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APHENE

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ABSTRACT

Synthesis of graphene from graphite was produced by electrolytic exfoliation using poly (sodium-4-styrenesulfonate) as an effective electrolyte. Two graphite rods were placed in an electrolysis cell filled with the electrolyte. As the result, we will obtain dry graphene powders and the dried sediment. Advantage of graphene has high mobility of charge carriers, unique transport performance, high mechanical strength, and extremely high thermal conductivity. It's suitable for many technological applications scanning and transmission electron microscopy and atomic force microscopy confirmed the existence of monolayer graphene sheets and stacks containing a few graphene sheets. Graphene powder will be characterized by FTIR, BET, and CV. Why we use graphene? It's because graphene has high electrical conductivity gives these materials consistently good performance over a wide range of voltage scan rates. Graphene has the potential to enable major advances in energy storage.

ABSTRAK

Sintesis graphene dari grafit dihasilkan oleh pengelupasan elektrolitik menggunakan poli (natrium-4-styrenesulfonate) sebagai elektrolit yang berkesan. Dua batang grafit ditempatkan dalam sel elektrolisis diisi dengan elektrolit. Sebagai hasilnya, kami akan mendapatkan serbuk graphene kering dan sediment. Kelebihan graphene mempunyai mobiliti tinggi kos pembekal, prestasi pengangkutan unik, kekuatan mekanik yang tinggi, dan konduktiviti terma yang sangat tinggi. Its sesuai untuk Mengimbas banyak aplikasi teknologi. Mikroskop penghantaran elektron, dan gaya atom mikroskopi membenarkan adanya lembaran graphene monolayer dan tumpukan mengandungi beberapa lembaran graphene. Serbuk graphene akan dianalisis yang dengan FTIR, BET, dan CV. Mengapa kita menggunakan graphene? kerana graphene mempunyai konduktiviti elektrik tinggi memberikan bahan-bahan ini konsisten prestasi yang baik atas berbagai-bagai nilai kadar scan voltan. Graphene mempunyai potensi yang tinggi untuk membolehkan kemajuan besar dalam simpanan tenaga super.

TABLE OF CONTENTS

	Page
SUPERVISOR'S DECLARATION	ii
STUDENT'S DECLARATION	iii
ACKNOWLEDGEMENTS	iv
ABSTRACT	v
ABSTRAK	vi
TABLE OF CONTENTS	vii
LIST OF TABLES	xi
LIST OF FIGURES	xiii
LIST OF ABBREVIATIONS	xx

CHAPTER 1 INTRODUCTION

1.1	Introduction	1
1.2	Problem Statement	2
1.3	The Objective of the Research	2
1.4	Scope of Research	2

CHAPTER 2 LITERATURE REVIEW

2.1	History of Graphene	3
	2.2.1 Grapehene	5
2.3	Supercapacitor	7
2.4	Poly (sodium-4-styrenesulfonate)	9
	2.4.1 Chemical Properties	10
2.5	Electrochemical properties of graphene	11

CHAPTER 3 METHODOLOGY

3.1	Introduction	13
3.2	Synthesis of graphene by electrolytic exfoliation	13
	3.2.1 List of materials.	13
	3.2.2 Procedure	14
3.3	Characterization of graphene	15
	3.3.1 Principal of (FTIR)	15
	3.3.2 Principal of (CV)	16

CHAPTER 4 RESULT AND DISUCSSION

4.1	Material Characterization	17
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CHAPTER 5 CONCLUSION AND RECOMMENDATION

5.1	Conclusion	21
5.2	Recommendation.	22

REFERENCES	23
-------------------	----

APPENDICES	24
-------------------	----

LIST OF TABLES

Table No.		Page
2.1	Table of Poly (sodium-4-styrenesulfonate)	9

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
FTIR	Fourier Transform Infrared Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
CV	Cyclic Voltammetry
GIC	Graphite Intercalation Compounds
EDLC	Electrochemical Double Layer Capacitance
2D	Two-Dimensional

