ELECTROCHEMICAL STUDY OF NICKEL NANOPARTICLE GRAPHENE COMPOSITE

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ABSTRACT

This project entitled the electrochemical study of Nickel nanoparticle graphene composite. Graphene is a two-dimensional crystal consisting of a monolayer of carbon atoms arranged in a honeycomb lattice which is extracted from graphite. It is capable to produce a high conductivity of electricity and has a high surface area. Nanoparticles are generally considered an invention of modern science. The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large surface area of the material, which dominates the contributions made by the small bulk of the material. Aside from graphene and nanoparticle interesting solid state chemistry and structural attributes, these two compounds exhibit interesting magnetic, optical, and electrochemical properties and thus have great potential for device applications (e.g. molecular magnets, electrodes and rechargeable batteries). Thus, these materials have raised renewed and growing interest in the electrochemical field. In this project, graphene was synthesized from graphite by electrolytic exfoliation using poly(sodium-4-styrenesulfonate) as an effective electrolyte while Nanosized nickel was prepared by a simple co-precipitation method. The surface area of graphene was measured using BET method and functional group was characterized by FTIR. X-ray diffraction was performed on the as-prepared nickel nanoparticle and confirmed its crystal structure. These two materials were grinded together to produce nickel nanoparticle graphene composite. The electrochemical behavior of the sample was studied by cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS).

ABSTRAK

Projek ini bertajuk kajian elektrokimia Nikel bersaiz nano graphene komposit. Graphene ialah satu hablur dua dimensi mengandungi satu ekalapisan atom-atom karbon menyusun dalam kekisi sarang lebah yang mana dikeluarkan dari grafit. Ia adalah berupaya menghasilkan satu kekonduksian tinggi bekalan elektrik dan mempunyai satu luas permukaan tinggi. Zarah nano adalah umumnya sebuah rekaan sains moden. Ciri-ciri menarik dan kadang-kadang tidak diduga yang terdapat pada zarah bersaiz nano adalah sebahagian besarnya disebabkan luas permukaan besar, yang mana dihasilkan daripada bahan-bahan yang kecil. Selain daripada sifat kimia berkeadaan pepejal serta sifat-sifat struktur graphene dan zarah nano, sifat-sifat struktur, kedua-dua sebatian ini mempamerkan cirri-ciri magnetik, optik , dan elektrokimia dan demikian mempunyai potensi yang besar untuk peranti (contohnya magnet-magnet molekul, elektrod-elektrod dan bateri-bateri cas semula). Maka, bahan-bahan ini telah mempertingkatkan faedah yang baru dalam bidang elektrokimia. Dalam projek ini, graphene disintesiskan dari grafit oleh pengelupasan elektrolitik menggunakan poly(sodium-4-styrenesulfonate) sebagai satu elektrolit berkesan manakala nikel bersaiz nano telah disediakan dengan menggunakan kaedah pemendakan bersama yang ringkas. Luas permukaan graphene diukur menggunakan kaedah BET dan kumpulan berfungsi telah diketegorikan oleh FTIR. Belauan sinar-x telah digunakan untuk mengesahkan struktur hablur zarah nano nikel yang telah disediakan. Kedua-dua bahan ini dicampur bersama dan menghasilkan zarah nano nikel graphene komposit. Sifat elektrokimia sampel telah dikaji oleh voltammetri berkitar (CV), dan spektroskopi rintangan elektrokimia (EIS).

