Faculty of Engineering

REDUCTION OF GRAPHENE OXIDE FOR SOLAR CELL APPLICATION

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REDUCTION OF GRAPHENE OXIDE FOR SOLAR CELL APPLICATION

RAFIDAH BINTI KEMAT

A dissertation submitted in partial fulfilment of the requirement for the degree of
Bachelor of Engineering (Hons) in
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This is for my mum, who has taught me to never give up

This is for my dad, who has taught me to never stop dreaming

This is for my siblings, whom I hope to inspire

And lastly,

This is for you, who always be there when I’m in needed.

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ABSTRACT

Third generation of solar cell attracted research interest due to its simple production but not yet commercialize. This research focuses on increasing the solar cell's efficiency by using newly found carbon atom that have excellent electrical property which is reduced graphene oxide. The reduced graphene oxide are prepared and synthesized with method that produced good morphologies of both reduced graphene oxide and the solar cell. Then, characterization is carried out to analyses its performances. A good surface structures of reduced graphene oxide is obtained suggesting the reduction method is conducted successfully. The optical and electrical properties of reduced graphene oxide and the solar cell is at high conductivity and higher light harvesting capacity from the J-V plot. The results obtained satisfy the properties presence in reduced graphene oxide that can increased the efficiency of solar cell.

ABSTRAK

Sel solar generasi ketiga telah menarik minat penyelidikan disebabkan oleh proses pembuatannya yang ringkas tetapi masih belum dikomersialkan. Kajian ini memberi tumpuan kepada peningkatan tahap efisein sel solar dengan menggunakan karbon atom yang baru ditemui dan mempunyai sifat elektrik yang sangat baik iaitu grafin kurang oksida. Grafin kurang oksida disediakan dan disintesis dengan kaedah yang boleh menghasilkan morfologi yang baik untuk kedua-dua grafin kurang oksida dan sel solar. Kemudian, pencirian dijalankan untuk menganalisis prestasinya. Struktur permukaan yang baik untuk grafin kurang oksida diperolehi mencadangkan kaedah pengurangan ini telah dijalankan dengan jayanya. Sifat-sifat optik dan elektrik daripada grafin kurang oksida dan sel solar adalah di tahap kekonduksian yang tinggi dan keupayaan penuaian cahaya yang lebih tinggi daripada *J-V plot*. Keputusan yang diperolehi menepati ciri-ciri yang ada di dalam grafin kurang oksida yang bolehkannya meningkatkan tahap efisien sel solar.

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GO	-	Graphene Oxide
rGO	-	Reduced Graphene Oxide
DI	-	Deionized
$KMnO_4$	-	Potassium Permanganate
H_2SO_4	-	Sulfuric Acid
H_2O_2	-	Hydrogen Peroxide
O	-	Epoxy
OH	-	Hydroxyl
$NaNO_3$	-	Sodium Nitrate
HNO_3	-	Nitric Acid
$KClO_3$	-	Potassium Chlorate
$NaNO_2$	-	Sodium Nitrite
CIO_2	-	Chlorine Dioxide
H_3PO_4	-	Phosphoric Acid
sp^2	-	Hybridisation
HCl	-	Hydrochloric Acid
$NaBH_4$	-	Sodium Borohydride

Ar	-	Argon
Ar/H_2	-	Argon/Hydrogen
NO_2	-	Nitrogen Dioxide
CVD	-	Chemical Vapor Depositions
CCG	-	Chemically Converted Graphene
XPS	-	X-Ray Photo-Electron Spectrometry
TCF	-	Transparent Conductive Film
DSSC	-	Dye-Sensitized Solar Cell
ITO	-	Indium Tin Oxide
FE-SEM	-	Field Emission Scanning Electron Microscope
UV-Vis	-	Ultraviolet-visible Spectroscopy
I-V	-	Current-Voltage
C=C	-	Carbon-Carbon
C=O	-	Carbonyl

CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter contains the overview of the study, which consists of the research background and objectives that gained from the problem statements stated, scope of research and research outline.

