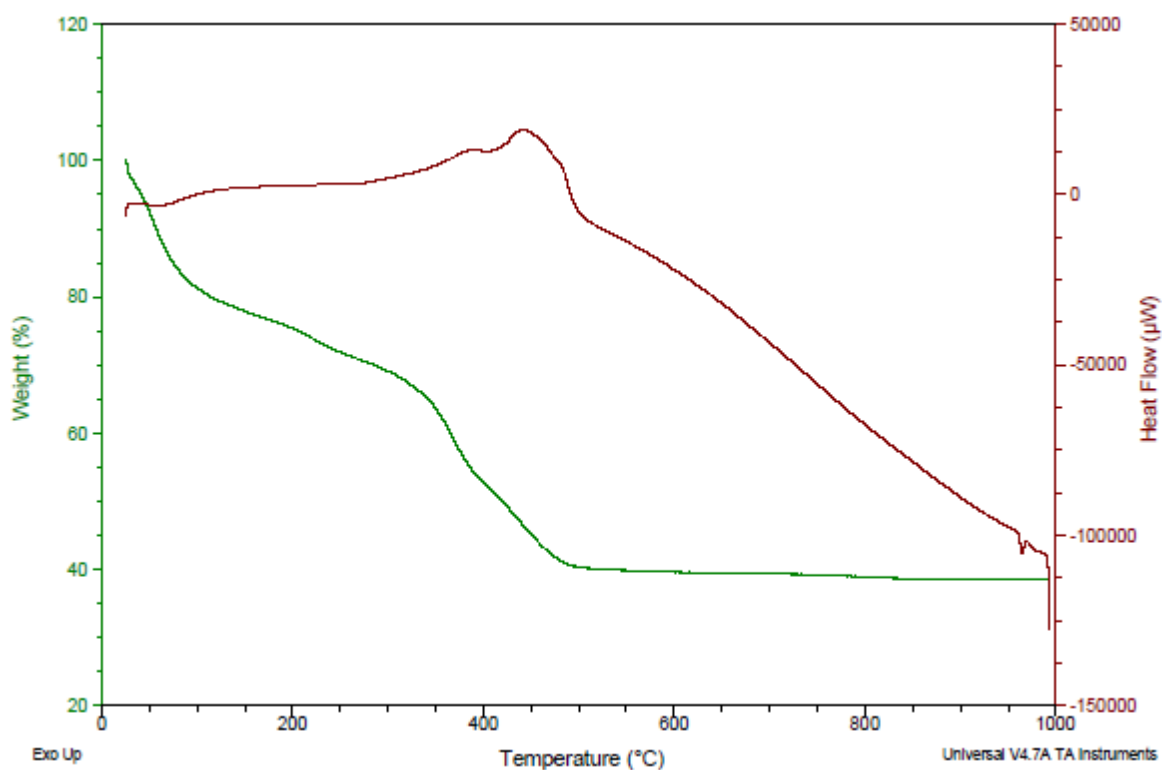
XRD of Ni-rGO



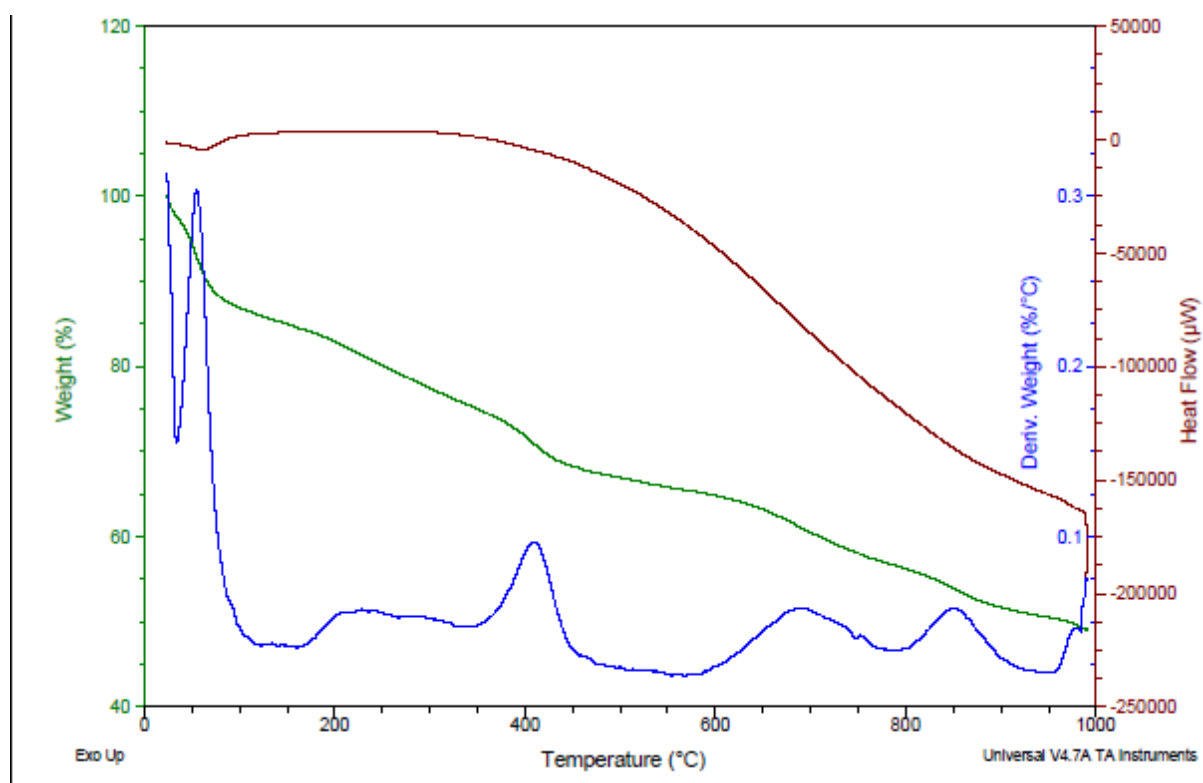
XRD of Co-NP



