ELECTROCHEMICAL LIQUID COMPOSITES

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ABSTRACT

This project entitled electrochemical study of graphene-ionic liquid composites. A unique combination of excellent electrical, thermal and mechanical properties has made graphene a multi-functional reinforcement for polymers. The objectives of this project are: to fabricate graphene by electrolytic exfoliation and to characterize graphene-ionic liquid composites by physical, chemical characterization and electrochemical study. In this project, graphene will be fabricated by using electrolytic exfoliation method. Then, FTIR spectroscopy and BET analyzer were used to characterize exfoliated graphene. In order to measure electrochemical behaviour of graphene-ionic liquid composite, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used. Results show that graphene-ionic liquid composites exhibit linear redox diffusion on the surface, a good criteria for electrode material. This can be observed via cylic voltammetry. Graphene-ionic liquid composites also show good conductivity with low impedance value in the Nyquist plot. This material can be a new versatile soft material with numerous advantages.

ABSTRAK

Projek ini bertajuk kajian elektrokimia komposit graphene-cecair ionik. Gabungan sifat-sifat unik elektrikal, therma dan mekanikal yang sangat baik membuatkan graphene mempunyai banyak fungsi untuk diaplikasikan di dalam bidang polimer. Objektif kajian ini ialah untuk menghasilkan graphene daripada pengelupasan elektrolitik dan untuk mengkaji ciri-ciri komposit graphene-cecair ionik dari segi fizikal, sifat kimia dan kajian elektrokimia. Dalam projek ini, graphene akan dihasilkan dengan menggunakan kaedah pengelupasan elektrolitik. Kemudian, spektroskopi FTIR dan alat penganalisis BET akan digunakan untuk mengkaji ciri-ciri graphene. Bagi mengukur sifat elektrokimia graphene-cecair ionik, voltammetry berkitar (CV) dan spektroskopi rintangan elektrokimia (EIS) akan digunakan. Data menunjukkan komposit graphene-cecair ionik mempamerkan resapan redok yang selari pada permukaannya, kriteria yang baik untuk bahan elektrod. Ini boleh dilihat dari data CV. Komposit graphene-cecair ionik juga menunjukkan konduktiviti yang baik dengan nilai rintangan yang rendah dalam Nyquist plot. Bahan ini boleh menjadi bahan lembut serba boleh dengan pelbagai kebaikan.

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Z_{im}	Imagery component (ohm)
Z_{re}	Real component (ohm)

LIST OF ABBREVIATIONS

CVD	Chemical Vapour Deposition
SiC	Silicon Carbide
IUPAC	International Union of Pure and Applied Chemistry
AFM	Atomic Force Microscopy
HOPG	Highly ordered pyrolytic graphite
MBE	Molecular Beam Epitaxy
FET	Field-Effect Transistor
SiO_2	Silicone Oxide
MOSFET	Metal–Oxide–Semiconductor Field-Effect Transistor
MWCNT	Multi Walled Carbon Nanotubes
CNT	Carbon Nanotubes
EMIM-BF_4	1-ethyl-3-methylimidazolium
BMIM-OtF	1-butyl-3-methylimidazolium trifluoromethane
BMPyrr-Ntf_2	1-butyl-1-metyl pyrolidinium bis (trifluoromethylsulfonyl) imide
BMIM-PF_6	1-Butyl-3-methylimidazolium hexafluorophosphate
LUMO	Lowest Unoccupied Molecular Orbital
HOMO	Highest Occupied Molecular Orbital
FTIR	Fourier Transform Infrared
BET	Brunauer-Emmett-Teller
CV	Cyclic Voltammetry
EIS	Electrochemical Impedance Spectroscopy
PSS	Poly (sodium-4-styrenesulfonate)

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

In response to the changing global landscape, energy has become a primary focus of the major world powers and scientific community. There has been great interest in developing and refining more efficient energy storage devices. One such device, the supercapacitor, has matured significantly over the last decade and emerged with the potential to facilitate major advances in energy storage. So far, different materials such as various carbon materials, mixed metal oxides and conducting polymers have been used as supercapacitor electrode materials.