LIST OF FIGURES

Figure No.		Page
2.0	Graphene is an atomic-scale honeycomb lattice made of carbon atoms.	5
3.1	Diagram of the apparatus for synthesis of graphene via electrolytic exfoliation.	13
3.2	Cyclic Voltammetry Circuit	16
4.1	Full Report Set (BET)	17
4.2	FTIR Spectra of Graphene	18
4.3	Cyclic voltammetric curves of the graphene composite electrode in Fe ²⁺ /Fe ³⁺ solution at various scan rates	19
4.4	Peak Current (I) Vs $\sqrt{\text{Scan Rate}}$	20

INTRODUCTION

THE ELECTROCHEMICAL STUDY OF GRAPHENE

1.0 INTRODUCTION

Generally, graphene is an atomic-scale honeycomb lattice made of carbon atoms. Graphene is the basic structural element of some carbon allotropes including graphite, charcoal, carbon nanotubes and fullerenes. It can also be considered as an indefinitely large aromatic molecule. Advantages of graphene properties that are high mobility of charge carriers, unique transport performance, high mechanical Strength, and extremely high thermal conductivity and it's suitable for many suitable technological applicant. The inherent properties of graphene appeal to many industries, including the electronics industry. As example as graphenebased electronics, composite materials, molecular gas sensors, and energy storage and conversion. All of these engineering applications demand massive production of high quality graphene materials.

There are many methods have been developed to produce graphene but by using highly efficient synthesis of graphene by electrolytic exfoliation from graphite, which can be easily scaled up for large-scale production to produce graphene.

Scaling-up production of graphene is still a big challenge. Graphene nanosheets are stable in aqueous solution. It will ready to be isolated as monolayer or multilayer graphene sheets. The capability to produce graphene in large quantity is the versatile practical applications of graphene.

1.1 Problem statement

There has been a lot of discussion over the years about using graphene as based ultracapacitors. Graphene is the one of most effective energy storage of capacitor. Encouraging result could be obtained from graphene that may have interesting properties that give this material consistently good performance. However, there are several aspects that we should take as our main problem. We should know how to synthesis graphene by electrolytic exfoliation method, characterized and analyze the electrochemical study of graphene as a supercapacitor. The extraction and analysis which is important to know the electrochemical study towards graphene as supercapacitor is a challenging issue and an impediment to expanded commercialization.

1.2 Objective of Research

- 1.2.1 To synthesize Graphene using electrolytic exfoliation method.
- 1.2.2 To characterize the obtain Graphene.
- 1.2.3 To study the electrochemical of graphene.

1.3 Scope of Research

The obtain graphene from synthesizing graphene is an electrochemical way to characterize physical and chemical properties of graphene. Thus it will enable us to dertermine the electrochemical properties of graphene towards supercapacitor.

CHAPTER 2

LITERATURE REVIEW

2.1 History of Graphene

The theory of graphene was first explored by P. R. Wallace in 1947 as a starting point for understanding the electronic properties of more complex. Hanns-Peter Boehm who described single-layer carbon foils in 1962. Graphene is most easily visualized as an atomic-scale chicken wire made of carbon atoms and their bonds. The crystalline or "flake" form of graphite consists of many graphene sheets stacked together. The basic structural element of some carbon allotropes including graphite, charcoal, carbon nanotubes and fullerenes. It can also be considered as an indefinitely large aromatic molecule, the limiting case of the family of flat polycyclic aromatic hydrocarbons. The term graphene first appeared in 1987 to describe single sheets of graphite as one of the constituents of graphite intercalation compounds (GICs); conceptually a GIC is a crystalline salt of the intercalant and graphene. The term was also used in early descriptions of carbon nanotubes, as well as for epitaxial graphene, and polycyclic aromatic hydrocarbons. Single layers of graphite were also observed by transmission electron microscopy within bulk materials in particular inside soot obtained by chemical exfoliation. A key advance in the science of graphene came when Andre Geim and Kostya Novoselov at Manchester University managed to extract single-atom-thick crystallites (graphene) from bulk graphite in 2004. The Nobel Prize in Physics for 2010 was awarded to Andre Geim and Konstantin Novoselov "for groundbreaking experiments regarding the two-dimensional material graphene".

Epitaxial graphene research evolved from work on carbon nanotubes. Early research showed that nanotubes had fabulous electronic properties, but the inability to manufacture well-controlled tubes and scale them up from single-tube transistors to large-scale integrated circuits has prevented serious technological applications. In 2001, Walt de Heer realized that two-dimensional graphene (essentially unrolled nanotubes) would have many of the same properties as carbon nanotubes, and this idea has opened the way to a new approach to carbon electronics.