1.2 Background

Graphene is a novel 2-dimensional carbon material that has excellent electrical, thermal, mechanical and optical properties [1]. This properties of graphene makes it suitable for energy conversion and storage. Graphene oxide (GO), a product by exfoliation of graphite oxide, has layered structure similar to graphite with various functional groups, epoxy, carbonyl, carboxylic acid and lactol group covalently bounded to its basal plane and edges [2-3]. GO that considered as precursor for graphene, attracted research interest due to its good solubility in water and other solvents, which allows it to be easily deposited onto a wide range of substrates [4].

Graphene oxide was first prepared on 1840, when it was first made by chemical treatments of graphite with potassium chlorate ($KClO_3$) and nitric acid (HNO_3) by British chemist, Brodie and Staudenmaeir. 60 years after that, a new method is developed by chemist named Hummers which used potassium permanganate ($KMnO_4$), concentrated sulfuric acid (H_2SO_4) and sodium nitrate ($NaNO_3$). This chemicals was prepared and maintained below 50^oC to oxidize graphite for twelve hours. In this research, GO was prepared by using improved Hummer's method [5-6], which sodium nitrate ($NaNO_3$) is replaced with phosphoric acid (H_3PO_4) and 9:1 mixture of H_2SO_4: H_3PO_4.

Reduced graphene oxide (rGO), is partially reduced product of GO to graphene-like sheets by removing the oxygen-containing groups with the recovery of the conjugated structure. Reduced graphene oxide is the intermediate state between GO and graphene. By controlling the ratio of sp^2 carbon atoms to sp^3 carbon atoms via reduction chemistry, the band gap for rGO which increase with the oxidation level can be tuned that transformed GO from insulator to a conductor graphene [7]. With this characteristic, rGO has a great potential to be applied in solar cells, biosensors and optical devices [8-10]. The reduction of GO is achieved by chemical reduction which hydrazine hydrate is added to GO solution at 80^{o}C for 24 hours and 10:7 mixture of hydrazine hydrate and GO solution [10-11].

Next, the rGO solution is used in Dye-Sensitized Solar Cell (DSSC) assembly. DSSC is a solar cell that belongs to the third generation of solar cell. DSSC is a thin film solar cell that partly by passes the photosynthesis reaction and makes a shortcut conversion of sunlight into electrical current [13]. The concept of DSSC is to reduce the production cost and energy harvesting time is significant compared to silicon cell or other thin film solar cells. The rGO film was fabricated in the DSSC as a counter electrode. The working principle of DSSC is photon are converted into an electric current by charge injection of excited dye molecules into a wide energy gap semiconductor. Upon exposure to light, the dye present at the photoanode gets excited and photo-induced electrons from dye is transferred towards conduction band of the photoanode, which accompanying the oxidation of redox species in the electrolyte (iodine) and simultaneously, the reaction of reduction occurs at the counter electrodes by accepting electrons [13-16].

In this research, the synthesis, characterization and the application of reduced graphene oxide in the fabrication of Dye-Sensitized Solar Cell were studied and discussed. The performance rGO thin film is varied by the concentration of GO solution, the stirring speed and reaction temperature to enhance the energy efficiency of DSSC.

1.3 Problem Statement

Renewable energy such as solar energy caught the world attention to compete with non-renewable energy such as fossil fuels and others. The aim is to commercialize the third generation of solar cell and to increase its efficiency significance with its low production cost. In conjunction, deposition of rGO thin film and its fabrication into DSSC will fully utilize the properties of graphene that have excellent electrical and optical properties to increase DSSC efficiency.

In order to absorb large amount of photon energy the negative layer of the solar cell have to be thick. However, this will increase the production cost and the construction become more complex. DSSC used thin film in its fabrication which is cheap to produce. As for the graphene, the challenge is to synthesis it in a large quantity. The reduction of GO to rGO restore half of the graphene properties which might be answer on how to produce graphene in large quantity.

Therefore, an ideal concentration of GO solution, stirring speed and reaction temperature while synthesizing GO solution is important to gain excellent analysis of rGO and its performance as thin film in DSSC. The electrical properties of DSSC is analyzed as the fabrication of rGO thin film may increase the efficiency of DSSC.