Particularly, carbon, in its various forms, has been used as electrode materials of supercapacitor, aiming at high specific capacitance together with high power density and energy density. Although, porous carbon materials have high specific surface arca, the low conductivity of porous carbon materials is limiting its application in high power density supercapacitor. Graphene, with one thick layer 2-D structure is emerging as a unique morphology carbon material with potential for electrochemical energy storage device applications due to its superb characteristics of chemical stability, high electrical conductivity and large surface area. In order to investigate graphene as supercapacitor material, its electrochemical behavior will be studied in this project. Its combination with ionic liquid will be studied to increase the composite's conductivity.

1.2 PROBLEM STATEMENT

There are few engineering applications demand massive production of high quality graphene materials. So, scaling-up production of graphene is still a big challenge. Therefore, it has been reported that highly efficient synthesis of graphene by electrolytic exfoliation from graphite, which can be easily scaled up for large-scale production. The prepared 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.

Current supercapacitors have energy densities well below the values required to provide power assists in various applications including hybrid electric vehicles or other high energy uses. Hence, recent efforts have been focused on the development of supercapacitors with high energy densities, which may be achieved both by enhancing the operating voltage of the devices and by improving the accessibility of the ions from the electrolyte to the active regions of electrode materials.

Toward this goal, graphene-based electrodes combined with ionic liquid electrolytes can provide an attractive alternative for supercapacitors since such combinations result in an optimal pairing of high specific surface area electrodes and wider operating potentials that may be afforded by some ionic liquid electrolytes. Generally, ionic liquids feature moderately high ion conductivity, non volatility, high decomposition temperatures, and wide electrochemical stability windows, and many ionic liquids are being considered as electrolytes to increase supercapacitor operating voltages. Despite the potential of ionic liquids as electrolytes, further work is needed to explore their potential for supercapacitors assembled with graphene- ionic liquid based electrodes.

1.3 OBJECTIVE OF RESEARCH

There are two objectives of this research:

a) To synthesize graphene using electrolytic exfoliation method.
b) To determine electrochemical behavior of graphene-ionic liquid composites.

1.4 SCOPE OF RESEARCH

Ionic liquid have attracted a great deal of attention due to their high thermal stability good conductivity, non flammability, suitable polarity, wide electrochemical window and recyclability. Furthermore, the physical and chemical properties of ionic liquids can be tuned by altering the cation, anion and attached substituent. This research presents the applications of graphene as active material and the addition of ionic liquid as graphene-ionic liquid composites, which combines the excellent natures of both graphene and ionic liquid. The main purpose of the work is to synthesize graphene by electrolytic exfoliation and study the electrochemical behavior of graphene-ionic liquid composites that can be apply to develop a new kind of supercapacitor which exhibits wide cell voltage and high energy densities and power.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Although the usage of graphite started 6000 years ago, when Marican in Europe used it to decorate pottery, the research about graphene, essentially an isolated single-atom plane of graphite, dates back to the 1960's when surprisingly higher basal-plane conductivity of graphite intercalation compounds were discovered compared to that of the original graphite [1-3].

While the scientific community was excited about the discovery that might lead to a lighter, cheaper substitute for existing metal conductors, they were puzzled by the cause of the high conductivity of graphite intercalation compounds and cautious about the future applications. The research of graphene has grown slowly in late 20th century with the hope to observe superior electrical properties from thin graphite or graphene layers while obtaining graphene was considered to be a formidable task in both theoretical and experimental aspect. Figure 2.1 shows the structure of functionalized graphene.

