Synthesis and Characterization of Reduced Graphene Oxide (rGO)/TIPS-Pentacene Composite Material for Organic Thin Film Transistor (OTFT) Sensor Platform

by

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Although this thesis only have one author's name on its cover, but this research will not been accomplished without the support from few number of people

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LIST OF ABBREVIATIONS

3D	Three dimensional
AFM	Atomic force microscope
CVD	Chemical vapour deposition
DMF	Dimethylformamide
DTA	Differential thermal analysis
EDX	Energy dispersive X-ray spectroscopy
FAS	Formamidinesulfinic acid
FESEM	Field Emission Scanning Electron Microscopy
FET	Field effect transistor
FTIR	Fourier transforms infrared spectroscopy
GO	Graphene oxide
I_{on} / I_{off}	Current on/off ratio
ITO	Indium thin oxide
I-V	Current-voltage
LAA	L-ascorbic acid
MOSFET	Metal oxide semiconductor field effect transistor
ODCB	Ortho-dichlorobenzene
OFET	Organic field effect transistor
OTFT	Organic thin film transistor
rGO	Reduced graphene oxide
RMS	Root mean square
rpm	Revolution per minutes

SPA	Semiconductor parameter analyser
TFT	Thin film transistor
TGA	Thermal Gravimetric Analysis
TIPS-pentacene	6, 13- Bis(triisopropylsilylethynl) pentacene
T_{sub}	Substrate temperature
TTF	Tetrathiafulvalene
UV	Ultraviolet
XPS	X-ray photoelectron spectroscopy
XRD	X-Ray Diffraction

LIST OF SYMBOLS

I	Magnitude of current
I_{DS}	Source-drain current
ϴ	Theta
S	Distance between the probes
s	Second
V	Magnitude of electric field
V	Voltage
V_{DS}	Source-drain voltage
V_G	Gate voltage
ρ	Resistivity
σ	Conductivity

Sintesis dan Pencirian Graphene Oksida (rGO) Terturun/TIPS-Pentacene Bahan Komposit Bagi Pelantar Sensor Transistor Organik Filem Nipis (OTFT)

ABSTRAK

Transistor organik filem nipis (OTFT) telah menarik minat pelbagai pihak berikutan kelebihan yang dimilikinya seperti fleksibel, telus, mudah difabrikasi dan kos pengeluaran yang murah. Namun begitu, masalah terbesar yang wujud ketika proses fabrikasi OTFT adalah jumlah mobiliti ion yang rendah tetapi nisbah I_{on}/I_{off} yang tinggi telah menjadi penghalang bagi OTFT digunakan pada peranti berprestasi tinggi. Graphene merupakan bahan yang mempunyai sifat pembawa mobiliti ion terbaik ketika ini tetapi mempunyai masalah dengan nisbah I_{on}/I_{off} yang rendah. Oleh itu, penyelidikan ini dijalankan bertujuan untuk menghasilkan graphene oksida terturun (rGO)/TIPS-pentacene bahan komposit bagi pelantar sensor OTFT untuk mengatasi kekangan ini. Graphene oksida (GO) dihasilkan mengikut kaedah Tour's dan diturunkan secara proses kimia menggunakan Vitamin C (LAA), asid sulfinik *formamidine* (FAS) dan natrium sulfit (Na_2SO_3). Bagi memastikan pernurunan rGO telah berjaya dilakukan, rGO telah dicirikan dengan menggunakan spektroskopi inframerah (FTIR), pembelauan sinar X-ray (XRD), analisis thermogravimetrik (TGA), medan pelepasan mengimbas elektron mikroskop (FESEM), *probe* empat titik dan analisis parameter semikonduktor (SPA). Daripada pencirian ini, didapati bahawa rGO-FAS merupakan agen penurunan terbaik yang menunjukkan prestasi peranti terbaik. Ketika proses fabrikasi peranti OTFT ini, *polymethylmethacrylate* (PMMA) dan TIPS-Pentacene diletakkan di atas substrat *polyethylene terephthalate* (PET) melalui kaedah salut putaran. Parameter yang telah dikaji adalah kesan terhadap perbezaan suhu substrat (T_{sub}) TIPS-pentacene, perbezaan kelikatan, ketebalan dan kelajuan putaran PMMA. Keputusan yang diperoleh daripada prestasi elektrik PMMA menunjukkan bahawa arus-voltan (I-V) semakin menurun apabila kelikatan meningkat. Bagi TIPS-pentacene, substrat telah dikeringkan pada suhu berbeza iaitu 40, 60, 80 dan 100 °C. Apabila suhu meningkat, purata saiz butiran, kekasaran punca kuasa min (RMS) dan ketebalan filem meningkat. Keputusan ini mengakibatkan peningkatan ciri keluaran dan pemindahan OTFT pada T_{sub} 100 °C yang telah menunjukkan nilai arus saliran (I_{DS}) tertinggi. Setelah semua pencirian dijalankan, rGO/TIPS-pentacene bahan komposit telah difabrikasi dan dioptimumkan melalui kaedah melarutkan bahan komposit ke dalam larutan yang berbeza seperti orto-diklorobenzena (ODCB), *anisole*, *toluene* dan kloroform. Keputusan menunjukkan bahawa bahan komposit ini menunjukkan I_{DS} paling tinggi dalam larutan ODCB. Setelah dibandingkan dengan rGO dan TIPS-pentacene tulen, bahan komposit ini tetap menunjukkan prestasi elektrik terbaik berbanding peranti lain.

