



Faculty of Engineering

The Temperature Effects of Titanium Dioxide (TiO_2) Doped Reduced Graphene Oxide (rGO) for Perovskite Solar Cell Application

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The Temperature Effects of Titanium Dioxide (TiO₂) Doped Reduced Graphene Oxide (rGO) for Perovskite Solar Cell Application

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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 is the result of my work, unless otherwise indicated or acknowledged as referenced work. This thesis has not accepted for any degree and is not concurrently submitted in candidature for any other degree.

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ABSTRACT

Perovskite solar cells (PSC) are evolving in spectacular pace and emerging as the most promising future generation of photovoltaic devices. In the present study, reduced graphene oxide (rGO) is introduced to titanium dioxide (TiO₂) as electron transport layer (ETL) in perovskite solar cell (PSC). TiO₂ doped rGO (TiO₂/rGO) was prepared by combining titanium (IV) oxide nanopowder as precursor for TiO₂ and chemically reduced graphene oxide for rGO. The TiO₂/rGO is varied with different annealing temperature and its effect on TiO₂/rGO properties and on electrical performance of PSC is studied. The surface morphologies of TiO₂/rGO thin films is characterized via Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM) and X-Ray Diffraction (XRD). Meanwhile, Ultraviolet-visible spectroscopy (UV-Vis) and X-ray Photoelectron Spectroscopy (XPS) are used to characterize the optical properties and chemical bonding respectively. Lastly, (I-V) analysis for electrical properties is performed. Structural and morphological evidences from SEM, AFM and XRD results confirmed that the TiO₂/rGO samples existed in anatase phase, rutile phase and the porosity as well as the surface roughness of TiO₂/rGO thin films increased as the annealing temperature increased. The absorption spectra and the band gap obtained at 326 nm and 2.48 eV respectively for TiO₂/rGO that annealed at 550 °C portraits better performances due to increment in grain size in higher annealing temperature. The formations of Ti-O and Ti-O-C bonds are confirmed from XPS analysis that fastening the rate of electron transfer in PSC. The electrical properties of TiO₂/rGO confirming that 550 °C TiO₂/rGO has better conductivity at 18.83×10^{-3} S/cm in conjunctions with its performance in optical properties.

Keywords: Doping, perovskite solar cell, reduced graphene oxide, titanium dioxide.

Kesan Suhu Doping Titanium Dioksida (TiO₂) dengan Grafin Kurang Oksida (rGO) untuk Aplikasi Sel Solar Perovskite

ABSTRAK

Sel solar perovskite (PSC) telah berkembang dengan pesat dan muncul sebagai prospektif generasi masa depan untuk peranti fotovoltaiik. Dalam kajian ini, grafin kurang oksida (rGO) dicampurkan dengan titanium dioksida (TiO₂) sebagai lapisan electron penghantar (ETL) dalam sel solar perovskite (PSC). Doping TiO₂ dengan rGO (TiO₂/rGO) telah dihasilkan melalui penggabungan titanium oksida (IV) dalam serbuk nano sebagai pendahulu untuk TiO₂ manakala rGO melalui pengurangan kimia daripada grafin oksida. TiO₂/rGO dihasilkan dengan suhu penyepuhlindapan yang berbeza dan kesannya terhadap sifat TiO₂/rGO dan prestasi elektrik dalam PSC dicatatkan. Mofologi permukaan filem tipis TiO₂/rGO dianalisa melalui Pengimbasan Elektron Mikroskop (SEM), Mikroskop Angkatan Atom (AFM) dan Difraksi X-Ray (XRD). Sementara itu, Spektroskopi Ultraviolet (UV-Vis) dan X-ray Photoelectron Spektroskopi (XPS) digunakan untuk mendapatkan sifat optik dan ikatan kimia. Akhirnya, analisis (I-V) untuk prestasi elektrik dilakukan. Struktur dan morfologi yang diperolehi daripada keputusan SEM, AFM dan XRD mengesahkan bahawa sampel TiO₂/rGO wujud dalam fasa anatase, fasa rutil dan keliangan serta kekasaran permukaan filem nipis TiO₂/rGO meningkat apabila suhu penyepuhlindapan meningkat. Spektrum penyerapan dan jurang band yang diperolehi pada 326 nm dan 2.48 eV menunjukkan bahawa TiO₂/rGO yang anil di 550 °C mempamerkan prestasi yang lebih baik disebabkan kenaikan dalam saiz butiran dalam suhu penyepuhlindapan yang lebih tinggi. Pembentukan ikatan Ti-O dan Ti-O-C disahkan dari analisis XPS mengawal kadar pemindahan elektron dalam PSC. Prestasi TiO₂/rGO dari segi elektrik mengesahkan