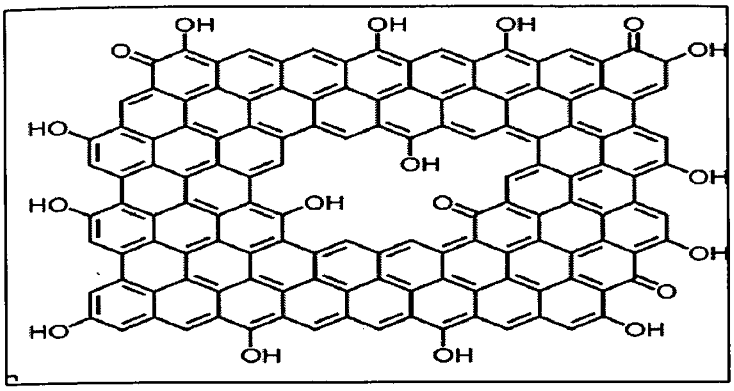

Figure 2.1: Structure of funtionalized graphene

In the graphite intercalation systems, large molecules were inserted between atomic planes, generating isolated graphene layers in a three-dimensional matrix. The subsequent removal of the larger molecules produced a mixture of stacked or scrolled graphene layers without the control of the structure. Various attempts were made to synthesize graphene including using the same approach for the growth of carbon nanotubes (producing graphite with 100 layers of graphene) [4], chemical vapor deposition (CVD) on metal surfaces (a few layers of graphene) [5, 6], or the thermal decomposition of SiC [7]. Although these approaches did not produce perfect monolayer graphene, the studies showed high-charge mobility of a few layers of graphene and the CVD approach has been optimized and become a major technique to produce graphene nowadays [8-10].

It was until 2004 that Andre Geim and Konstantin Novoselov used a method to isolate graphene, a method similar to what young Kaleb did, drawing with a piece of graphite or peeling graphite with adhesive tape till the graphene is found. Such a simple approach can provide high quality graphene with size in hundreds of microns [10]. These high quality graphene crystals realize the investigation of their amazing properties. Since then, the research of graphene including the control of the graphene layers on substrates, functionalizing graphene and exploring the applications of graphene has grown exponentially. Figure 2.2 shows the TEM images of graphene.

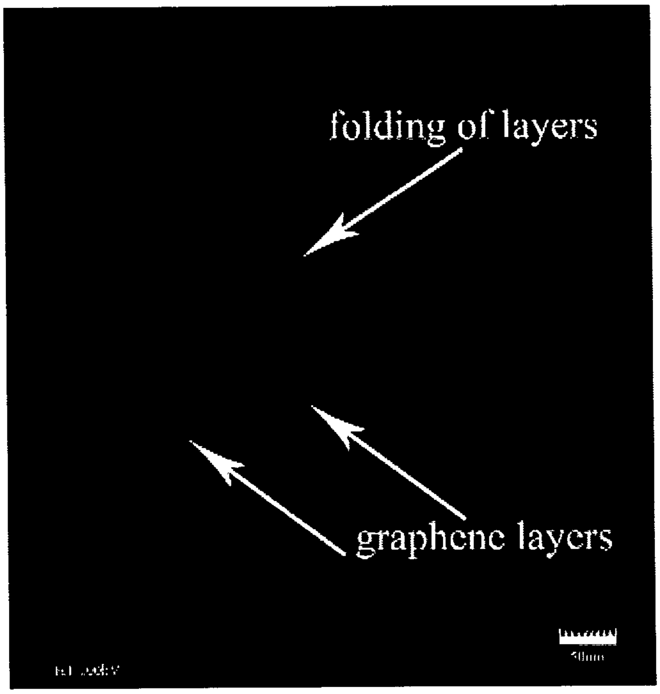

Figure 2.2: TEM images of graphene.

As shown in Figure 2.3, the number of publications on graphene (according to ISI Web of Knowledge^{SM}) increases dramatically after 2004. The term of 'graphene' was recommended by the relevant IUPAC commission to replace the older term 'graphite layers' that was unsuitable in the research of single carbon layer structure, because a three-dimensionally (3D) stacking structure is identified as 'graphite'. The recent definition of graphene can be given as a two-dimensional monolayer of carbon atoms, which is the basic building block of graphitic materials (i.e. fullerene, nanotube, graphite).