Synthesis and Characterization of Reduced Graphene Oxide (rGO)/TIPS-Pentacene Composite Material for Organic Thin Film Transistor (OTFT) Sensor Platform

ABSTRACT

Organic thin film transistor (OTFT) has drawn a lot of attention due to their advantages of flexible, transparent, easy to fabricate and cost effective production. The main problem occurred in OTFT was its lower ion mobility but higher I_{on}/I_{off} ratio which could prevent their application for high performance electronic devices. Graphene material displayed an excellent carrier mobility but lower I_{on}/I_{off} ratio. So, the objective of this research was to develop a reduced graphene oxide (rGO)/TIPS-pentacene composite material based OTFT sensor platform to overcome these limitations. Graphene oxide (GO) was synthesized using Tour's method and chemically reduced using ascorbic acid (LAA), fomamidinesulfinic acid (FAS) and sodium sulphite (Na_2SO_3). The rGO were characterized using Fourier transforms infrared spectroscopy (FTIR), X-Ray Diffraction (XRD), Thermal Gravimetric Analyzer (TGA), Field emission scanning electron microscopy (FESEM), four point probe and semiconductor parameter analyzer (SPA) to confirm the reduction of rGO. From this characterization, it was found that rGO-FAS was a better reducing agent, which resulted better device performance. For fabrication of OTFT device, polymethylmethacrylate (PMMA) and TIPS-pentacene were deposited on Poly (ethylene terephthalate) (PET) substrate by spin coating method. The parameters that have been studied were the effect of different substrate temperature (T_{sub}) of TIPS-pentacene, different concentration, thickness and spinning speed of PMMA. The results for electrical performance of PMMA demonstrated that the current-voltage (I-V) measurement of the PMMA thin film was continued to decrease as the PMMA concentration increased. For TIPS-pentacene, the substrate were annealing at various temperatures of 40, 60, 80 and 100 °C. As the temperature increased, the average grain size, root mean square (RMS) roughness and thickness of the film were increased. This result lead to the increasing in the output and transfer characteristics of OTFT with T_{sub} of 100 °C showed higher source-drain current (I_{DS}) compared to other devices. After all characterization have been carried out, rGO/TIPS-pentacene composite material was fabricated and optimized by dissolved the composite material in different solvent consisted of ortho-dichlorobenzene (ODCB), anisole, toluene and chloroform. The performance of this composite material discovered that dissolving the composite material in ODCB exhibited higher I_{DS} and after compared with pure rGO and TIPS-pentacene, this composite material maintained better electrical performance than other devices.

CHAPTER 1

INTRODUCTION

1.1 Overview

Nanotechnology can be defined as anything smaller than micro technology such as nano powders or other things that were in nanoscale size which was about 1 to 100 nanometres (nm). As technology continued to advance in almost every scientific field, development of nanotechnology instrumentation was encouraged in order to view the nanoworld. This process has opened up the possibilities to apply this nano size material in various applications.