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π	pi
μL	Micro Liter
Ω	ohm

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller / Surface Area Analyzer
CV	Cyclic Voltametry
CVD	Chemical Vapor Depositio
DI	De-ionized
DNA	Deoxyribonucleic Acid
EIS	Electrochemical Impedence Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
K^+	Potassium Ion
$K_3[Fe(CN)_6]$	Potassium hexacyanofarrate (III)
KCl	Potassium Cloride
KNO_3	Potassium Nitrate
Li^+	Lithium Ion
$LiNO_3$	Lithium Nitrate
Na^+	Sodium Ion
$NaNO_3$	Sodium Nitrate
$Ni(NO_3)_2 \cdot 6H_2O$	Nickel (II) Nitrate hexahydrate
OLED	Organic Light Emitting Diodes
PSS	Poly (sodium-4-styrenesulfonate)
SiC	Silicon Carbide
TEM	Transmission Electron Microscopes
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Graphene, a single atomic layer of graphite, first isolated in 2004 by Andre Geim's group, has made a quantum leap in the exploration of the physics of two-dimensional electron systems. Graphene is a single sheet of carbon atoms arranged in a honeycomb (hexagonal) lattice which is a molecular chicken wire where one carbon atom sits at each 120° corner (Figure. 1) (Chakraborty, 2010). Graphene is a bipartite lattice made up of two interpenetrating triangular sublattices. There are two carbon atoms (commonly referred to as A and B) per unit cell. Each carbon atom has one s orbital and two in-plane p orbitals which make up the strong covalent bonds responsible for the mechanical stability of the graphene sheet.

This new material has leapt to the forefront of material science and has numerous possible applications. It also allows for the observation of electrons in an almost zero resistance environment. Graphene has some extremely interesting properties not yet

observed in any other element or compound. In the field of electronics, graphene could let electronics to process information and produce information and produce radio transmission many times better than silicon based devices such as transistors, supercapacitors, and future electronic devices (Chintapalli,2010). Despite the difficulties of producing graphene sheets on top of the appropriate substrate, graphene's high carrier mobility and low noise to be used as the channel in a field-effect transistor make of it an excellent material for integrated circuits and graphene can be used for the conductive plates for ultra capacitors due to its high area-to-mass ratio (Lammert T., Rozo L. and Whittier E., 2009).

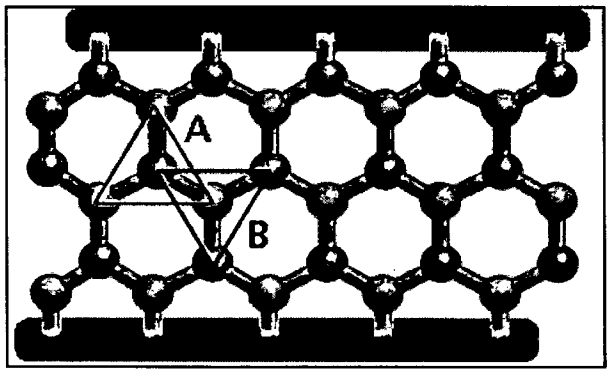

Figure 1.0: Graphene lattice. The unit cell contains two atoms, atoms A and B.

Source: Chakraborty, 2010

Nanoparticles are generally considered an invention of modern science. Similar to ultrafine particles, nanoparticles are sized between 1 and 100 nanometers. Nanoparticle synthesis has been widely investigated in recent years because of its many unique characteristics in physical and chemical properties. Due to their unique characteristics, nanomaterials and nanotechnologies are changing many basic scientific

concepts in a great variety of fields, and are receiving intensively increasing interest in the relative research and industrial applications. Nanostructured noble metals are potentially used in catalysis, optoelectronics, microelectronics etc. The ultrafine and nanometer nickel powders have attracted a great deal of attention over past decades due to their specific properties such as magnetism, thermal resistance, chemical activity and have a wide range of applications including batteries, hard alloy, catalyst, electricity and so on (Ying et al. 2005).

1.2 PROBLEM STATEMENT

Aside from graphene and nanoparticle interesting solid state chemistry and structural attributes, these two compounds exhibit interesting magnetic, optical, and electrochemical properties and thus have great potential for device applications (e.g. molecular magnets, electrodes and rechargeable batteries). Thus, these materials have raised renewed and growing interest in the electrochemical field. In this work, graphene will be combined with nickel nanoparticle to produce nickel nanoparticle graphene composite in case to study the electrochemical behavior. Cyclic voltametric method was implemented in this work to carry out the best result.

1.3 RESEARCH OBJECTIVE

The objective of this project is to study the electrochemical behavior of Nickel nanoparticle graphene composite.

1.4 SCOPES OF STUDY

The scopes of this study include:

(i) To synthesis graphene materials from graphite by the electrolytic exfoliation.