A simple way to make graphene is to peel it off from a piece of graphite (the Geim approach). While this is easy, defect concentrations, structural disorder, poor electronic transport, and lack of scalability to large circuits make it a dead end for graphene electronics. A better approach, developed by de Heer and used by Graphene Works, is to start with silicon carbide, a wide-gap semiconductor. Using thermal sublimation, silicon is removed from the surface, leaving a carbon-rich interface that forms graphene sheets. This SiC-graphene system allows the lithographic patterning of, potentially, millions of seamlessly-connected graphene devices. This method of graphene production enables the scalability and ease of fabrication necessary in an electronic material.

2.2.1 Graphene

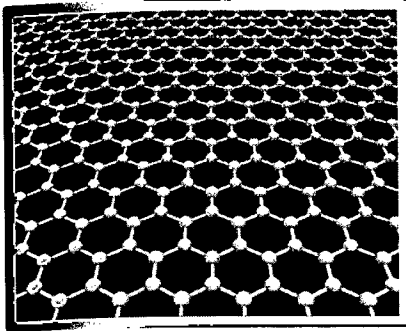


Figure 2.0 - Graphene is an atomic-scale honeycomb lattice made of carbon atoms.

Graphene is one of the hottest new material in physics today. The remarkable properties of graphene, such as its thermal conductivity, the mobility of its charge carriers and a high predicted specific surface area, together with the exotic transport phenomena it exhibits make it a serious candidate for numerous future studies.

Graphene, a monolayer form of carbon with a two-dimensional (2D) honeycomb lattice, has shown many interesting properties, including high mobility of charge carriers, unique transport performance, high mechanical strength and extremely high thermal conductivity and etc. In other words graphene can be describe as one atom-thick sheet of hexagonal carbon, is attracting interest due to its material properties. The 2-dimensional structure of pristine graphene results in electron-lattice interactions that differ from conventional 3-dimensional semiconductors and gives rise to electronic properties. Graphene also appeal to various kind of industry such as electronic industry, optoelectronics industry and many more.

Many methods have been developed to produce graphene. These include

- (i) Micromechanical cleavage - This approach can only produce a very limited quantity of graphene sheets for fundamental research.
- (ii) Epitaxial growth via ultra-high vacuum graphitization -This allows the fabrication of patterned graphene structure, which is desirable for electronics. However, the combination of high cost and small wafer size limits its application.

(iii) Synthesis of graphene by electrolytic exfoliation from graphite - graphene nanosheets are stable in aqueous solution, ready to be isolated as monolayer or multilayer graphene sheets. The capability to produce graphene in large quantity paves the way for versatile practical applications of graphene. This it is the method that I will use.

Graphene has many potential applications such as :

(i) Electronic device - Current electronic devices depend on material properties such as mobility and carrier lifetime. The high conductivity and high mobility of graphene make it a good fit for state-of the-art and next generation electronic application.

(ii) Fuel cells - hydrogen storage using graphene. Nissan Motor Co. Claims graphite with disordered stacks of graphene that allow large amounts of hydrogen stored for use in a vehicle fuel cell.

(iii) Composite material - The graphene imparts some improvement to the composite properties such as increased strength, increased conductivity, and increased thermal stability.

Besides that, charge storage device, medical devices, thermal application and many more are also been use a lot in industry nowadays.

2.3 Supercapacitor

Also known as ultracapacitors or electrochemical capacitors, utilize high surface area electrode materials and thin electrolytic dielectrics to achieve capacitances several orders of magnitude larger than conventional capacitors. super capacitors do not have a dielectric, an electrical insulator that can be polarized with the application of an electric field. Instead, the plates of a super capacitor are filled with two layers of the identical substance. This allows for separating the charge. Without the need for a dielectric, the plates are packed with a much larger surface area, resulting in high capacitance.

