Faculty of Engineering

Characterization of Titanium Dioxide (TiO_2) doping on Reduced Graphene Oxide (rGO) for Dye Sensitized Solar Cell (DSSC) Application

Afiqah binti Baharin

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. It is original and the result of my work, unless otherwise indicated or acknowledged as reference work. This thesis has not been accepted for any degree and is not concurrently submitted in candidate of any other degree.

Name of student	: Afiqah bt Baharin
Student ID No.	: 17020129
Program Degree	: Master of Engineering (Electronic Engineering)
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Signature of Student	:
Date	:

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ABSTRACT

This research is to fabricate dye sensitized solar cell with introduction of graphene layers and examine the structural, optical, electrical properties and chemical bonding of different doping ratio of TiO_2-rGO for Dye Sensitized Solar Cell (DSSC) application. Titanium Dioxide solution was prepared using precipitation peptization method and reduced graphene oxide solution was prepared by using chemical reduction method. The effects of different doping ratio of TiO_2-rGO were studied and fabricated for DSSC application. The performance of the thin film was characterized by Scanning Electron Microscope (SEM), X-ray Diffraction (XRD) and Atomic Force Microscopy (AFM) for structural properties. Meanwhile, Ultraviolet-visible spectroscopy (UV-Vis) and Fourier Transform Infrared spectroscopy (FTIR) for optical properties, I-V measurement by using Keithley sourcemeter to analyse the electrical properties of the thin film while X-ray Photoelectron Spectroscopy (XPS) measurement to analyse the chemical bonding between TiO_2 and rGO. It is observed that a low content of rGO (0.1 wt%) was successfully incorporated with TiO_2 and form Ti-O-C bond, which enhance the power conversion efficiency up to 1.21% compared to pure TiO_2 (0.19%). This was also supported by UV-Vis spectra with highest absorption and lowest band gap energy of 2.87 eV. However, 0.5 wt% TiO_2-rGO resulted in poor photoconversion efficiency performance due to the over photocatalytic reaction occurred leaving extra holes on the counter electrode. Therefore, rGO is potentially to be coupled with TiO_2 and applied as photoanode in DSSC application to lower the recombination loss.

Keywords: Doping, DSSC, titanium dioxide, reduced graphene oxide, thin films.

Pencirian Doping Titanium Dioksida (TiO_2) dengan Grafin Kurang Oksida (rGO) terhadap Pewarna Sel Solar Sensitif (DSSC)

ABSTRAK

Projek ini memperkenalkan lapisan grafin untuk difabrikasi ke dalam pewarna sel solar sensitif (DSSC) dan mengkaji kesan nisbah campuran yang berlainan antara TiO_2-rGO daripada segi struktur, optikal, elektrikal dan ikatan kimia. Larutan Titanium Dioksida (TiO_2) disediakan melalui proses pemendakan peptisasi manakala grafin kurang oksida disediakan melalui proses pengurangan kimia. Kesan nisbah campuran yang berlainan antara TiO_2 dan rGO telah disiasat dan filem nipis tersebut akan difabrikasi ke dalam aplikasi DSSC. Beberapa kaedah telah digunakan untuk menkaji struktur filem nipis tersebut. Kesan struktur dapat dikaji menggunakan kaedah imbasan mikroskop elektron (SEM), sistem pembelauan sinar-X (XRD) dan daya atom mikroskop (AFM). Sementara itu, kaedah spektrofotometer ultra lembayung-nampak (UV-VIS) dan spektrofotometer infra-merah (FTIR) digunakan untuk menganalisis kesan optikal filem. Selain itu, ciri-ciri elektrikal filem dapat diukur menggunakan kaedah ukuran I-V menggunakan mesin Keithley manakala ikatan kimia dapat dianalisa menggunakan kaedah spektroskopi fotoelektron sinar-X (XPS). Kajian mendapati bahawa kandungan rGO yang rendah (0.1 wt%) berjaya digabungkan dengan TiO_2 dan membentuk ikatan Ti-O-C, yang meningkatkan kecekapan penukaran kuasa sehingga 1.21% berbanding TiO_2 yang tulen (0.19%). Penemuan ini juga disokong oleh spektrum UV-Vis dengan penyerapan tertinggi dan tenaga jarak jalur terendah sebanyak 2.87 eV. Oleh itu, TiO_2-rGO berpotensi untuk dijadikan sebagai photoanode dalam aplikasi DSSC. Bagaimanapun, 0.5 wt% TiO2-rGO menghasilkan prestasi kecekapan fotokonversi yang kurang baik kerana reaksi fotokatalitik yang berlebihan dan menyebabkan wujudnya lubang tambahan di elektrod kaunter. Oleh itu, rGO *berpotensi untuk digabungkan dengan TiO_2 dan digunakan sebagai fotoanod dalam aplikasi DSSC untuk mengurangkan kehilangan rekombinasi.*