(ii) To synthesis $Ni_3(Fe(CN)_6)_2(H_2O)$ nanoparticle by a simple co-precipitation method.

(iii) To characterize composite by chemical characterization method and electrochemical method.

CHAPTER 2

LITERATURE REVIEW

2.1 GRAPHENE

Graphene and Graphite are the two dimensional sp_2 hybridized forms of carbon found in pencil lead (Bunch, 2008). Graphite is a layered material formed by stacks of graphene sheets separated by 0.3 nm and held together by weak van der Waals forces (Kelly, 1981) while graphene is a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice,and is a basic building block for graphitic materials of all other dimensionalities (Novoselov, Geim et al. 2004).The term graphene was coined as a combination of graphite and the suffix-ene by Hanns-Peter Boehm, who described single-layer carbon foils in 1962.

A single 2-D sheet of graphene is a hexagonal structure with each atom forming 3 bonds with each of its nearest neighbors (Figure. 2.2). These are known as the σ bonds oriented towards these neighboring atoms and formed from 3 of the valence electrons. These covalent carbon-carbon bonds are nearly equivalent to the bonds holding diamond

together giving graphene similar mechanical and thermal properties as diamond (Bunch, 2008). The fourth valence electron does not participate in covalent bonding. It is in the 2pz state oriented perpendicular to the sheet of graphite and forms a conducting π band. The remarkable electronic properties of carbon nanotubes are a direct consequence of the peculiar band structure of graphene, a zero bandgap semiconductor with 2 linearly dispersing bands that touch at the corners of the first Brillouin zone (Wallace, 1947).

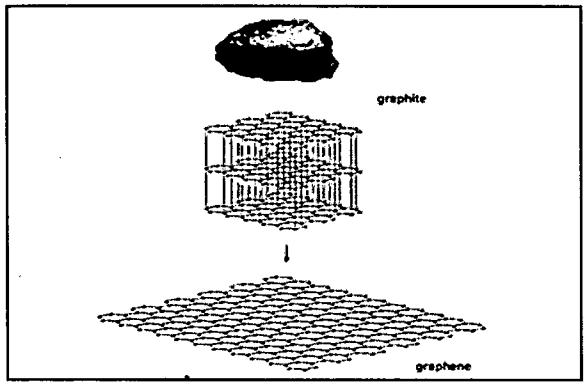

Figure. 2.1: Single layer of graphene from graphite

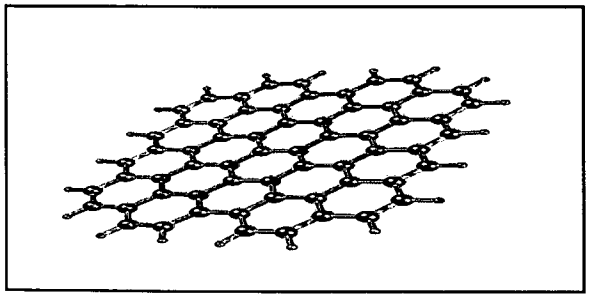

Figure. 2.2: hexagonal structure of graphene

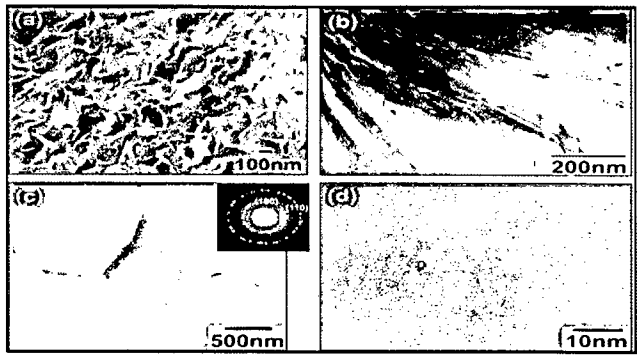

Figure. 2.3: (a) FESEM image of the bulk graphene powders. (b) TEM image of many graphene sheets. (c) TEM image of a largegraphene flake. The insetis the corresponding SAED pattern. (d) HRTEM image of graphene sheets, showing the featureless basal planes and a cross-sectional view of the edges of folded graphene sheets.