Over the past decade, many scientists have been working on the development of nanomaterial. This was due to their great advantages in various material, size and shapes which have lots of potential to be used especially in biomedical and electronic application. As a result of this progress, government and private sector have been funding large amount of money for continued research in this area in order to look for improvement and capabilities of these materials for being used in future. One of the most important nanomaterial was the nanocomposite. It can be derived from a metal, polymer or ceramic. Nanocomposites were attracting enormous interest because they demonstrate combination of properties from the individual components.

This research work focuses on the synthesis of reduced graphene oxide (rGO)/TIPS-Pentacene composites for organic thin film transistor (OTFT). Transistor was a semiconductor device that used to amplify or to convert electronic signals from the sensing material.

Organic semiconductors were carbon-rich and pi-conjugated materials with semiconductor properties that have the ability to transport charge when the electrical bias was applied due to the extended conjugated pi (π) system (Coropceanu et al., 2007). Usually, thermal evaporation method was used for fabrication of organic semiconductor on top of the substrate, but in this research spin coating method will be used. Among all organic semiconductors, TIPS-Pentacene was found as the most suitable organic semiconductor material due to its higher solubility in organic solvents and did not required high temperature for processing (Mansouri et al., 2013). By introducing organic semiconductor into rGO, electron mobility and device performance will be improved after considered few parameter (Basu et al., 2014).

Graphene is a single atom thick planar sheet of hexagonally arranged, sp^2 bonded carbon atom (Feng et al., 2011). It has extraordinary properties in term of mechanical, electrical, optical and thermal properties (Thakur & Karak, 2012). These properties have been practically used in many applications for producing composite material. It is recently become new composite material to blend rGO with organic semiconductor and lead to the development of highly conductive and sensitive material for sensor application.

Organic thin film transistor (OTFT) has been chosen as the transducer because it has drawn a huge number of consideration for applying it in several applications due to its promising benefits like simple device architecture, large-area compatible fabrication, low temperature processing and low cost manufacturing (Kim et al., 2008). Among all the organic semiconductor used as semiconductor layer in OTFT, pentacene is the most favourable organic compound which have excellent electrical properties (Kim et al., 2008). This study investigated the fabrication of rGO-organic semiconductor composite material used in the OTFT sensor platform.

1.2 rGO/TIPS-Pentacene composite for sensing material platform

Recently, organic semiconductor were fabricated using solution processing which ensure their promising application in radio frequency identification tag (RFID), display driver, e-paper and chemical sensor (Basu et al., 2014). OTFT produced by using solution-processed organic semiconductor method will be inexpensive due to low temperature processed. It also can formed large area manufacturing and flexibility OTFT (Kim et al., 2007).

Development of rGO process was the main idea for a big scale exploitation of graphene's unique properties. Most potential application of graphene was for electronic devices, but due to its zero-band gap and poor process ability to be deposited onto insulator layer, it has become serious problems that prevent this potential technological development. Zero band gap of graphene will limits the achievable on/off current ratio (Meric et al., 2008). However, organic semiconductor, TIPS-Pentacene have a clear and adjustable band gap (Schlierf & Samorì, 2014). So, by blending together rGO and TIPS-Pentacene means that their electrical properties will also be improved. Soluble rGO-organic semiconductor composite material was believed to have lots of potential compared to other graphene produced by other methods.

1.3 Problem Statement

Synthesis of rGO through chemical process mostly involved the use of toxic chemicals such as hydrazine/ hydrazine derivatives (Park et al., 2011), hydroquinone

(Wang et al., 2008) and sodium borohydride ($NaBH_4$) as a reducing agent. However, these reducing agent were highly toxic or explosive and very difficult to handle for large scale production (Ma et al., 2013) that will give effect to the environment and living organisms. Nowadays, researchers have more focused on reducing GO using green nanotechnology which were cost-effectiveness, massive scalability, versatile and easy processability (Fernandez-Merino et al., 2010). Therefore, alternative chemicals or material to reduce GO by green reduction, which was by applying environmental friendly reducing agent such as amino acid (Chen et al., 2011), carrot root (Kuila et al., 2012), vitamin C (Fernandez-Merino et al., 2010) and thiourea dioxide (Chua et al., 2012). Hence, in this research, green reducing agent were used to overcome this problem, these include ascorbic acid (LAA), formamidinesulfonic acid (FAS) and sodium sulphite (Na_2SO_3). Different reducing agents were important to study for determination of the best reducing agent that can be used to replace toxic chemical during reduction process. After obtained the suitable reducing agent, the optimization parameter such as reaction temperature and time were very important to study in order to get the perfect research methodology to achieve best result in producing rGO.