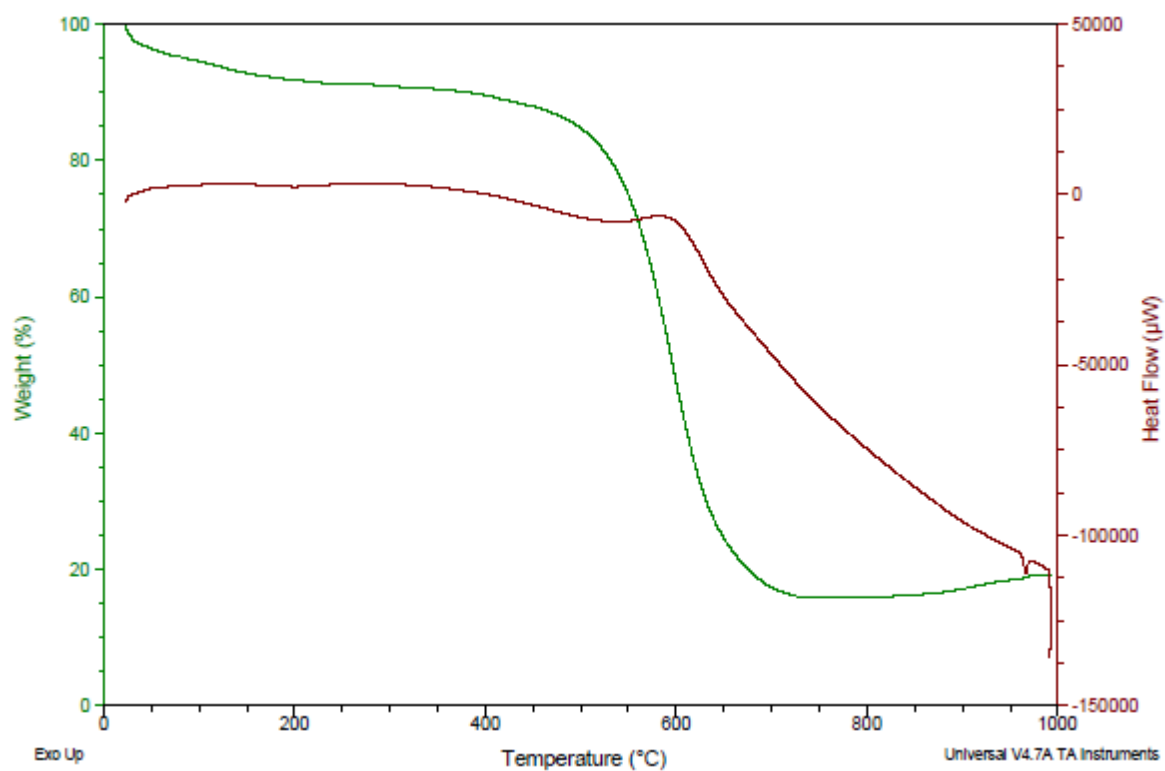
XRD of Co-rGO



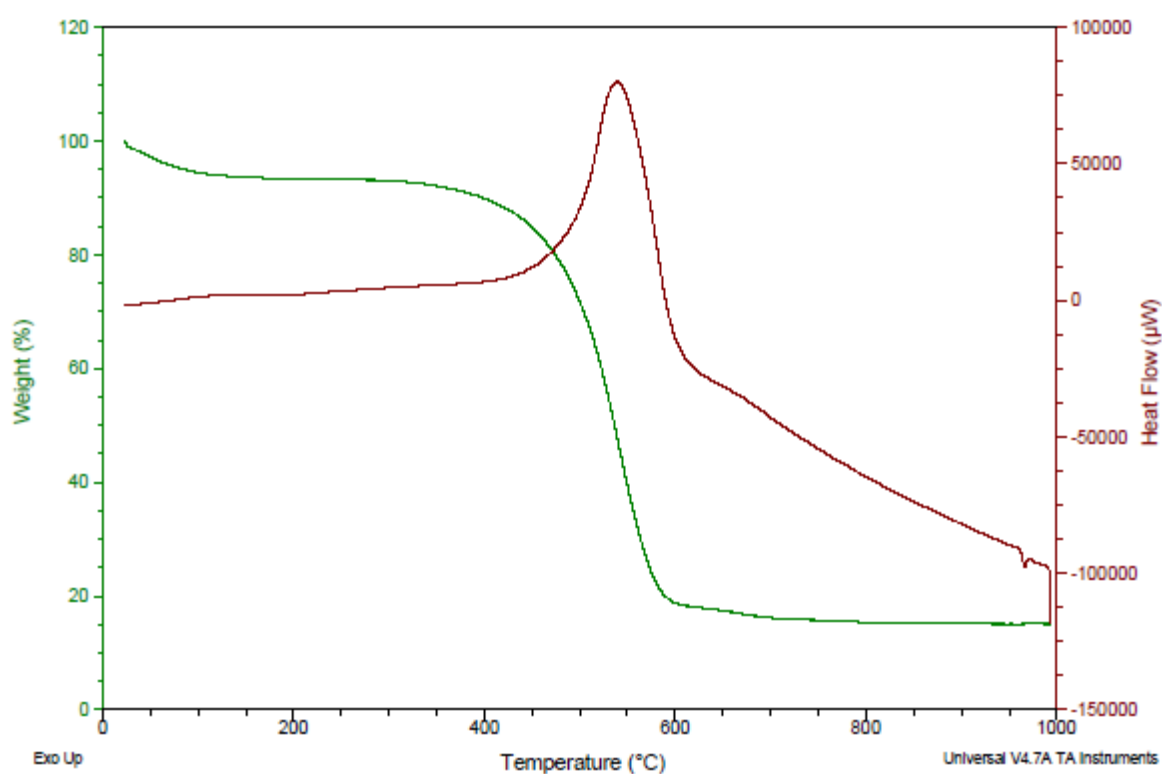
Simultaneous TGA and DSC of Ni-rGO