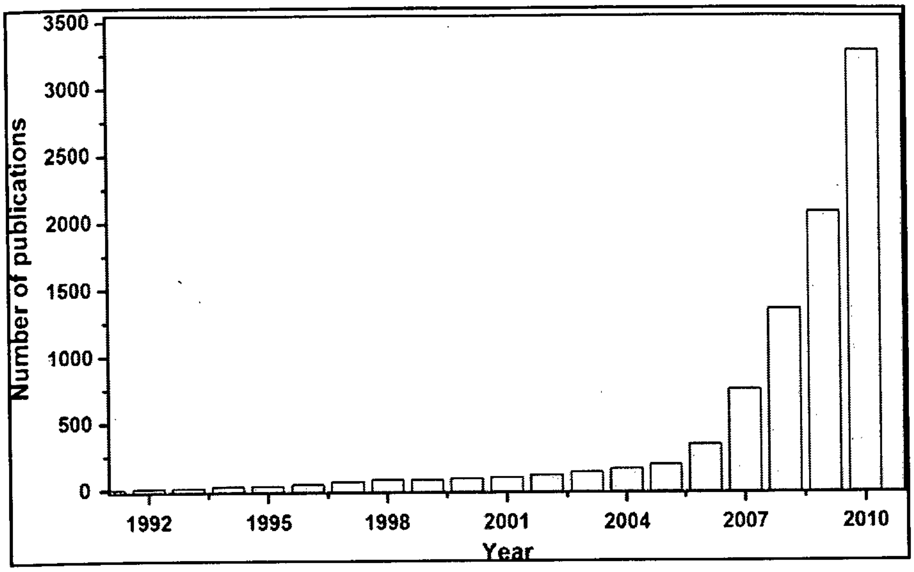

Figure 2.3: Number of publications on graphene in past 20 years.

2.2 GRAPHENE FABRICATION

The most common method of graphene fabrication is exfoliation which finds its roots with a technique that has been around for centuries which is writing with a graphite pencil. By writing with a pencil you create many graphene sheets spread over your paper. Unfortunately this method is uncontrollable and we are typically left with many sheets of varying thicknesses. If we want to study a single graphene sheet you need to locate it. The problem amounts to trying to find a needle in a haystack. A way around this problem was solved by Andre Geim's group in Manchester [11].

By gently rubbing or pressing a freshly cleaved graphite crystal on oxidized silicon wafer graphene flakes with the correct thickness of oxide, single atomic layers are visible under an optical microscope due to thin film interference effects [12, 13]. This technique simplifies the process of finding single graphene sheets but obviously limits this fabrication scheme to devices for research purposes. For the case of suspended graphene sheets as discussed in this thesis, this process may take approximate 1 hour to find relatively thin approximate 1-5 nm thick suspended graphene devices but could take several days or weeks to find a suitable single suspended layer.

There are recent attempts to improve the quality and yield of exfoliation techniques. These include stamping methods which use silicon pillars to transfer graphene flakes and electrostatic voltage assisted exfoliation which uses electrostatic forces to controllably separate graphene from bulk crystals [14, 15]. These are very recent developments and only time will tell whether they yield significant improvement over standard exfoliation.

Another common graphene fabrication technique is to disperse graphene from solution. In this method graphite flakes are sonicated in a solution and then dispersed onto a wafer. An AFM is used to locate individual sheets making this technique very time consuming relative to the optical detection scheme. Long sonication times are needed to break the graphite down and this typically results in small flakes. Recently a similar technique was used to fabricate graphene ribbons with nm-scale widths [16]. One of the difficulties in dispersing graphene from solution is separating the layers without breaking them. A way around this is to intercalate the graphite and dissolve it in a solvent. When the intercalant dissolves it separates the graphene sheets. This technique was shown to work effectively for graphene oxide. However, the success of similar techniques on graphene is limited due to the chemistry required to keep individual graphene sheets from aggregating in solution.