Ultracapacitors based on electrochemical double layer capacitance (EDLC) are electrical energy storage devices that store and release energy by nanoscopic charge separation at the electrochemical interface between an electrode and an electrolyte. Capacitors have an extremely high energy density compared to conventional dielectric capacitors. Able to store a large amount of charge which can be delivered at much higher power ratings than rechargeable batteries. There are several advantages of super capacitors relative to batteries:

1. Super capacitors also have a low cost per cycle.
2. Having a long life with little wear and tear occurring over many cycles.
3. Charge rapidly and use simple methods of charging.

There are several disadvantages of super capacitors relative to batteries :

- (i) Low energy densities.
- (ii) Holding less energy per unit of weight when compared to electrochemical batteries.
- (iii) Cells of super capacitors also have low voltages, requiring them to be connected in series with other super capacitors to obtain higher voltages.
- (iv) Lack of market penetration
- (v) Packaging problems, and self-discharge and High Cost.

Supercapacitors, is in electrically powered vehicles similar to rechargeable batterie is One of the uses of high-capacity electrolytics. Combining a supercapacitor with a battery in a single unit creates an electric vehicle battery. Electric vehicle batteries are long lasting, less expensive and much more powerful than other technologies.

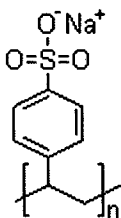
Hybrid vehicles and electric vehicles use a system of storing energy, which is rechargeable. The rechargeable electricity energy system, as it is commonly known, uses supercapacitors as its storage system. Flywheel energy storage also used as storage systems.

Another use of supercapacitors is in self-powered equipment, which can be powered by human muscle. The mechanically powered flashlight, driven by a supercapacitor, is a promising alternative to rechargeable batteries for electricity storage. Other applications include enhancing performance for portable fuel cells, such as generators, and improving the handling of batteries.

2.4 Poly (sodium-4-styrenesulfonate)

Poly(sodium-4-styrenesulfonate) is a type of polymer and ionomer based on polystyrene. It is the sodium salt of polystyrene sulfonic acid. This is used as effective electrolyte in synthesis of graphene by electrolytic exfoliation from graphite.

Table 2.1 – Properties of Poly (sodium-4-styrenesulfonate)

Identification	
Name	Poly(sodium-p-styrenesulfonate)
Synonyms	Poly(Sodium 4-Styrenesulfonate); Poly(sodium styrenesulfonate); 4-Ethenyl-benzenesulfonic acid sodium salt homopolymer
Molecular Structure	
Molecular Formula	$(C_8H_7NaO_3S)_n$
CAS Registry Number	25704-18-1
Properties	
Density	0.801
Melting point	460 °C (dec.)
Water solubility	SOLUBLE

2.4.1 Chemical properties

The polyanion is readily soluble in water, and insoluble in lower alcohols. The solid appears as white or off-white powder. It may be prepared by polymerization or copolymerization of sodiumstyrene sulfonate or by sulfonation of polystyrene. The harsh conditions used in this procedure lead to the occurrence of a number of side reactions. Double substitutions of the phenyl rings are known to occur, even with conversions well below 100%. Crosslinking reactions are also found, where condensation of two sulfonic acid groups yield a sulfonyl crosslink. On the other hand, the use of milder conditions such as acetyl sulfate leads to incomplete sulfonation. Recently, the atom transfer radical polymerization (ATRP) of protected styrenesulfonates has been reported, leading to well defined linear polymers, as well as more complicated molecular architectures.

2.5 Electrochemical properties of graphene

Physics of monolayer and bilayer graphene from a theorist's perspective. We discuss the physical properties of graphene in an external magnetic field, reflecting the chiral nature of the quasiparticles near the Dirac point with a Landau level at zero energy. We address the unique integer quantum Hall effects, the role of electron correlations, and the recent observation of the fractional quantum Hall effect in the monolayer graphene.

The quantum Hall effect in bilayer graphene is fundamentally different from that of a monolayer, reflecting the unique band structure of this system. The theory of transport in the absence of an external magnetic field is discussed in detail, along with the role of disorder studied in various theoretical models. We highlight the differences and similarities between monolayer and bilayer graphene, and focus on thermodynamic properties such as the compressibility, the plasmon spectra, the weak localization correction, quantum Hall effect, and optical properties.