1.4 Research Objectives

The aim of this research is to study the characterization of reduced graphene oxide and its performance as thin film in Dye-Sensitized Solar Cell. In order to achieve the aim above, objectives of the research are as below:

i) To synthesis graphene oxide (GO) from graphite powder by using improved Hummer's Method.

ii) To reduce graphene oxide (rGO) from graphene oxide (GO) by using chemical reduction.

iii) To examine the surface morphology, optical and electrical properties of reduced graphene oxide for Dye-Sensitized Solar Cell application.

1.5 Scope of Research

This study focuses on preparing GO from graphite powder via improved Hummer's method through mixing with potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4). The concentration of GO solution, stirring speed and reaction temperature are varied in this project with 1.0ml, 1.5ml and 2ml for concentration, 100rpm, 200rpm, and 300rpm for the stirring speed and 60^{o}C, 80^{o}C and 100^{o}C for the reaction temperature. Then, hydrazine hydrate solution is poured into the GO solution to produce rGO solution. This method is called chemical reduction. Next, spray pyrolysis technique is used to deposit the rGO solution as rGO thin film that then fabricated into DSSC.

The performance analysis of rGO thin film and DSSC has been carried out focusing on its surface morphology, optical and electrical properties. Various methods are used to analyze this characterization which are Scanning Electron Microscope (SEM) for surface morphology, Ultraviolet-visible spectroscopy (UV-Vis) for optical properties and I-V characteristic for electrical properties.

1.6 Research Outline

This report is organized to represent the developmental stages of the whole research. This report consists of five chapters. Chapter 1 is generally about the introduction of the research detailing the research background and application of the research which includes the problem statement of the research, the objectives of the research, scope and the outlines of the research. The overview of reduced graphene oxide and Dye-Sensitized solar cell application are also discuss in this chapter.

Chapter 2 covers the literature review, which describes the fundamental and the existing researches and studies related to the research are obtained from journal and articles. In this chapter, further elaboration about solar cell generations, the thin film of rGO, synthesizing and coating method of rGO are stated. This chapter also provides guidance and references for methodology in Chapter 3.

In Chapter 3, it focuses on the research methodology of the preparation of rGO, coating rGO as a thin film by using homemade spray pyrolysis and its fabrication into DSSC. Then, the characterization of the rGO and DSSC will be conducted. The steps and procedures are expressed with flow charts. Chapter 3 represent a brief summary about all the information gathered and studied in Chapter 2.

Then, in Chapter 4 the findings and the analysis of the research are discussed, which include the results obtained from the characterization and the problems that have encountered during the period of completing the research. The obtained results is validated by comparing with the previous researches.

Lastly, Chapter 5 provides the conclusion of the accomplishment of the research. Some future recommendations also included in this chapter. This chapter conclude everything that had been done and observed, and the research objectives that have been achieved. Based on the problem that faced while doing the research, recommendations for further improvement of the research are given.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter consists of explanation on development of graphene. The characteristic of each synthesis and reduction method of graphene oxide is reviewed. Next, the solar cell generations and DSSC is discussed, referring to its efficiency and its performance.

2.2 Development of Graphene

Graphene, a single layer of graphite which also a member of carbon family is often considered as the basic unit for others member of carbon family [1]. Derived from graphite, graphene is a unique atom-thick two dimensional (2D) crystal that is stable under ambient condition due to its specific electronic structures. This structures gives unusual electronic properties such as the anomalous quantum Hall effect and high carrier mobility at relatively high charge carrier concentrations at room temperature [2]. A few and single-layer transferable graphene nanosheets is first obtained by mechanical exfoliation of bulk graphite and by epitaxial chemical vapor deposition. However, graphene is less effective for large scale manufacturing due to its complex method of synthesis [3].

One of the way to produced graphene is by chemical reduction. Solution-based reduction of graphene oxide is attractive for its easy operation in recent year [5-7]. There are a few steps to synthesis graphene. First, graphene oxide (GO) is synthesis from graphite oxide by using Improved Hummer's method. Then, the graphene oxide (GO) is reduced by using chemical reduction method.