Usually, a fabrication of TIPS-Pentacene thin film requires vacuum deposition process which was not really suitable for the fabrication of large area device due to their low solubility in solvent. So, spin coating method was used to replace the common method for fabrication of OTFT. Normally, solution processed of TIP-Pentacene used have higher on-off ratios but experience lacking in field effect mobility. While, rGO shows high value of mobility but suffer from low on/off ratio (Basu et al., 2014). By blended this rGO with TIPS-Pentacene, it was believed can overcome the problems that occur during the previous fabrication of OTFT and improve the electrical performance of OTFT.

1.4 Research Objectives

The main objective of this research was to prepare a composite material for OTFT sensor platform in order to improve performance of the material when compared to the pure organic material and reduced graphene oxide (rGO). This main objective was accomplished by the following specific objectives:

Specific Objectives:

i. To synthesis, characterize and optimize the performance of grapheme oxide (GO) and reduced graphene oxide (rGO)
ii. To fabricate and evaluate the performance of OTFT using different parameters
iii. To optimize the performance of rGO/TIPS-Pentacene composite for improved device performance using different solvents

1.5 Scope of Research

To achieve the objectives of this research, five scopes have been identified:

i. Synthesis and optimization of rGO

Synthesis of GO was done by using Tour's method. Graphite was used as raw material. The optimization part was done by varying the temperature and time for the reduction process of rGO.

ii. Characterization of rGO

This study was conducted to identify the structural characteristics of rGO by different reducing agents. Several instruments were used for the characterization such as Fourier transform infrared spectroscopy (FTIR), Thermal gravimetric analyzer (TGA), X-Ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Four point probe and UV-visible spectrophotometer.

iii. Fabrication of OTFT

Fabrication of OTFT was done by modifying the process of fabrication TIPS-Pentacene. Normally, it needs vacuum deposition to deposit the material on top of substrate but in this research, new approach has been applied by using spin coating method. Some optimization was also carried out in this part, which were the effect of concentration and spinning speed dielectric material. For organic semiconductor, different substrate temperature was used in order to determine the optimum parameter of the OTFT. The current-voltage (I-V) measurement was tested by using semiconductor parameter analyser (SPA).

iv. rGO/TIPS-Pentacene composite for OTFT

rGO/TIPS-pentacene composite material for fabrication of OTFT was done by blending the rGO with organic semiconductor which was TIPS-pentacene. For this part, different solvents was optimized in order to obtain the highest current-voltage (I-V) measurement for this composite material. The I-V measurement was examined by using semiconductor parameter analyzer (SPA).

v. Comparison of TIPS-Pentacene, rGO-FAS and FAS/TIPS-Pentacene composite material

These three materials were compared in order to prove that FAS/TIPS-pentacene composite material was better than the other two materials, TIPS-pentacene and rGO-FAS. The I-V measurement was examined by using semiconductor parameter analyser (SPA).

1.6 Thesis Organization

A brief overview of the rest of the chapter are described as below:

Chapter 2: Literature Review

This chapter discusses the literature review of the research. It begins with the background and production of graphene. The reason for choosing chemical synthesis method for graphene production was discussed in this chapter. Besides, fabrication of OTFT which consist of the element present, operation and structure in the transistor also be explained in this chapter. Lastly, at the end of this chapter, it will explain previous research of other rGO-organic semiconductor material that have been study.

Chapter 3: Methodology

In this chapter, list of chemicals and materials that were used in this research was introduced. Next, the synthesis method of GO and rGO are presented. Then, fabrication of OTFT were explained and lastly, the preparation of rGO/TIPS-Pentacene composite