Confinement of electrons in graphene is nontrivial due to Klein tunneling. Various theoretical and experimental studies of quantum confined structures made from graphene. The band structure of graphene nanoribbons and the role of the sublattice symmetry, edge geometry and the size of the nanoribbon on the electronic and magnetic properties are very active areas of research. Also, the effects of substrate interactions, adsorbed atoms, lattice defects and doping on the band structure of finite-sized graphene systems.

The best known carbon crystal is diamond, whose hardness and high dispersion of light make it useful for industrial applications and jewelry. Under ambient pressures and at room temperature, however, the most stable form of carbon is graphite, which is used as an industrial lubricant and as the 'lead' in pencils. Graphite is a layered material in which each layer consists of a sheet of carbon atoms forming hexagonal structures similar to benzene rings. A monolayer of graphite is called graphene, and a carbon nanotube is a cylinder made of graphene.

This leads to unique electronic and transport properties in graphene and carbon nanotubes, such as the absence of backscattering, which causes metallic carbon nanotubes to behave as perfect conductors even in the presence of scatterers. Graphene and nanotubes will continue to attract attention because of their considerable potential for device applications as well as their purely scientific interest.

CHAPTER 3

METHODOLOGY

3.1 Introduction

Electrochemical synthesis of graphene sheets is a one step treatment by using electrolytic exfoliation. In this case, two high purity graphite rods are used as electrodes. In the electrochemical cell they are immersed in the electrolyte bath. Before starting the experiments, several things needed to be done in order to run the experiments smoothly and accurately. Basically, all the instrument and the material should be in good form. The obtain graphene will be analyze using Infrared Spectroscopy (IR), Surface Area Measurement (BET) and Cyclic voltammetry (CV)

3.2 Synthesis of graphene by electrolytic exfoliation

3.2.1 List of materials.

There are several material that will be use in this method that is :

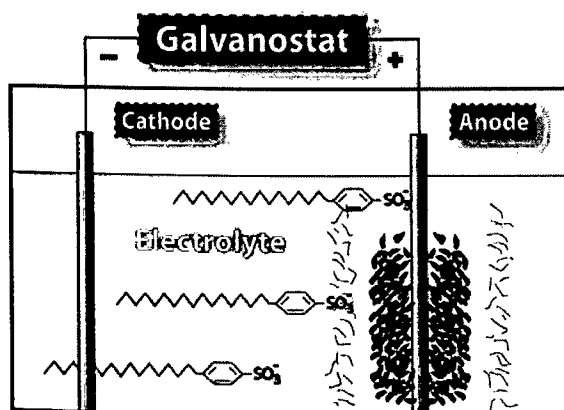
High purity graphene rod (electrode)

Poly (sodium-4-styrenesulfonate)

Deionized water

Ethanol.

Constant potential of 5 V (DC voltage)



Source: Highly efficient and large scale synthesis of graphene by electrolytic exfoliation (2009)

Figure 3.1 – Diagram of the apparatus for synthesis of graphene via electrolytic exfoliation.

3.2.2 Procedure

At 1st Poly (sodium-4-styrene) will be dissolve in deionized water to form electrolyte. Two graphite rod places in electrolysis filled with the electrolytic. A constant potential of 5 V (DC voltage) was applied to the two electrodes. A diagram of the synthesis apparatus is shown in Fig. 1. After 24hours of electrolysis, black product gradually appeared at the positive electrode (anode). Then the product dispersion was taken from the electrolysis cell. The dispersion was centrifuged at low speed (1000 rpm) to remove large agglomerates for 1hour. The top of the dispersion was then decanted. This graphene–PSS suspension is very stable in nature. After around 1-2 days storage, there is no any precipitation. To obtain dry graphene powders, the dispersion was washed with DI water and ethanol, and then dried in a vacuum oven at 80°C. The yield of graphene was estimated by weighting the dried graphene powders and the dried sediment. Our electrolytic exfoliation method results in producing graphene. Purpose method that will require to characterize the graphene by using Fourier Transform Infrared Spectroscopy (FTIR), Brunauer-Emmett-Teller (BET), Cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS).

3.3 Characterization of graphene

The obtained graphene will be analyzed by Fourier Transform Infrared Spectroscopy (FTIR) Technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. This technique is used to identify chemical compounds based on how infrared radiation is absorbed by the compounds' chemical bonds. FTIR or IR is ideal for identification and quantification of organic species even at trace levels. These include polymers (plastics), paints, binders, adhesives as well as unknown organic compounds, stains and solvents, even when tiny amounts of sample are only available.

