CHAPTER 1 INTRODUCTION

1.1 Introduction

Carbon is a unique and very versatile element which is capable of forming different structures at the nanoscale [1]. Nanographite and graphene are allotrope of carbon. Nanographite consists of small stack of graphene. It has a thickness of 10 - 100 nm and a well preserved crystalline order. Nanographite is of potential interest in the realization of high temperature gaskets, as electrodes in lithium recharged batteries, adsorption substrates, or as a reinforcing material in nanocomposites, and they can be produced by chemical or mechanical methods [2]. Chemical methods are generally based on the intercalation of graphite followed by rapid thermal annealing [2]. The electronic properties of nanographite change with the number of graphene layers and by the relative position of atoms in adjacent layers (stacking order). As the number of graphene layers increase, the stacking order and the band structure can become more complicated, several charge carriers appear and the conduction and valence bands start notably overlapping [1].

Graphene has attracted significant attention in many research topics since it has been discovered by Geim, Novoselov and coworkers in 2004 [3, 4]. Graphene is a two dimensional sheet of carbon monolayer film that carbon atoms are arranged in hexagonal array [5]. It has unique physical, optical, mechanical, electrical and thermal properties, such as the thinnest material in the universe (97.7% transparency), excellent mechanical strength, high flexibility (Young's modulus ≈ 1 TPa), superior thermal conductivity (~5000 W/m·K), high surface area (2630 m^2/g) and high capacity [5-10]. In addition, the intrinsic carrier mobility in a graphene is much higher than that in silicon (~200,000 cm^2/V·s) [9]. Theoretically, graphene is the most stable electrical conducting material due to its periodic structure of carbon atoms that arrange in the orderly repeating pattern of two-dimension and non-defect. Thus electrons can travel very long distances without scattering [5-10]. Graphene has shown great promise in many applications such as chemical filters, electrical batteries, nanoelectronic devices, nanoelectromechanical devices and molecular storage devices [11]. Moreover, many researchers believe that graphene is set to revolutionize electronics and photonics, such as novel computers, solar cells and sensors [11, 12].

Many researchers have developed various methods to synthesize graphene and nanographite. The isolation of graphene and nanographite from graphite was first introduced by mechanical exfoliation or scotch tape method [5]. The method exhibits a high quality of graphene and nanographite, but it cannot offer a large size of graphene and nanographite and a large scale production. Hummers' method is one of the low cost approachs; however, this oxidation process causes damage on the honeycomb structure of graphene and nanographite [7]. Chemical vapor deposition (CVD) methods have shown to be another suitable technique for achieving a large scale production of graphene and nanographite, but the process requires high temperature (~1,000 ºC) for operating and costs a lot of money [7]. Graphene and nanographite can also be exfoliated from graphite using sonication or ultrasonic treatment. It is an easy technique with a simple preparation and low cost. However, it may decrease the planar size of graphene and nanographite [12].

The application of nanographite is versatile, such as super lubricant, energy-storing, high conductor, diamond, etc. [2]. For the feature of small and homogeneous particle dimension, it can be used as nanoscaled compound-material or compound-paint additive. For the feature of high-purity and high specific surface area make it better to be hydrogen storage material than other materials. For the feature of high thermal-stability, electric/anti-corrosion performance and thermal-conduction features make it to be good electric and thermal conductive material [13].

Graphene has outstanding properties which will lead to an application in many technology areas. It can be used to make ultra-fast microchip (1,000 GHz) which can improve the rate of data transfer for electronic device [14]. Graphene-based transistor can run at high frequency which can increase the speed and capacity of computing [14]. Graphene-based ultracapacitor is light, flexible and easy to maintain [14]. Graphene-based electrodes can be used in term of electrocatalytic activity and macroscopic scale conductivity which demonstrated higher performance than carbon nanotubes based ones. In addition, graphene which has low electrical noise can be used as ultra-sensitive and ultra-fast electronic sensor [15, 16].

