SYNTHESIS AND CHARACTERIZATION OF POLYANILINE, GRAPHENE AND GRAPHENE/POLYANILINE NANOCOMPOSITES

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UNIVERSITI SAINS MALAYSIA

2018

SYNTHESIS AND CHARACTERIZATION OF POLYANILINE, GRAPHENE AND GRAPHENE/POLYANILINE NANOCOMPOSITES

by

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Thesis submitted in fulfilment of the

requirements for the degree of

Master of Science

August 2018

ACKNOWLEDGEMENT

First of all, I would like to take this opportunity to thank School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia for offering me the Master program. I would like to express my deepest appreciation to my supervisor, Prof. Ir. Dr. Mariatti Jaafar, who led me into the interesting research topic of graphene. Without her great mentorship, invaluable guidance, and helpful advice, this thesis could not have been completed. I have learnt a lot of new knowledge during completion of this Master project. I would also like to thank my co-supervisor, Dr. Tuti Katrina for her help to complete my project.

Secondly, I would like to express my profound gratitude to the Dean, Prof. Dr. Zuhailawati Hussain, for providing me all necessary facilities during my research work. I would like to acknowledge the technical support to all the laboratory technicians for their valuable help.

Besides, I would like to extend my thanks to Ministry of Education (MOE) for awarding Fundamental Research Grant (Grant, no. 6071284) that made this research possible. Also, special thanks to Ministry of Higher Education (MOHE) for awarding My Brain 15 (under My Master scheme) sponsorship throughout the Master study.

Lastly, I would like to give my heartfelt thanks to my friends for helping me the relevant and useful information in the process of completing this project. I am heartily thankful to my beloved parents and family members for their unconditional love and financial support.

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LIST OF SYMBOLS

0-D	Zero-dimensional
1-D	One-dimensional
2-D.	Two-dimensional
3-D.	Three-dimensional
m^2g^{-1}	Square meter per gram
$cm^2V^{-1}s^{-1}$	Square centimeter per volt second
TPa	Terapascal
$Wm^{-1}K^{-1}$	Watts per meter kelvin
um^2	Square micron
°C	Degree Celsius
V	Volt
2θ	Two-teta
°	Degree
eV	Electronvolt
S/cm	Siemens per centimetre
Σ	Electrical conductivity
P	Electrical resistivity
%	Percentage
wt%	Weight percentage
nm	Nanometers
Ǻ	Angstrom

LIST OF ABBREVIATIONS

APS	Ammonium persulfate
CH_4	Methane
$CHCl_3$	Chloroform
Cu	Copper
CMOS	Complementary metal-oxide-semiconductor
CNTs	Carbon nanotubes
CPs	Conducting polymers
CVD	Chemical vapour deposition
CTAB	Cetyltrimethyl ammonium bromide
ED	Electron diffraction
DBSA	Dodecylbenzenesulfonic acid
DMF	Dimethylformamide
FESEM	Field-emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
GO	Graphene oxide
H_2	Hydrogen
HCl	Hydrochloric acid
HNO_3	Nitric acid
HOPG	Highly oriented pyrolytic graphite
HRTEM	High-resolution transmission electron microscopy
H_2SO_4	Sulphuric acid
ICPs	Intrinsically conducting polymer
IL	Ionic-liquid
$KClO_3$	Potassium chlorate
K_2SO_4	Potassium sulfate
LE	Leucoemeraldine
$NaBH_4$	Sodium borohydride

$NaClO_4$	Sodium perchlorate
$NaNO_3$	Sodium nitrate
Na_2SO_4	Sodium sulfate
N_2H_4	Hydrazine
$(NH_4)_2SO_4$	Ammonium chloride
Ni	Nickel
O_2	Oxygen
PA	Polyacetylene
PANI	Polyaniline
PE	Polyethylene
PEDOT	Poly(3,4-ethylene dioxthiophene)
PMMA	Poly(methylmethacrylate)
PP	Polypropylene
PPY	Polypyrrole
PS	Polystyrene
PTH	Polythiophene
PVA	Poly(vinyl alcohol)
PVC	Poly(vinyl chloride)
Pt	Platinum
rGO	Reduced graphene oxide
SAED	Selected area electron diffraction
SDBS	Sodium dodecylbenzene sulfonate
SDS	Sodium dodecyl sulphate
SO_2	Sulphur dioxide
SEM	Scanning electron microscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
UV-vis	Ultraviolet-visible
TEM	Transmission electron microscopy