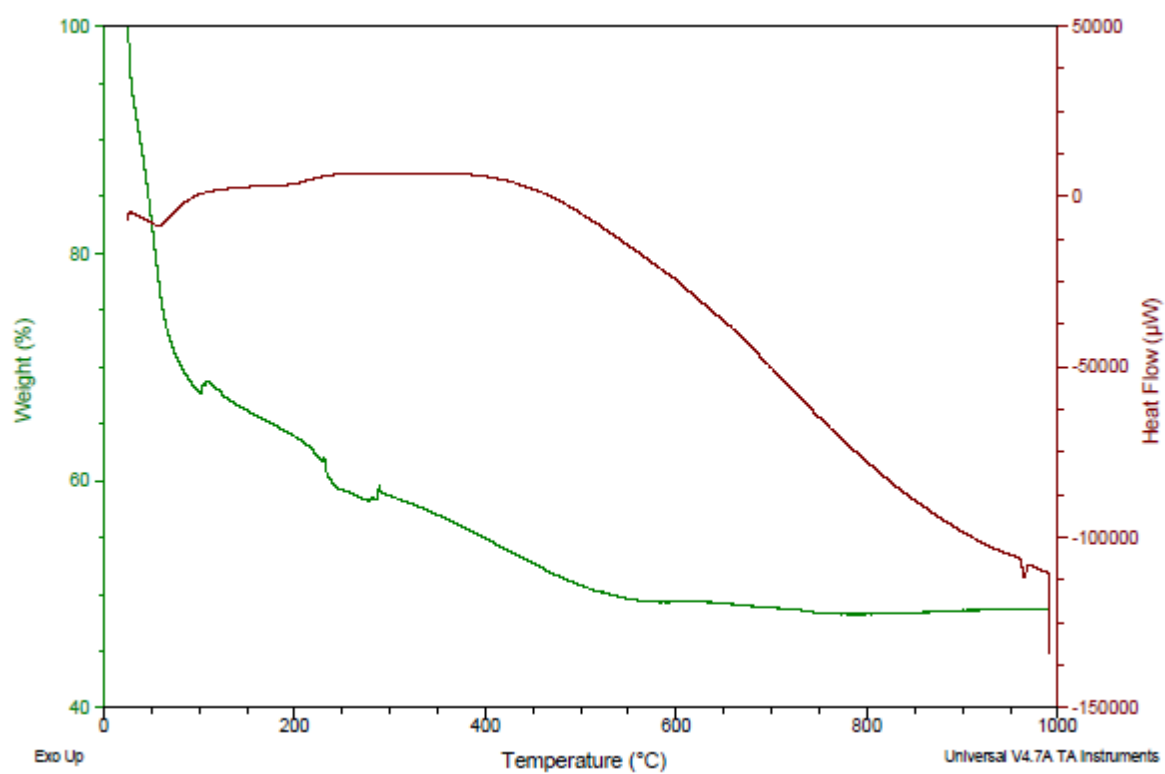
Simultaneous TGA and DSC of FeCo-rGO



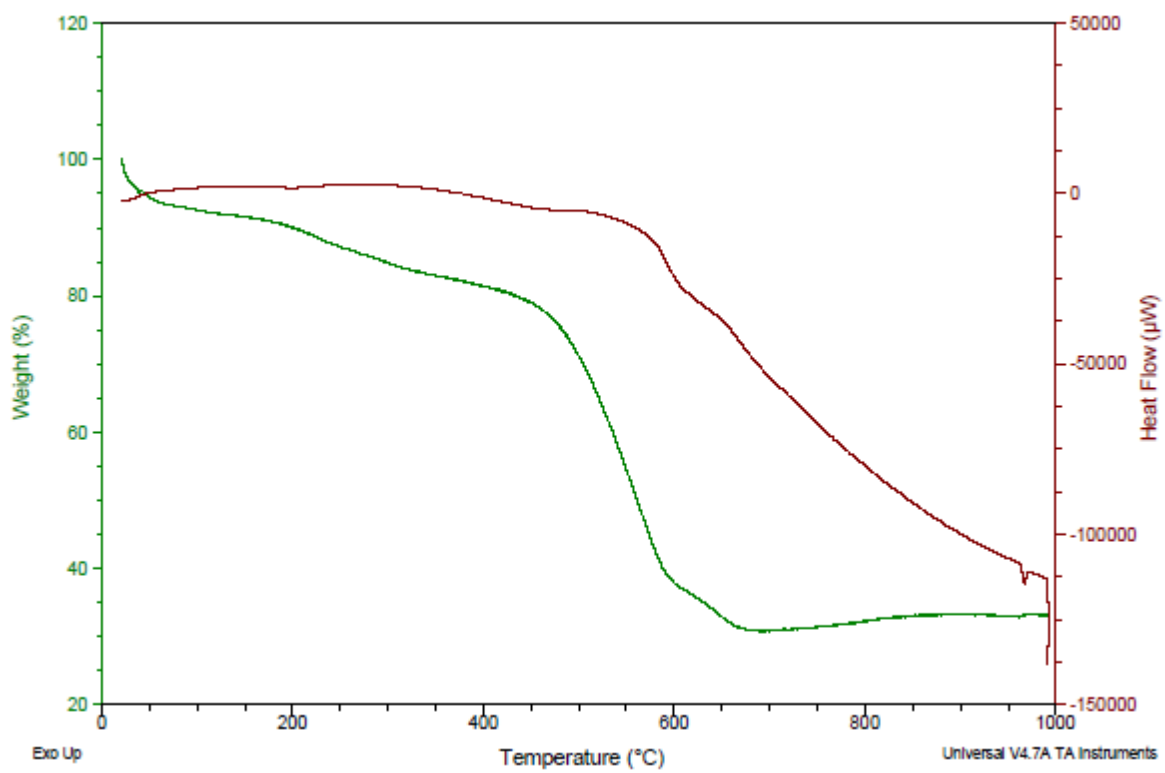
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