2.1.1 Fabrication of Graphene

There are several ways of producing graphene but none of them have yielded samples as pure as "the scotch tape method" (Lammert et al. 2009). The most common method of graphene fabrication is exfoliation which finds its roots with a technique that has been around for centuries – 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 you are typically left with many sheets of varying thicknesses (Bunch, 2008). If you 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 (Novoselov, Geim et al. 2004). By gently rubbing or pressing a freshly cleaved graphite crystal on an 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 (Novoselov, Jiang et al.

2005; Blake, Hill et al. 2007). This technique simplifies the process of finding single graphene sheets but obviously limits this fabrication scheme to devices for research purposes.

Other methods that have been developed to produce graphene includes: (i) Epitaxial growth via ultra-high vacuum graphitization (Berger, Song et al. 2004). Typically this is accomplished by heating a SiC wafer which results in the partial graphitization of the upper layer (Berger, Song et al. 2004). This allows the fabrication of patterned graphene structure, which is desirable for electronics. 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 (Berger, Song et al. 2006). (ii) Chemical synthesis through oxidation of graphite. The whole process involves oxidation of graphite to graphite oxide, exfoliation of graphite oxide to yield graphene oxide sheets, and chemical or thermal reduction to graphene (Wang, Park et al. 2009). Chemical processing inevitably introduces defects in graphene sheets (Li, Zhang et al. 2008). (iii) Chemical vapor deposition (CVD) growth of graphene either on a substrate or substrate free (Kim, Zhao et al. 2009; Dato, Radmilovic et al. 2008). (iv) Solvothermal synthesis combined with pyrolysis (Choucair et al. 2009) and liquid phase exfoliation of graphite (Lotya et al. 2009). Scaling-up production of graphene is still a big challenge. For the time being, exfoliation remains the preferred method for most of the experimental research groups around the world.

In this research, highly efficient synthesis of graphene by electrolytic exfoliation from graphite is used (Figure 2.4). The as-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 (Wang, Park et al. 2009).

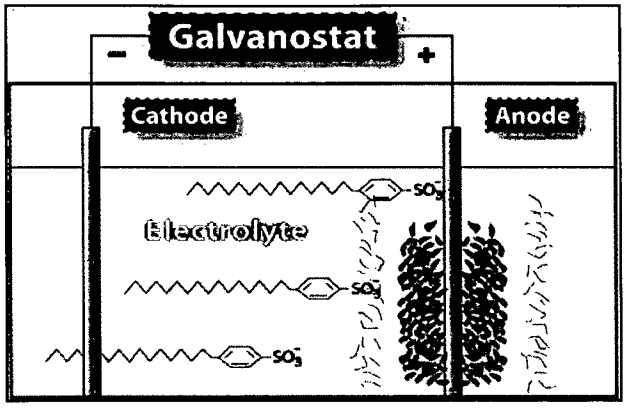

Figure. 2.4: Diagram of the apparatus for synthesis of graphene via electrolytic exfoliation.

2.1.2 Electrical properties of graphene.

Most of the experimental research on graphene focuses on the electronic properties. The most notable feature about the early work on graphene transistors was the ability to continuously tune the charge carriers from holes to electrons. An example of the gate dependence in single layer graphene is shown in Figure. 2.5a. According to Bunch (2008), this effect is most pronounced in the thinnest samples whereas samples from multiple layers show much weaker gate dependence due to screening of the electric field by the other layers.

At low temperatures and high magnetic fields, the exceptional mobility of graphene allows for the observation of the quantum hall effect for both electrons and holes (Figure. 2.5b) (Novoselov, Geim et al. 2005; Zhang, Tan et al. 2005). Due to its unique band structure, the graphene quantum hall effect exhibits a subtle difference from the conventional quantum Hall effect in that plateaus occur at half integers of $4e2/h$ rather than the typical $4e2/h$ (Bunch, 2008).