SINTESIS DAN PENCIRIAN POLIANILIN, GRAFIN DAN NANO KOMPOSIT GRAFIN/POLIANILIN

ABSTRAK

Kebelakangan ini, nanokomposit dengan grafin dan polimer konduktif telah menarik perhatian kerana kekonduksian elektriknya yang unggul. Tujuan utama kajian ini adalah untuk meningkatkan kekonduksian elektrik Polianilin (PANI) dengan penambahan grafin yang difungsikan. Objektif bagi kajian ini dibahagikan kepada dua bahagian. Dalam bahagian pertama, kesan penggunaan natrium dodekil benzenesulfonat (SDBS) sebagai surfaktan dan kaedah berbeza untuk menghasilkan PANI (konvensional fasa tunggal dan pempolimeran antara muka) telah dikaji. Dalam bahagian kedua, grafin telah dihasilkan melalui pengelupasan elektrokimia grafit dengan menggunakan voltan electrokimia yang berbeze iaitu 5V dan 10V. Grafin/PANI-SDBS nanokomposit telah dihasilkan dengan melalui satu-langkah pempolimeran antara muka yang mudah dengan kandungan grafin yang berbeza. Keputusan menunjukkan bahawa nanogentian PANI yang seragam dengan diameter yang kecil (55 nm) dapat dihasilkan dengan menggunakan pempolimeran antara muka. Penambahan SDBS semasa pempolimeran antara muka PANI berjaya mengurangkan aglomerasi nanogentian PANI. Voltan yang rendah, 5V dapat menghasilkan grafin yang nipis dengan kecacatan yang rendah (I_D/I_G=0.36), meningkatkan kestabilan terma serta kekonduksian elektrik yang tinggi iaitu 2.53 $\times 10^{-1}$ S/cm. Kajian morfologi menggunakan FESEM dan HRTEM menunjukkan bahawa nanogentian PANI cenderung untuk menyalut di atas permukaan grafin. Nanokomposit yang mengandungi 5% berat badan grafin telah menunjukkan kekonduksian elektrik yang paling tinggi iaitu 2.53 $\times 10^{-1}$ S/cm, dengan empat kali ganda lebih tinggi daripada PANI (9.99 $\times 10^{-6}$ S/cm). Kestabilan terma dan kekonduksian elektrik nanokomposit telah meningkat bertambahnya kandungan grafin.

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ABSTRACT

Recently, nanocomposites with graphene and conducting polymers have attracted considerable attention because of their superior electrical conductivity. The main aim of this study is to enhance electrical conductivity of polyaniline (PANI) by addition of functionalized graphene. The objectives of the present study are divided into two parts. In the first part, effect of using sodium dodecylbenzenesulfonate (SDBS) as surfactant and two different methods to synthesize PANI (conventional single-phase and interfacial polymerization) are considered in the study. In the second part, graphene were synthesized through electrochemical exfoliation of graphite with different electrochemical applied bias of 5V and 10V. The graphene/PANI-SDBS nanocomposites have been synthesized through a simple one-step interfacial polymerization by varying the amount of graphene content. Results indicate that more uniform with smaller diameter (55 nm) of PANI nanofibers are produced using interfacial polymerization. The growth of PANI nanofibers into agglomeration was successfully suppressed with the addition of SDBS during the interfacial polymerization of PANI. The low applied bias, 5V yields thin graphene sheets with relatively low defect (I_D/I_G=0.36), enhanced thermal stability as well as show high electrical conductivity of 2.53 $\times 10^{-1}$ S/cm. The morphological analysis via field emission scanning (FESEM) and high resolution transmission electron microscopy (HRTEM) showed that PANI nanofibers tend to coat on the surfaces of graphene sheets. The nanocomposites containing 5 wt% graphene content exhibit the highest electrical conductivity of 2.53 $\times 10^{-1}$ S/cm, which is four orders of magnitude higher than that of PANI (9.99 $\times 10^{-6}$S/cm). The thermal stability and electrical conductivity of nanocomposites was found to be improved with the increased in graphene content.

CHAPTER ONE

INTRODUCTION

1.1 Background of Research

Carbon nanomaterials including zero-dimensional (O-D) fullerenes, one-dimensional (1-D) carbon nanotubes (CNTs) and two-dimensional (2-D) graphene have been widely investigated due to their versatile characteristics and properties. Graphene, a two-dimensional honeycomb sp^2 carbon lattice has received enormous attention in recent years for its potential application in next generation composite materials as well as electronic and energy storage devices. Graphene was considered as the basic unit for other carbon materials and it can be wrapped up into 0-D buckyballs, rolled into 1-D nanotubes or stacked into three-dimensional (3-D) graphite as shown in Figure 1.1. As opposed to other carbon nanomaterials, the special two dimensional structure makes graphene displays a number of unique material properties including large theoretical specific surface area (2630 m^2g^{-1}), high intrinsic mobility (200 000 $cm^2V^{-1}s^{-1}$) (Bolotin *et al.*, 2008; Morozov *et al.*, 2008), high Young's modulus (~1.0 TPa) (Lee *et al.*, 2008), superior thermal conductivity (~5 000 $Wm^{-1}K^{-1}$) (Balandin *et al.*, 2008), high optical transmittance and good electrical conductivity.