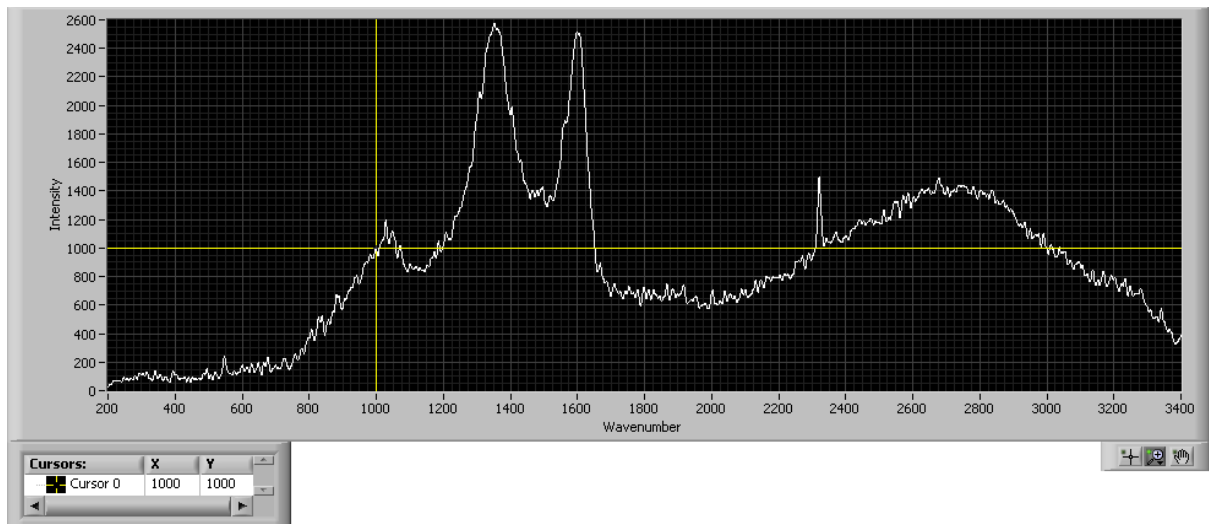
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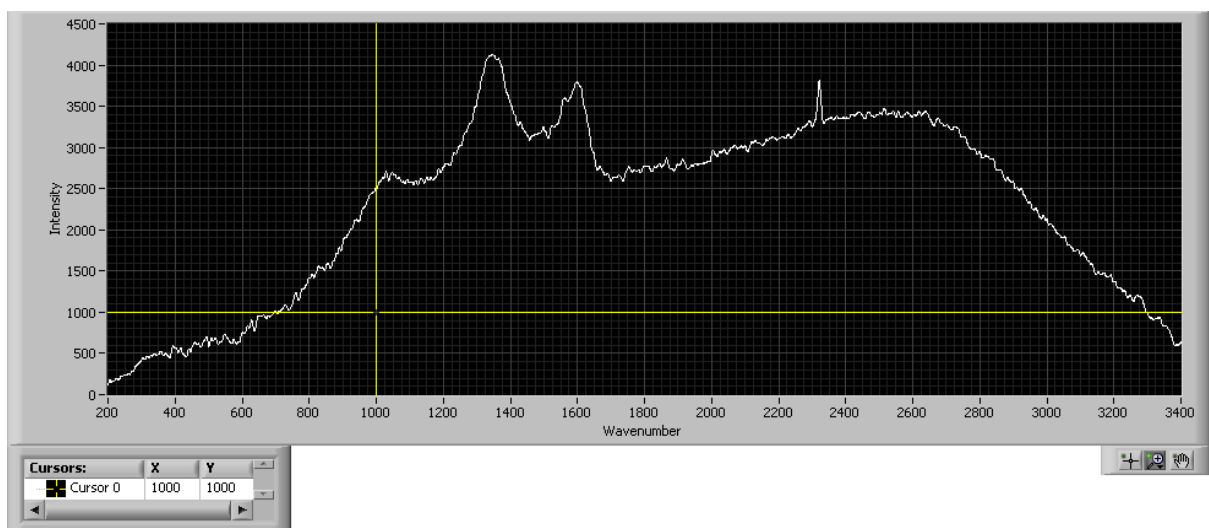