pH value is important in medicine, food science, nutrition, water treatment, water purification and environmental science, etc [17-20]. Monitoring the pH of a material is important because it reduces product spoilage, ensures that optimum levels of yield are achieved and enables the processor to meet legal requirements [20]. However, recent problem on developing pH sensor is detector cannot withstand strong acid or base solutions. Most pH measurement is carried out using glass electrode combinations, but glass is susceptible to chemical attack [20]. Moreover, it is not easy to maintain and clean. pH sensor need material, such as nanographite and graphene, which is robustness, easy cleaning and maintaining and high metering precision and reliability, at any one time. Properties of graphene and nanographite are useful for fabrication of pH sensor which is an electronic device used for measuring the pH (acid or base) of a liquid. A typical pH sensor consists of a special measuring probe connected to an electrode that measures and displays the pH reading. Graphene and nanographite-based pH sensor can detect the change of pH because of excellent electric conductivity, high surface area, high capacity and high carrier mobility of graphene and nanographite. Moreover, graphene is capable of observing distinct and discrete step changes in resistance, corresponding to single molecules of the gas absorbing to and deabsorbing from the graphene flake. This advance could lead to devices that could sense a single molecule within a given space [14].

In this experiment, we demonstrate the procedures of preparation and characterization of nanographite by sonication and reduced graphene oxide by Hummers' method and reflux. pH sensor made from thin film of assembly of nanographite sheets and reduced graphene oxide sheets was compared and reported. The change in resistance when contacting with liquids of different pH value of both devices was reported. Understanding this simple sensing mechanism may lead to further development on a low cost sensor which is different from a field-effect transistor (FET) sensor that requires high technology.

1.2 Research objectives

1.2.1 To study and synthesize nanographite by ultrasonic treatment
1.2.2 To study and synthesize reduced graphene oxide by Hummers' method
1.2.3 To study physical properties of nanographite and reduced graphene oxide
1.2.4 To use nanographite and reduced graphene oxide for pH sensor

1.3 Literature review

Novoselov *et al.* [16] described monocrystalline graphitic films which are a few atoms thick but are nonetheless stable under ambient conditions, metallic and of remarkably high quality. The films are found to be a two dimensional semimetal with a tiny overlap between valence and conduction bands. They exhibit a strong ambipolar electric field effect such that electrons and holes in concentrations up to 10^{13} cm^{-2} and with room temperature mobilities of about 10,000 $cm^2/V\cdot s$ can be induced by applying gate voltage.

Paredes *et al.* [21] prepared graphite oxide by Hummers' method using $NaNO_3$, H_2SO_4, and $KMnO_4$. Graphite oxide was dispersed in various organic solvents such as acetone, methanol, ethanol, 1-propanol, ethylene glycol, dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), pyridine, tetrahydrofuran (THF), dichloromethane, *o*-xylene and *n*-hexane. For DMF, NMP, THF, and ethylene glycol, as-prepared graphite oxide can form dispersions with long-term stability. Furthermore, the graphite oxide material in these solvents is exfoliated mostly into individual, single-layer graphene oxide sheets with lateral dimensions between a few hundred nanometers and a few micrometers.

Si *et al.* [5] prepared graphite oxide by oxidizing graphite flakes with acid, and, then, graphite oxide was sonicated to yield graphene oxide. Graphene was prepared from graphene oxide in three steps. First, the majority of the oxygen functionality in graphene oxide was removed by prereduction with sodium borohydride. Second, it was sulfonated with the aryl diazonium salt of sulfanilic acid in an ice. Finally, it was reduced with hydrazine to remove any remaining oxygen functionality. The addition of more sodium borohydride immediately precipitates graphitic carbon. When hydrazine was used in the final reduction step, there was no sign of precipitation. Aqueous dispersion of graphene show good stability. There is no sign of coagulation of graphene sheets after more than one month. The water soluble graphene exists in the form of single carbon sheets exhibiting an electrical conductivity comparable to graphite.

Su *et al.* [7] demonstrated that the natural graphite flakes was employed as an electrode and source of graphene for fast electrochemical exfoliation. The graphite flake was adhered to a tungsten wire by a silver pad and then was inserted as anode into the ionic solution. A grounded platinum wire was placed parallel to the graphite flake with a separation of 5 cm. The ionic solution was prepared by taking 4.8 g of sulfuric acid and diluted in 100 mL of deionization water. The electrochemical exfoliation process was carried out by applying DC bias on graphite electrode (from -10 to +10 V). The electrochemical exfoliation of graphene using H_2SO_4 generally produced thin sheets with high defect level due to the fact that the H_2SO_4 itself also results in strong oxidation of graphite. However, oxidation by H_2SO_4 was reduced by adding KOH into the H_2SO_4 solution to lower the acidity of the electrolyte solution. All of the graphene sheets had a thickness lower than 3 nm and more than 65% of the sheets were thinner than 2 nm. The lateral size of graphene sheets ranges from 1 to 40 μm. The layer number of these electrochemically exfoliated graphene ranges from 1 to 4 with the most frequently seen graphene as bilayer (>60%).