For more practical applications one would like to utilize the strong gate dependence of graphene for either sensing or transistor applications. Unfortunately, graphene has no band gap and correspondingly resistivity changes are small. Therefore, a graphene transistor by its very nature is plagued by a low on/off ratio. However one way around this limitation, is to carve graphene into narrow ribbons. By shrinking the ribbon the momentum of charge carriers in the transverse direction becomes quantized which results in the opening of a band gap. This band gap is proportional to the width of the ribbon. This effect is pronounced in carbon nanotubes where a nanotube has a band gap proportional to its diameter. The opening of a band gap in graphene ribbons has recently been observed in wide ribbon devices lithographically patterned from large graphene flakes (Han, Ozyilmaz et al. 2007) and in narrow chemically synthesized graphene ribbons (Li, Wang et al. 2008).

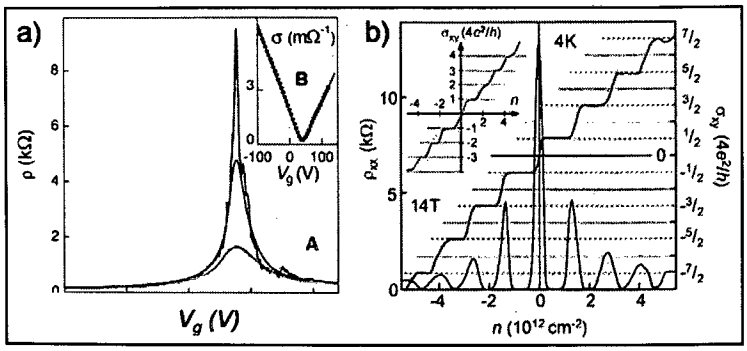

Figure 2.5: a) The resistivity of a single layer of graphene vs. gate voltage. b) The Quantum Hall Effect in single layer graphene.

Source: Novoselov, Geim et al. 2005

2.1.3 Potential application of Graphene

The properties of graphene, carbon sheets that are only one atom thick, have caused researchers to consider using this material in other fields. Graphene can be used as components with higher strength to weight ratios. Researchers have found that adding graphene to epoxy composites may result in stronger/stiffer components than epoxy composites using a similar weight of carbon nanotubes. Graphene appears to bond better to the polymers in the epoxy, allowing a more effective coupling of the graphene into the structure of the composite. This property could result in the manufacture of components with high strength to weight ratio for such uses as windmill blades or aircraft components.

Graphene also can be use as transistors that operate at higher frequency. The ability to build high frequency transistorswith graphene is possible because of the higher speed at which electrons in graphene move compared to electrons in silicon. Researchers are also developing lithography techniques that can be used to fabricate integrated circuits based on graphene.

For mobile devices, graphene can act as a lower cost of display screens. Researchers have found that graphene can replace indium-based electrodes in organic light emitting diodes (OLED). These diodes are used in electronic device display screens which require low power consumption. The use of graphene instead of indium not only reduces the cost but eliminates the use of metals in the OLED, which may make devices easier to recycle.

Storing hydrogen for fuel cell powered cars. Researchers have prepared graphene layers to increase the binding energy of hydrogen to the graphene surface in a fuel tank, resulting in a higher amount of hydrogen storage and therefore a lighter weight fuel tank. This could help in the development of practical hydrogen fueled cars.

Graphene also can be use as sensors to diagnose diseases. These sensors are based upon graphene's large surface area and the fact that molecules that are sensitive to particular diseases can attach to the carbon atoms in graphene. For example, researchers have found that graphene, strands of DNA, and fluorescent molecules can be combined to diagnose diseases. A sensor is formed by attaching fluorescent molecules to single strand DNA and then attaching the DNA to graphene. When an identical single strand DNA combines with the strand on the graphene a double strand DNA if formed that floats off from the graphene, increasing the fluorescence level. This method results in a sensor that can detect the same DNA for a particular disease in a sample.

High surface area of graphene can make ultracapacitors with better performance than batteries possible. These ultracapacitiors store electrons on graphene sheets, taking advantage of the large surface of graphene to provide increase the electrical power that can be stored in the capacitor. Researchers are projecting that these ultracapacitors will have as much electrical storage capacity as lithium ion batteries but will be able to be recharged in minutes instead of hours.