Simultaneous TGA and DSC of Co-rGO



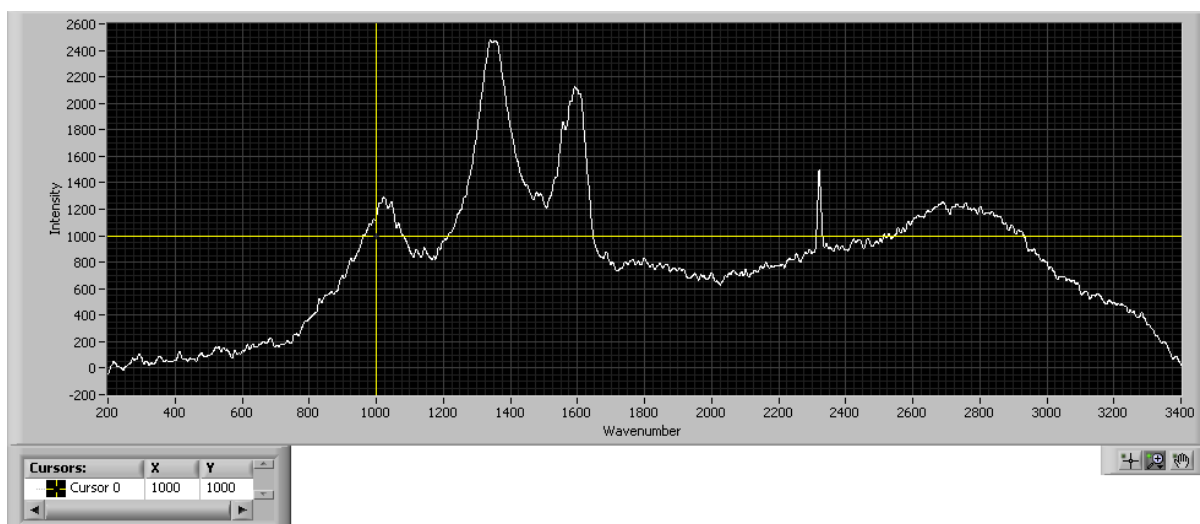
Simultaneous TGA and DSC of B-rGO