To date, several methods have been demonstrated for graphene synthesis using both top-down and bottom-up approaches. In recent years, mechanical exfoliation, chemical exfoliation, chemical synthesis and thermal chemical vapour deposition (CVD) synthesis are the most commonly used methods. Although mechanical exfoliation using scotch tape was the first method of synthesized graphene sheets by Geim and Novoselov in 2004 and this discovery igniting the field of graphene, but the yield is limited (Chia *et al.*, 2014). A popular low-cost method to produce graphene in large quantities is obtained from chemical exfoliation of graphite via Hummers method. However, this process has the disadvantages with the resulting reduced graphene oxide (rGO) sheets having structural defects, giving poor quality in terms of low electrical conductivity which depends largely on removal of the functional groups through chemical or thermal reduction. Moreover, this method involves the usage of hazardous or corrosive chemicals (Liu *et al.*, 2015).

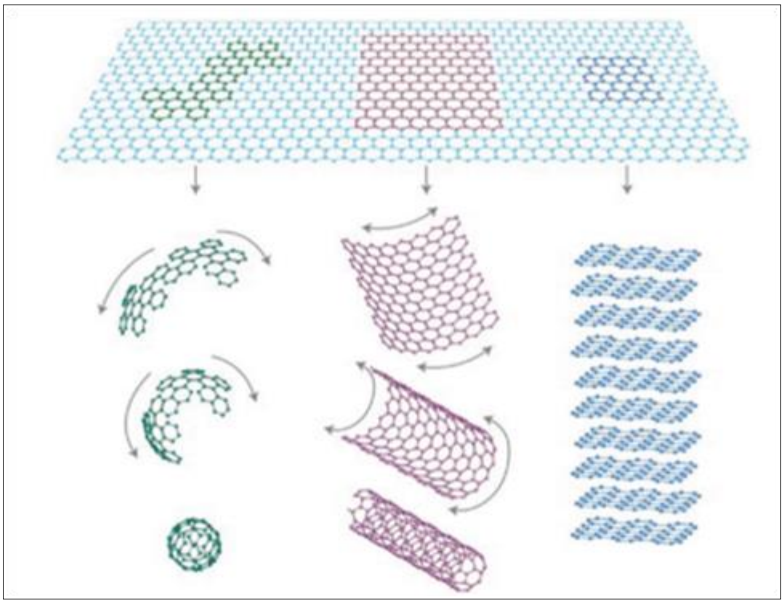

Figure 1.1: Graphene is a 2D building material for carbon materials of all other dimensionalities (Geim & Novoselov, 2007).

CVD method has been most widely used to grow large area graphene. However, this method requires the use of high temperature or expensive equipment process (Oyer *et al.*, 2012; Soldano *et al.*, 2010). Recently, the electrochemical method have drawn much attention and it is considered as a promising low-cost route for the mass production of graphene (Zhong *et al.*, 2015). This method takes several minutes to hours, producing gram scale quantities of graphene at the laboratory-scale. The quality of graphene is strongly affected by the operating voltages, graphite precursors and electrolyte (Yang *et al.*, 2016). Electrochemical exfoliation of bulk graphite can generate graphene with a diverse range of characteristics.

There are still some challenges in order to utilize the great potential of graphene for various applications. It has been found that the graphene sheets tend to agglomerates and would result in insoluble in water and organic solvents due to the π-π stacking interactions. In order to overcome this, functionalization of graphene such as chemically introduced a new functional groups onto the surface of graphene is considered as an approach to address the challenges. Moreover, the presence of hydrophilic groups such as carboxylic and sulfonate groups can be introduced onto the basal planes of graphene to prevent aggregation.

Graphene have shown a great promise in preparing the nano-scale sensors, conductors, capacitors, batteries and other (Huang *et al.*, 2012). In addition, one of the most significant applications of the graphene is to incorporate them into some polymers as the reinforcing fillers to synthesize nanocomposites. Organic polymers possess some limitations such as low thermal stability and poor mechanical, electrical and optical properties due to their intrinsic nature. The discovery of conducting polymers has generated a great interest in conductive nanocomposites. The most widely studied conducting polymers are polyaniline (PANI), polypyrrole (PPy) and poly(3,4-ethylene dioxthiophene) (PEDOT) (Flandin *et al.*, 2001).

Among the various conducting polymers, the PANI family of conjugated polymers has attracted much attention. Besides conductivities, PANI is favourable than other because the monomer aniline is less expensive and the synthesis of PANI is simple. Moreover, PANI has excellent environmental stability and tunable properties. Most recently, nanostructured PANI has received great potential because its