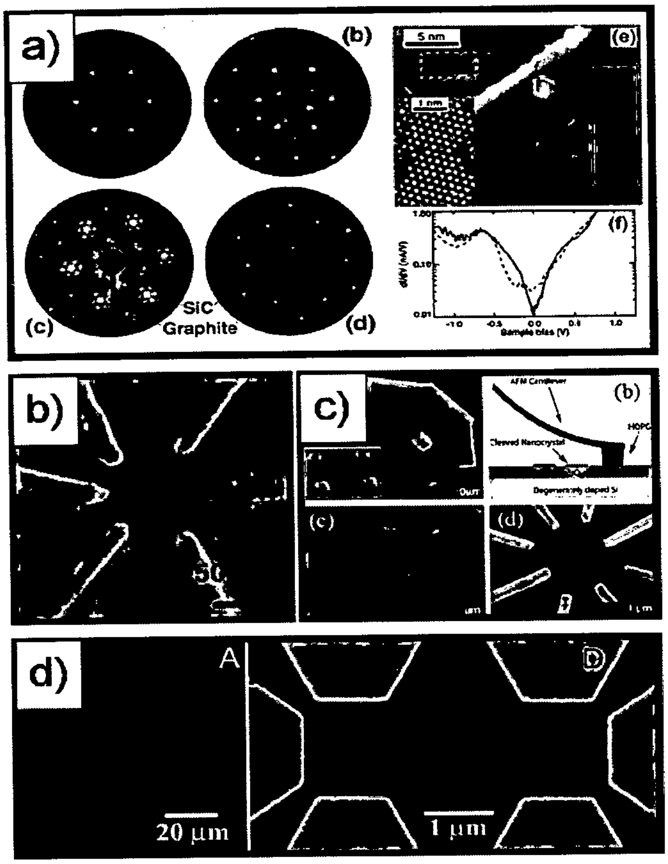

Figure 2.4: a) Growing few layer graphene on SiC

b) AFM image of a few layer graphene quantum dot fabricated by dispersion from solution.

c) Nanopencil used to extract few layer graphene flakes from HOPG.

d) Optical image of a few-layer graphene sheet.

The technique which currently seems to have the greatest potential for mass production is the direct growth of graphene. Typically this is accomplished by heating a SiC wafer which results in the partial graphitization of the upper layer [17]. However, controlling the number of layers as well as the grain sizes is difficult with this technique limiting the mobilities achieved so far with this form of graphene [18]. Furthermore, isolating single sheets is problematic and additional lithography is required to pattern electrostatic gates on top of the graphene. Making suspended mechanical structures from grown graphene has yet to be demonstrated.

Chemical vapor deposition (CVD) and molecular beam epitaxy (MBE) are two other potential routes to graphene growth. Carbon nanotubes and diamond are successfully grown using CVD and the preferred method of growth for high quality GaAs/AlGaAs heterostructures is MBE. For the time being, exfoliation remains the preferred method for most of the experimental research groups around the world. However as in diamond, wide spread applicability of graphene is limited by the crude and time consuming methods currently used to fabricate and isolate single graphene sheets. The research community is currently in need of a reliable and reproducible graphene fabrication method if graphene is ever to move beyond being a laboratory curiosity.

2.3 PROPERTIES OF GRAPHENE

In the past few years many fascinating properties were discovered through the investigation of pristine graphene including extremely high charge (electrons and holes) mobility (230,000 cm^2/Vs) with 2.3% absorption of visible light [19, 20], thermal conductivity (3000 W/mK), and the highest strength (130 GPa), and the highest theoretical specific surface area (2600 m^2/g) which has filled the research community with great enthusiasm. This section will focus on the graphene properties that lay foundation for their wider scope of applications. It is worth mentioning the important properties of graphene with single layer, bi-layers and few layers.

2.3.1 Electrical Transport Properties of Graphene

Pristine graphene, a two-dimensional honeycomb carbon lattice is a zero gap semiconductor. The sp_2 hybridized carbon atoms are arranged in hexagonal fashion in 2-dimensional layer. A single hexagonal ring comprises of three strong in-plane sigma bonds pz orbitals perpendicular to the planes. Different graphene layers are bonded by weak pz interaction while strong in-plane bonds keep hexagonal structure stable and facilitate de-lamination of 3-D structure (graphite) into individual graphene sheet just by applying mechanical stress. The scotch tape method micromechanically creates single layer of defect free graphene and provides a 2-D platform, to investigate many fundamental properties of this 2-D crystal. The high electronic conductivity in single layer is due to very high quality, i.e. low defect density of its crystal lattice. Defects in general act as scattering sites and inhibit charge transport by limiting the electron mean free path. There are evidences that pristine graphene is defect free, thus its conductivity must be affected by some extrinsic source.

Graphene is a potential material for the future generation electronic devices suffers from zero energy band gap even at the charge neutrality point, which is one of the hurdle for graphene to be useful as an electronic material, for example, in graphene-based FET. The zero band gaps do not allow its use in logic applications, which require frequent on/off switching. However, band structure of the graphene can be modified by lateral quantum confinement by constraining the graphene in nanoribbons [21-23] and in graphene quantum dots [24], and by biasing bi-layer [25-27] graphene. Band gap opening in both zigzag and armchair nanoribbons was observed and proven experimentally and theoretically which vary with the width of the ribbons and disorderness in the edges [28]. Doping and edge functionalization also change the band gap in nanoribbons [29]. It is important to note that the most of the primary work on graphene has been related to FET.