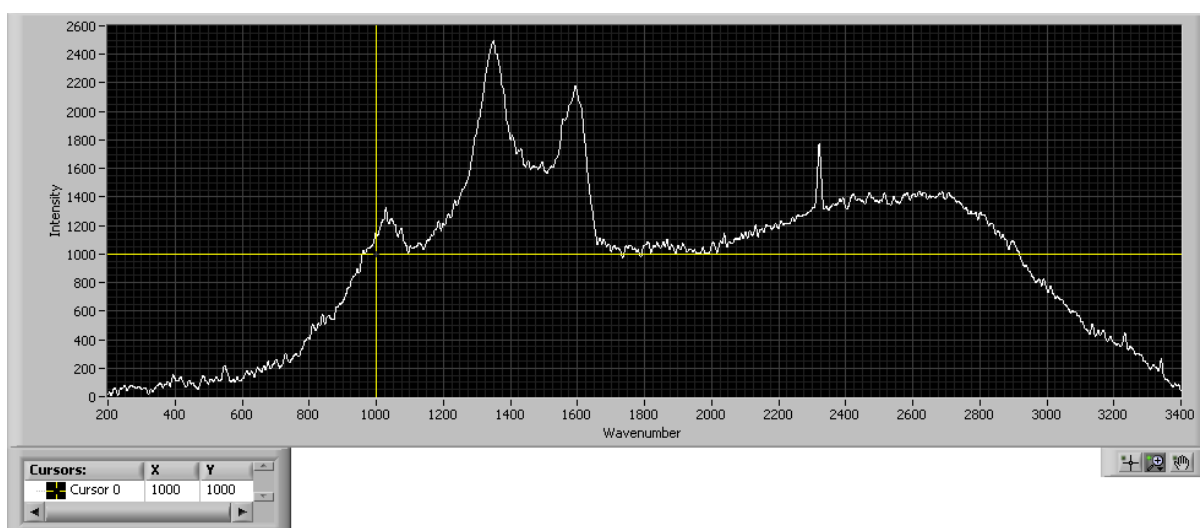
Raman of FeCo-rGO



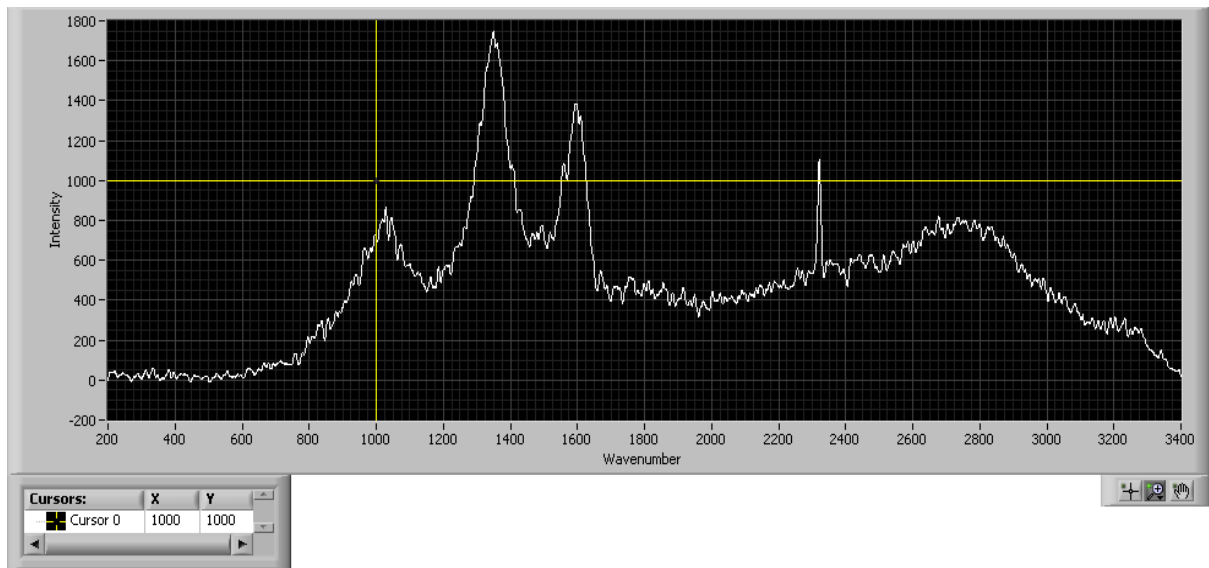
Raman of Ni-rGO