2.2.1 Graphite Oxide to Graphene Oxide (GO)

Graphite oxide is a compound made up of carbon, hydrogen and oxygen molecules [5]. It is artificially created by treating graphite with a water-free mixture of concentrated sulfuric acid. These oxidizers work by reacting with the graphite and removing an electron in the chemical reaction. This reaction is known as a redox (a portmanteau of reduction and oxidation) reaction, as the oxidizing agent is reduced and the reactant is oxidized [6]. Despite of that, graphite oxide has similar layered structured to graphite but the carbon atom in graphite is heavily decorated by oxygen group, which make graphite to have a thick hydrophilic layer [3-6].

Other than that, graphene oxide is effectively a by-product of graphite oxidization as when the oxidizing agents react with graphite, the interlayer distance between the layers of graphite is increased. The completely oxidized compound can then be dispersed in a base solution such as water, and graphene oxide is then produced. Differ from graphite oxide, graphene oxide contains only one or a few carbon atom like graphene and also have hydrophilic properties.

In addition, the main difference between graphite oxide and graphene oxide is the interlayer distance between the individual atomic layers of the compounds, caused by water intercalation [7]. As a result, graphene oxide can be described as a random distribution of oxidized areas with oxygen-containing functional groups, combined with non-oxidized regions where most of the carbon atoms preserve sp^2 hybridization [2-4].

Another properties of graphene oxide is it has good solubility in water and other solvents, which allows it to be easily deposited onto a wide range of substance. Besides, the optical, mechanical and electrical properties of graphene oxide can be tuned by controlling the degree of the oxidation.

2.2.2 Graphene Oxide (GO) to Reduced Graphene Oxide (rGO)

Reduced graphene oxide is the intermediate state between graphene oxide and graphene. The most attractive properties of graphene oxide is that it can be partly reduced to graphene-like sheets by removing the oxygen-containing groups with the recovery of the conjugated structures[2]. The reduction of graphene oxide produce graphene-like material both in structure and properties.

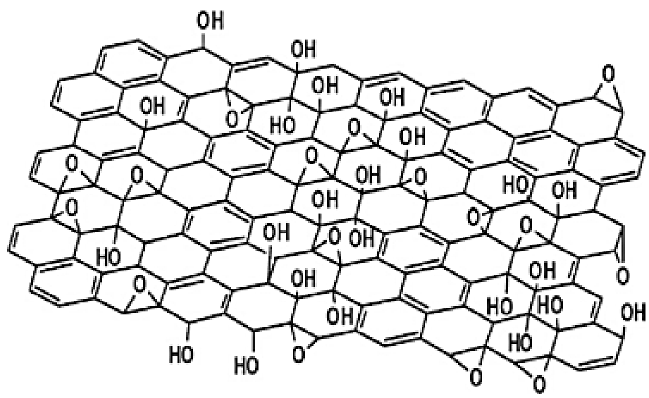

Figure 2.1: Lerf-Klinowski model of GO with the omission of minor groups (carboxyl, carbonyl, etc.) on the periphery of the carbon plane of the graphitic platelets of GO [2].

Oxygen-containing group, epoxy (O) and hydroxyl (OH) is decorated in carbon plane of graphene oxide as shown in graphene oxide model proposed by Lerf and Klinowski [2].Carbonyl groups are also present, most likely as carboxyl acids along the sheet edge but also as organic carbonyl defects within the sheets. All these functional groups are covalently bounded to its basal plane and edges [2-4]. The aim of reduction is to reduce the oxygen-containing groups that presence in graphene oxide.

The conductivity of graphene mainly relies on the long-range conjugated network of the graphitic lattice. Functionalized breaks the conjugated structure which results in a decrease of both carrier mobility and carrier concentration. However, the conductivity is blocked by the absence of percolating pathways between sp^2 carbon clusters to allow classical carrier transport to occur. Thus, reduced graphene sheets or films are typically insulating and exhibiting higher sheet resistance [2-5].