A schematic of the graphene-based FET is shown in Figure 2.5 consisting of the gate, a graphene channel connecting source and drain electrodes, and a dielectric barrier layer (SiO2) separating the gate from the channel. In most of the studies 300 nm SiO2 layer is used, under the graphene acted as a dielectric layer and silicon acted as a back gate. Due to large parasitic capacitance of the 300 nm SiO2 layer, it finds difficulty in integration with other electronic components. Thus, top gated graphene-based device have been developed in 2007 [30]. Top gated graphene-based MOSFETs have been prepared using exfoliated graphene [30-33], CVD grown graphene on Ni and Cu substrate [34] and epitaxial graphene [35, 36], whereas, Al_2O_3, SiO_2 and HfO_2 dielectric materials have been used for top gate [27].

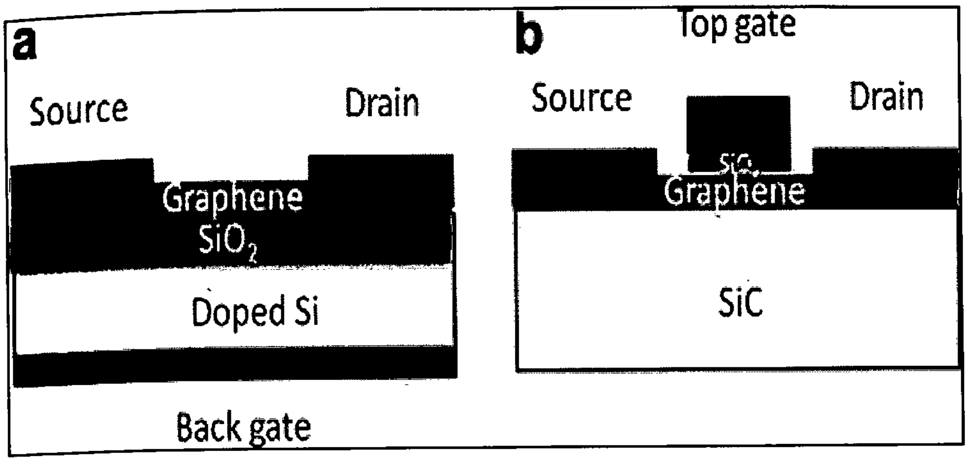

Figure 2.5: (a) Schematic diagram of back gated and (b) Top gated graphene field effect devices. The perpendicular electric field is controllable by applied back-gate voltage (Vg) and the top gate voltage (Vtop).

2.3.2 Thermal Properties of Graphene

Application of the graphene has been envisioned for electronic devices. Where, thermal management is one of the key factors for better performance and reliability of the electronic components. Considerable amount of heat generates during the device operation needs to be dissipated. Carbon allotropes such as graphite, diamond, and carbon nano tubes have shown higher thermal conductivity due to strong CAC covalent bonds and phonon scattering. Earlier carbon nanotubes are known for the highest thermal conductivity with room temperature value 3000 W/mK for MWCNT [37] and 3500 W/mK for single wall CNT [38]. However, a large thermal contact resistance is the main issue with CNTs based semiconductor.

Recently the highest room temperature thermal conductivity up to 5000 W/mK for the single layer graphene has been reported (pure defect free graphene) [39] whereas for supported graphene conductivity is 600 W/mK. Conductivity of the graphene on various supports is not studied much but their effect was predicted by Klemens [40]. A new approach of determining thermal conductivity of a thin atomic layer of graphene is shown in Figure 2.6 [40]. In this method a suspended graphene layer is heated by laser light (488 nm), the heat propagated laterally towards the sinks on side of the corner of the flakes.

The temperature change was determined by measuring the shift in the graphene G peak using co focal micro-Raman spectroscopy which acts as a thermometer. The thermal conductivity is affected by factors such as defects edge scattering and isotopic doping. In general, all these factors are detrimental to the conductivity due to phonon scattering at defect and phonons modes localization due to the doping.