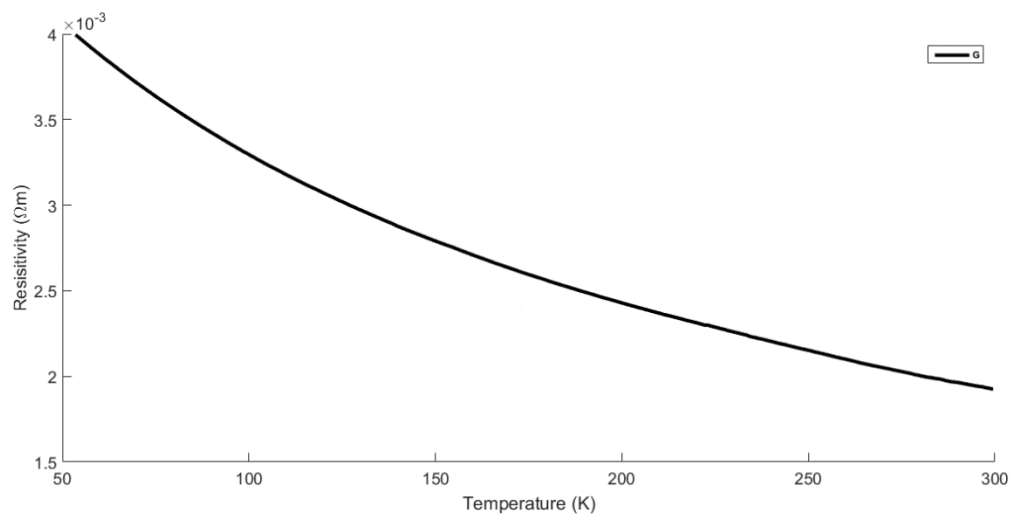
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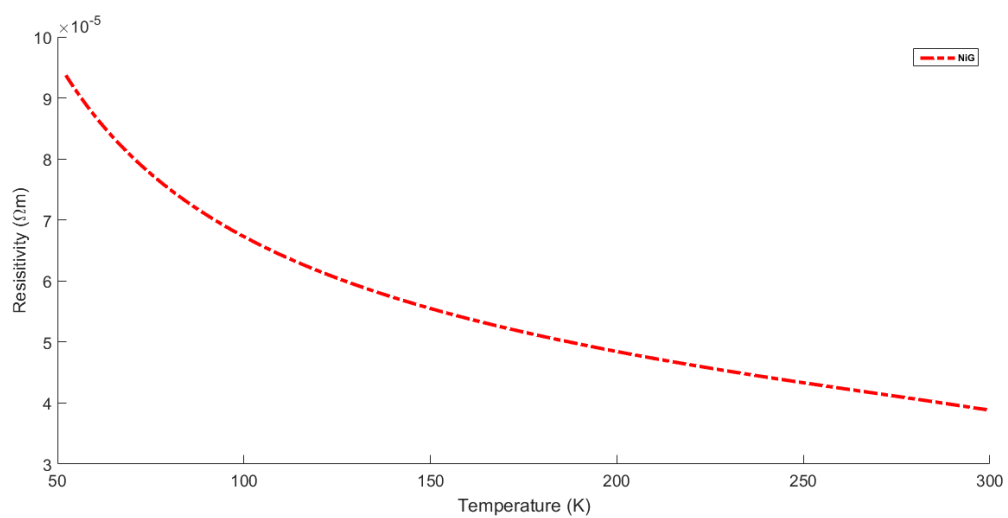
Raman of N-rGO