IR spectroscopy correlation table that lists some general absorption peaks for common types of atomic bonds and functional groups will be taken as references to obtain functional group on FTIR result. Brunauer-Emmett-Teller (BET) or can be called Surface Area Analysis of nanoparticles can obtain many useful properties of nanoparticles rise from their small size, making it very important to be able to determine their surface area.

3.3.1 Principles of FTIR

FTIR relies on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectrum. This absorption corresponds specifically to the bonds present in the molecule.

The background emission spectrum of the IR source is first recorded, followed by the emission spectrum of the IR source with the sample in place. The ratio of the sample spectrum to the background spectrum is directly related to the sample's absorption spectrum. The resultant absorption spectrum from the bond natural vibration frequencies indicates the presence of various chemical bonds and functional groups present in the sample. FTIR is particularly useful for identification of organic molecular groups and compounds due to the range of functional groups, side chains and cross-links involved, all of which will have characteristic vibrational frequencies in the infra-red range

3.3.2 Principal of Cyclic voltammetry

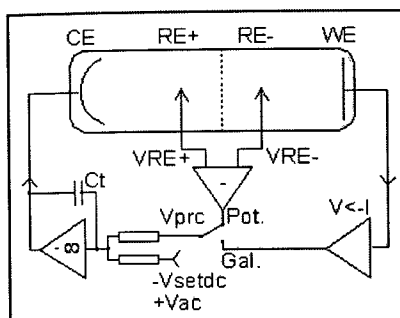


Figure 3.2 – Cyclic Voltammetry Circuit

Cyclic voltammetry (CV) is the most widely used technique for acquiring qualitative information about electrochemical reactions. It offers a rapid location of redox potentials of the electro active species.

For the moment we will focus on voltammetry in stagnant solution. Obviously there must be more than one electrode for current to flow. The electrode, the solvent, the background electrolyte and the reactant. In this case the voltage is swept between two values at a fixed rate, however now when the voltage reaches V_2 the scan is reversed and the voltage is swept back to V_1 . When the scan is reversed we simply move back through the equilibrium positions gradually converting electrolysis product (Fe^{2+}) back to reactant (Fe^{3+}).

The current flow is now from the solution species back to the electrode and so occurs in the opposite sense to the forward sweep but otherwise the behavior can be explained in an identical manner. For a reversible electrochemical reaction the CV recorded has certain well defined characteristics. For a reversible electrochemical reaction the CV recorded has certain well defined characteristics. The peak currents are proportional to the square root of the scan rate. The influence of scan rate is explained for a reversible electron transfer reaction in terms of the diffusion layer thickness

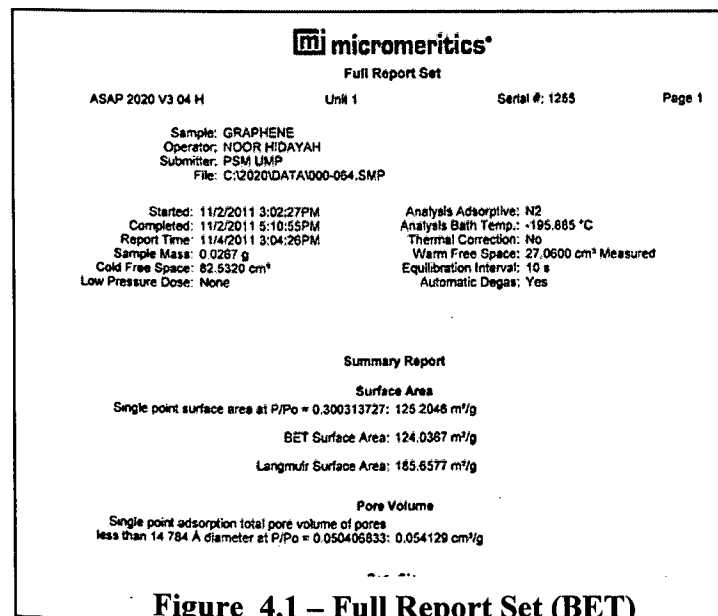
CHAPTER 4

RESULT AND DISCUSSION

4.1 MATERIAL CHARACTERIZATION

After electrolysis, stable graphene dispersion was obtained from synthesis of graphene by electrolytic exfoliation. This supernatant can be directly filtered to form graphene paper, or washed with DI water and ethanol, then dried in a vacuum oven to obtain bulk powders of graphene (as shown in Fig. 3.1). From the Figure 4.1, it show the result of measured by the N₂ absorption Brunauer-Emmett-Teller (BET) which determine the surface area of the graphene powders.