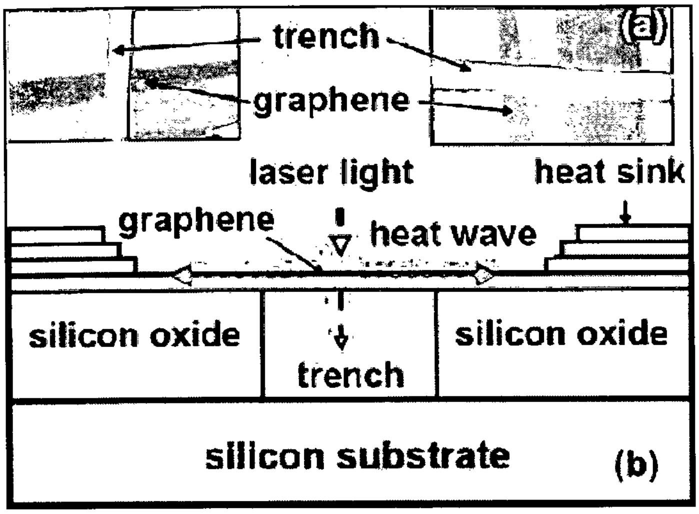

Figure 2.6: (a) High-resolution scanning electron microscopy image of the suspended graphene flakes.
(b) Schematic of the experimental setup for measuring the thermal conductivity of graphene.

2.4 APPLICATIONS OF GRAPHENE

Supercapacitor Construction

Supercapacitors are electrochemical capacitors that store energy through reversible ion adsorption onto active materials that have high specific surface area [41]. Because of their many advantageous properties, such as high power density, high capacitance, and long cycle life, these systems play an important role in electrical energy storage [41, 42]. To generate a high specific capacitance, the specific surface area of the electrode materials needs to be as high as possible to accommodate a large number of electrolyte ions at the electrode/ electrolyte interface thereby promoting the electrical double-layer capacitance [41, 42]. A wide variety of supercapacitor materials and processes for cell construction currently exist.

Supercapacitors therefore represent a new breed of technology that occupies a niche amongst other energy storage devices that was previously vacant. They have the ability to store greater amounts of energy than conventional capacitors, and are able to deliver more power than batteries. The current position of the supercapacitor is easily visualised by means of a Ragone plot in Figure 2.7, which graphically represents a device's energy and power capabilities.

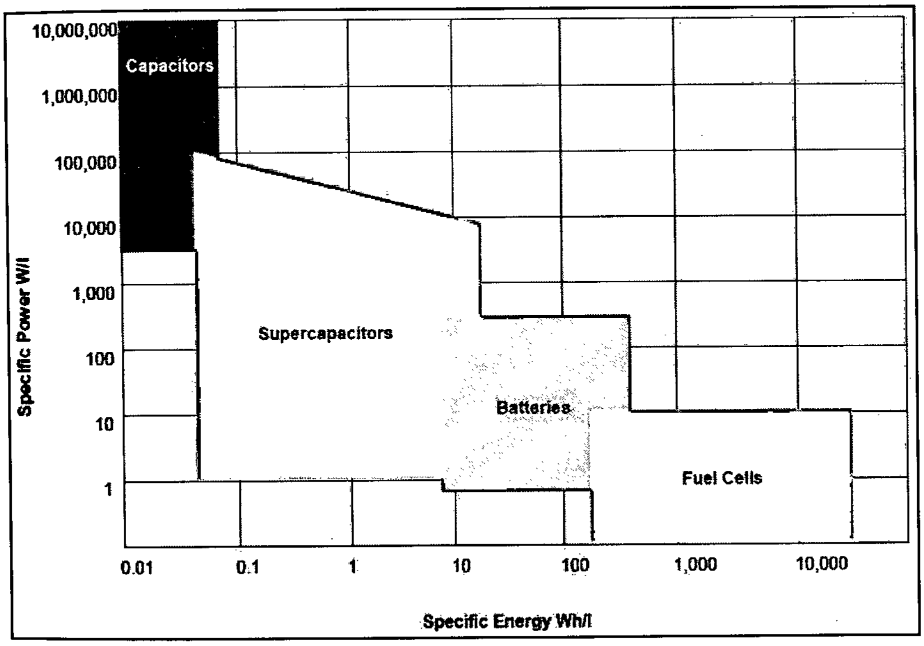

Figure 2.7: Ragone plot of various energy storage devices [41].

Here, I will propose the properties of various available materials and describes the aspects of each alternative that have a significant impact on device performance.