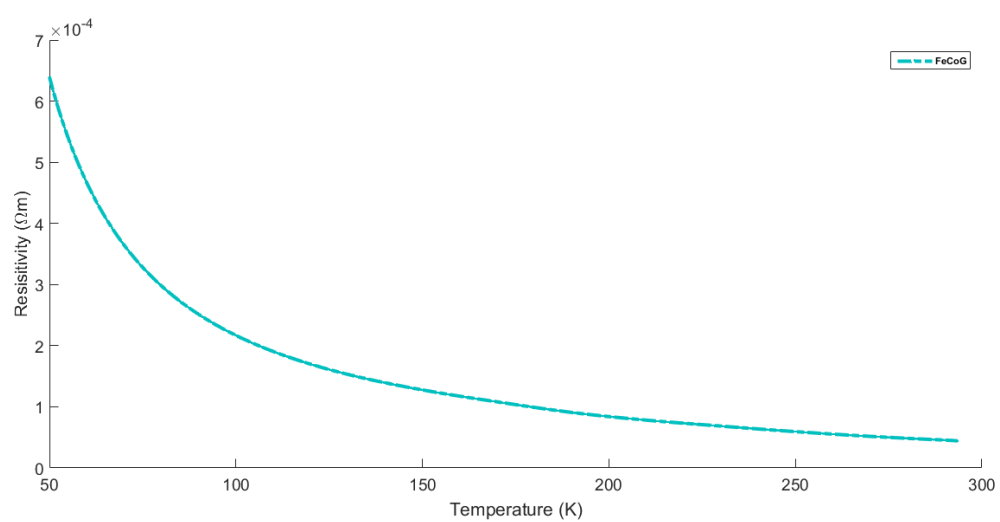
Raman of rGO



Conductivity of rGO



Conductivity of Ni-rGO



Conductivity of FeCo-rGO