Kata kunci: *Doping, DSSC, titanium dioksida, grafin kurang oksida, filem nipis.*

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AFM	Atomic Force Microscopy
CO_2	Carbon dioxide
CNT	Carbon nanotubes
CB	Conduction band
DMF	Dimethylformamide
DSSC	Dye-Sensitized Solar Cell
FF	Fill factor
FTO	Fluorine-doped Tin Oxide
FTIR	Fourier Transform Infrared Spectroscopy
GO	Graphene oxide
I_{max}	Maximum current
I_{sc}	Short circuit current
ITO	Indium Tin Oxide
mA	Miliampere
NC	Nanocomposites
PCE	Power conversion efficiency
P_{in}	Input power
P_{max}	Maximum power
rGO	Reduced Graphene Oxide
SEM	Scanning Electron Microscope
TCO	Transparent Conductive Oxide
TiO_2	Titanium Dioxide

TTIP	Titanium (IV) Isopropoxide
UV-Vis	Ultraviolet-visible spectroscopy
V	Voltage
VB	Valance band
V_{oc}	Open circuit voltage
XPS	X-ray Photoelectron
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Research Background

Recently, global warming results from the large scale emission of carbon dioxide (CO_2), development of green house effect and air pollution which can caused countless illness from year to year around the world (Lai et al., 2015; Low et al., 2018). This is also due to utilization of non renewable energy sources such as petroleum, natural gas, coal and fossil fuels in our daily activities (Lai et al., 2015). The energy demand of the world is growing from time to time.

Henceforth, the development of renewable energies such as wind, solar, biomass and hydropower have been widely studied to overcome the global issues (Low et al., 2018). The solar energy has been thoroughly analyzed. It is worth to mention that the solar energy is the ideal energy compared to other renewable energy due to abundance, natural friendly and endless support to the Earth to generate electricity (Siddick et al., 2017). The International Energy Agency (IEA) has predicted that 20% of the world's energy supply comes from solar energy in 2050 and supposed to increase up to 60% in 2100 (Lai et al., 2015). Therefore, there must be a continuous production of solar energy and made available at cheaper price for each and everyone to utilize it.

In the past decades, a new solar cell design which is based on nanostructured materials has been studied. It is called Dye Sensitized Solar Cell (DSSC) reported by M.Gratzel and O'Regan in 1991 (Elsanousi et al., 2013). In fact, DSSC was extremely promising low-cost materials and easy to fabricate while still providing energy conversion efficiency up to 11.5% (Mohammad et al., 2017). This solar cell enables conversion of sunlight into useful electrical energy. DSSC device has a sandwich structure which is include of photoanode, an electrolyte, dye and a counter electrode (Wei et al., 2016). The photoanode has derived great attention due to its function to transport photo-induced electrons and absorb dye which helps to determine the photo-current density (Wei et al., 2016). It plays a big role in the working process of DSSC. Among various semiconductors, Titanium Dioxide (TiO_2) has been largely used as photoanode in DSSC. This is due to its higher photoactivity, wide band gap, nanostructure mesoporous structure, low cost and relative non-toxicity (Zulkifli et al., 2015). Nevertheless, the enhancement of performance is compulsory by modifying the DSSC. Recently, it has been reported that TiO_2-rGO nanocomposite has been used in DSSC to improve the optical properties, high photo-catalytic and enhanced the power conversion efficiency (PCE) in DSSC (Low et al., 2017).

This research focused on the different doping ratio of TiO_2 and rGO which are 0.1 wt%, 0.3 wt% and 0.5 wt% to observe and enhance the effect of photocatalytic performance of TiO_2 when adding only small amount of rGO. The optical, structural and electrical characterization of the samples are carried out.

1.2 Problem Statement

Based on previous research, continuous work has been done in order to increase the photoconversion efficiency of DSSC. The TiO_2 photoanode has a main role throughout the light to electrical conversion in DSSC. It contains electron movement from the dye molecules to the conduction band of TiO_2. The excited electrons will flow across the Indium Tin-Oxide (ITO), external load and finally to the counter electrode (Eshaghi et al., 2015). However, the charge recombination is a main factor that limits the performance of DSSC (Mohammad et al., 2017). This is to say that the back-electron transfer in the TiO_2

photoanode-electrolyte interfaces before reaching the collecting electrode, such as ITO, is considered to be the major recombination pathway, which decrease the efficiency of DSSC system (Eshaghi et al., 2015; Raja et al., 2016). Moreover, TiO_2 has a wide band gap (3.2 eV) which also limits its utilization of visible light region (Lin et al., 2017). Therefore, to prevent the recombination process, several ways have been used including the use of composite semiconductor photoanode with different bandgaps and insertion of some doping elements in the TiO_2 photoanode (Eshaghi et al., 2015).