Kang *et al.* [22] prepared graphene by the Hummers' method. The electrochemical sensor was fabricated with graphene modified glassy carbon electrodes (GCEs) which used for sensitive detection of paracetamol with cyclic voltammetry and square-wave voltammetric (SWV) techniques. This work showed wrinkled graphene sheet with no aggregation, indicating that the functionalized graphene sheets were well dispersed in ethanol solvent, and the suspensions were stable at room temperature for about 3 weeks. Graphene modified electrode exhibited excellent performance for detecting paracetamol.

Lei *et al.* [3] synthesized graphene sheets by scotch tape method. Graphene sheets were used for fabrication of simple chemiresistor as pH sensor. Graphene device showed that the resistance of the device decreased linearly with increasing pH values (4–10) in the surrounding liquid environment. The resolution of this device was approximately 0.3 pH in alkali environment. The sensitivity of the device is calculated as approximately 2 $k\Omega\ pH^{-1}$.

Jo *et al.* [23] prepared mesocellular carbon foam which is functionalized with hollow nanographite. Hollow graphite nanoparticles are well-dispersed in mesocellular carbon foam. After nanographitic functionalization, the BET surface area and total pore volume decreased. Thermogravimetric analysis in air shows that the thermal stability of nanographite functionalized mesocellular carbon foam is improved relative to that of mesocellular carbon foam, and the one-step weight loss indicates that the nanographite is homogeneously functionalized on the mesocellular carbon foam particles. The nanographite functionalized mesocellular carbon foam electrode exhibited a very high area capacitance (C_{area}, 23.5 $\mu F/cm^2$) compared with that of the mesocellular carbon foam electrode. Nanographite functionalized mesocellular carbon foam exhibited high capacity retention (52%) at a very high scan rate of 512 mV/s, while only a 23% capacity retention at 512 mV/s was observed in the case of the mesocellular carbon foam electrode. The high rate capability of the nanographite functionalized mesocellular carbon foam electrode as charge storage was due to the low resistance derived from the nanographitic functionalization.

Antisari *et al.* [24] prepared graphite nano-sheets by a mechanical method (Low energy pure shear milling) based on the grinding of graphite powder under low energy pure shear milling using water as a lubricant. The small applied stress activates the plastic deformation process mainly on the easy gliding (001) hexagonal planes so that planar flakes bounded by the basal planes are obtained by a purely mechanical process.

Li *et al.* [25] prepared composite phase change materials from nanographite/paraffin composites. Nanographite can be prepared easily from exfoliated graphite and expanded graphite. Nanographite has the function of improving the thermal conductivity of the composite. The nanographite layers were randomly dispersed in the paraffin and the thermal conductivity increased gradually with the content of nanographite. The distributed nanographite enhanced the heat transmission and improved the performance of energy storage technologies in term of efficiency in phase change materials. Thermal conductivity of the material containing 10% nanographite was 0.9362 W/m·K. The phase change temperature of paraffin was slightly influenced by nanographite content. The phase change temperature of the nanographite /paraffin composite phase change materials was slightly less than that of paraffin. As the nanographite content increased, the thermal conductivity of the nanographite /paraffin composite increased while the latent heat gradually decreased.

1.4 Research boundaries

1.4.1 Nanographite will be synthesized by ultrasonic treatment at 20 kHz of frequency with various times
1.4.2 Reduced graphene oxide will be synthesized by Hummers’ method and refluxed
1.4.3 To study the optimal conditions for the synthesis of nanographite and reduced graphene oxide for pH sensor
1.4.4 To study physical properties of nanographite and reduced graphene oxide
1.4.5 To study the ability of nanographite and reduced graphene oxide for the detection of various variables such as pH