The Result show that the surface area obtained was 124.0367 m²/g while the pore size was 17.4560 Å. That result show that graphene has high surface area which h good electrical conductivity and very large (and in principle completely accessible) surface areas, are extremely promising candidates for EDLC ultracapacitors. Graphene cost-effective graphite and compatible with commonly used electrolyte systems. These materials could have the cost and performance that would dramatically accelerate their adoption in a wide range of energy storage applications. This is the best method producing graphene sheets in large quantity by electrolytic exfoliation of graphite under the assistance of PSS surfactant.



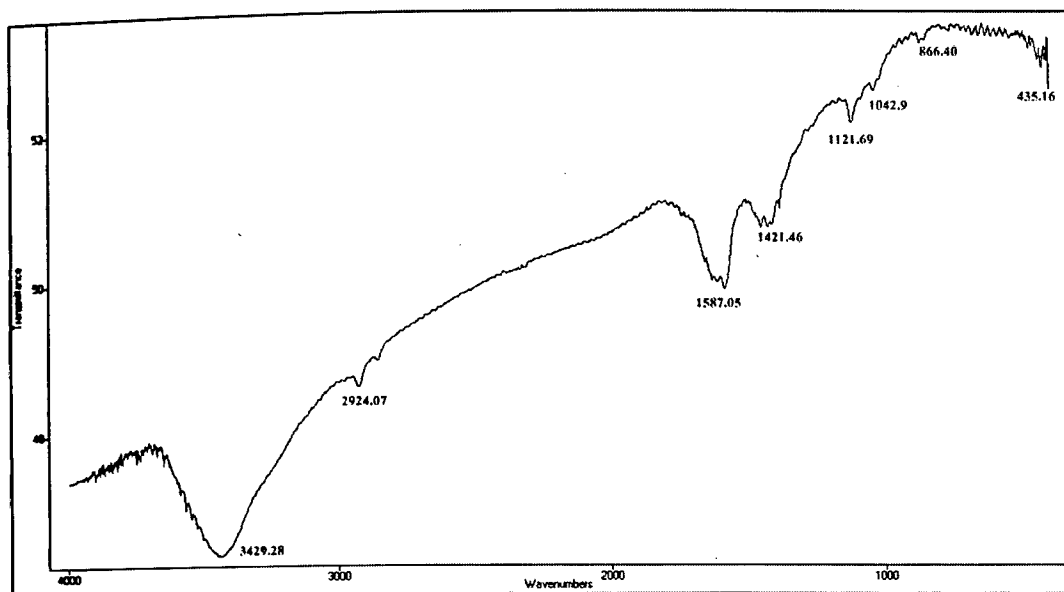


Figure 4.2 – FTIR Spectra of Graphene

Fig 4.2 shows FTIR spectra of graphene. The peak was found in graphene, the presence of different type of functional group of O–H stretching vibrations of adsorbed water molecules and structural OH groups was confirmed. The peak at 3429.28 cm^{-1} . The peak at 2924.07 cm^{-1} can be attributed to C–H stretching vibrations of the polymer chain. Peak at 1587.05 cm^{-1} , 1421.46 cm^{-1} , 1121.69 cm^{-1} , and 1042.9 cm^{-1} presence of carboxyl and epoxy functional respectively. The bands at 866.40 cm^{-1} originate from aromatic ring. Overall, functional group which presence in graphene is O–H group, C–H group, carboxyl and epoxy.

This result is obtained based on correlation table that lists some general absorption peaks for common types of atomic bonds which can be found in graphene. The dispersions can be easily cast into high-quality but with very different properties or functional group which can effect the properties of graphene which can enhance it to become good supercapasitor.