In the past two decades, one-dimensional (1D) and two-dimensional (2D) nanomaterials such as carbon nanotubes (CNTs) and graphene sheets have doped with TiO_2 photoanode to increase DSSC achievement (Eshaghi et al., 2015). The graphene may be more suitable than CNTs for charge separation due to its superior electron conductivity (2000 S/cm), high surface area (>2600 m^2/g), high electron mobility (15,000 cm^2/Vs) and good contact with metal oxide materials, TiO_2 nanomaterial is the potential candidate to couple with rGO to form composite film since graphene also have zero band gap (Lai et al., 2015; Low et al., 2016). Moreover, the band gap of TiO_2-rGO nanocomposite was reduced significantly due to formation of Ti-O-C bond between TiO_2 and rGO which results for a better electron transitions and lowered the recombination loss (Low et al., 2018; Awang et al., 2019). The usage of TiO_2-rGO as photoanode in DSSC was still limited and loosely used at the current stage as further study is still required. Thus, comprehensive studies have been conducted to optimize the concentration of TiO_2-rGO as photoanode in DSSC to improve the power conversion efficiency (PCE) results.

1.3 Research Questions

(i) What is the optimum doping ratio of TiO_2 and rGO for DSSC application?

(ii) What is the structural, optical, electrical and chemical bonding effects of different doping ratio of TiO_2 and rGO?

1.4 Research Hypothesis

RGO which is reduced by chemical reduction methods will doped with TiO_2 is expected to improve the structural, optical and electrical properties of Dye Sensitized Solar Cell.

1.5 Research Objectives

The objectives of this research are:

(a) To improve the performance of ITO photoanode layer by rGO doping.

1.6 Scope of Research

This research will focus on varying the doping ratio of Titanium Dioxide (TiO_2) and reduced Graphene Oxide (rGO) which is 0.1 wt%, 0.3 wt% and 0.5 wt%. The concentration of rGO played an important role to observe and improve the performance of photocatalytic of TiO_2 when adding only small amount of rGO. N-719 dye will be used as sensitizers. TiO_2 is prepared by using precipitation peptization method while rGO is synthesized via chemical reduction method. The solution is deposited by using doctor blade method. The annealing temperature for the thin film is fixed at 450 °C to minimize the interfacial defects as well as to ensure a good Ti ion substitution onto the rGO NC and maintain the anatase phase of TiO_2 (Luan et al., 2016; Low et al., 2017). All the works are carried out in the faculty laboratory.

1.7 Research Gap

Previous research showed that synthesization of TiO_2 with sol gel method has obtained low optical and PCE up to 1.07% only (Taya et al., 2015). In present study, TiO_2 is synthesized by precipitation peptization method that gives good optical and better electrical performance. It is important to address the effects of TiO_2 doped rGO. It may also have high efficiency compare to pure TiO_2. This doping process should be considered whether it can lead to higher wavelength, lower band gap and high efficiency. Previous study has reported that graphene has good electrical conductivity but has not been widely used as photoanode in DSSC (Nouri et al., 2016). In current study, doping of TiO_2 and rGO is utilized to obtain higher PCE.

1.8 Organization of Thesis

The project outlines are divided into five chapters which includes introduction, literature review, methodology, results and discussion and conclusion and recommendation.

Chapter 1 reviews the introduction of this research which includes the introduction, problem statement, research gap, research hypothesis, objectives of the study and scope of the research. The overview of TiO_2 doped rGO and Dye Sensitized Solar Cell (DSSC) are also discussed in this chapter.

Chapter 2 is devoted to literature review where existing studies and researches related to the project obtained from journals and articles. The study on generation of solar cells, working principles of DSSC, properties of TiO_2 and rGO and different synthesis of TiO_2 and rGO are elaborated in this chapter. This chapter helps to provide guidance and references for methodology in chapter three.

Chapter 3 explains about the research methodology. This chapter briefly explains on all the methods, equipments and materials used in this research. The preparation of TiO_2 and rGO, deposition method for TiO_2-rGO, preparation of electrodes and dye for DSSC fabrication are explained in this chapter. The steps and procedure are expressed with flow chart. In addition, the characterization technique used are also described in this chapter.

Chapter 4 discuss all the findings gain from the research, which also include the results obtained from characterization of the samples and problem encountered during the research. The obtained results are validated by comparing with the previous research.

Lastly, Chapter 5 reserves for conclusion and recommendation for this research for further improvement. This chapter conclude everything that had been done and observed, and the research objectives that have been achieved. Based on the problems faced during the research, recommendation for further improvement of the research is discussed.