bahawa 550 °C TiO₂/rGO mempunyai kekonduksian yang lebih baik pada $18.83 \times 10^{-3} \text{ S/cm}$ bertepatan dengan prestasinya dalam sifat optikal.

Kata kunci: *Doping, sel solar perovskite, grafin kurang oksida, titanium dioksida.*

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LIST OF ABBREVIATIONS AND SYMBOLS

Al_2O_3	Aluminium oxide
Au	Gold
C	Carbon
C-C	Carbon-carbon
C-O	Carbon-oxygen
COOH	Carboxylic
$\text{CH}_3\text{NH}_3\text{PbBr}_3$	Methylammonium lead bromide
$\text{CH}_3\text{NH}_3\text{PbI}_3$	Methylammonium lead iodide
DMF	Dimethylformamide
ETL	Electron transport layer
ETM	Electron transport material
FTO	Fluorine doped tin oxide
GO	Graphene oxide
HTL	Hole transport layer
HTM	Hole transport material
H_2O	Water
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
H_3PO_4	Phosphoric acid
KMnO_4	Potassium permanganate
Li-TFSI	Lithium bis(trifluoromethanesulfonyl)imide
O	Oxygen

OH	Hydrogen
PbI ₂	Lead (II) iodide
PEG	Polyethylene glycol
PSC	Perovskite solar sell
rGO	Reduced graphene oxide
Spiro-OMeTAD	2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene
TCO	Transparent conducting oxide
Ti	Titania
TiO ₂	Titanium dioxide
TiO ₂ /rGO	Titanium dioxide doped reduced graphene oxide
TTIP	Titanium isopropoxide
ZnO	Zinc oxide
σ	Resistivity
ρ	Conductivity

CHAPTER 1

INTRODUCTION

1.1 Research Overview

Renewable energy tender opportunity of carbon-free economy for a greener and sustainable energy development in the world whereas the non-renewable energy sources produced enormous amount of carbon dioxide (CO_2) that harmful to environment and contribute to the hikes in climate changes and global warming (Nematollahi et al., 2016). Solar energy harvesting has been done substantially through photovoltaic devices as energy supply from the sun is reliable, renewable, and sustainable with no worry of depletion (Papoola et al., 2018). Thin film based photovoltaics solar cell such as copper-indium-gallium-selenide (CIGS), cadmium telluride (CdTe), dye-sensitized solar cell (DSSC), organic solar cell and perovskite solar cell (PSC) especially have caught research attention whereas by 2030 photovoltaic are anticipated as the third of global electricity generation (Green et al., 2014).

Perovskite solar cell has shown an increase in power conversion efficiency (PCE) at phenomenal rate in just seven years as compared to other type of photovoltaics. Perovskite is an organic-inorganic material that have shown its own capabilities for the use in light-emitting diodes, sensors, field-effect transistors and photodetectors (Assadi et al., 2018). Perovskite solar cells belong to the family of third generation of solar cell. The third generation of solar cell uses organic material in its fabrication that cut down the cost of making a solar cell. Perovskite solar cell also has display special combination of ambipolar charge transport properties, good broadband absorption and long carrier diffusion (Tonui et al., 2018).

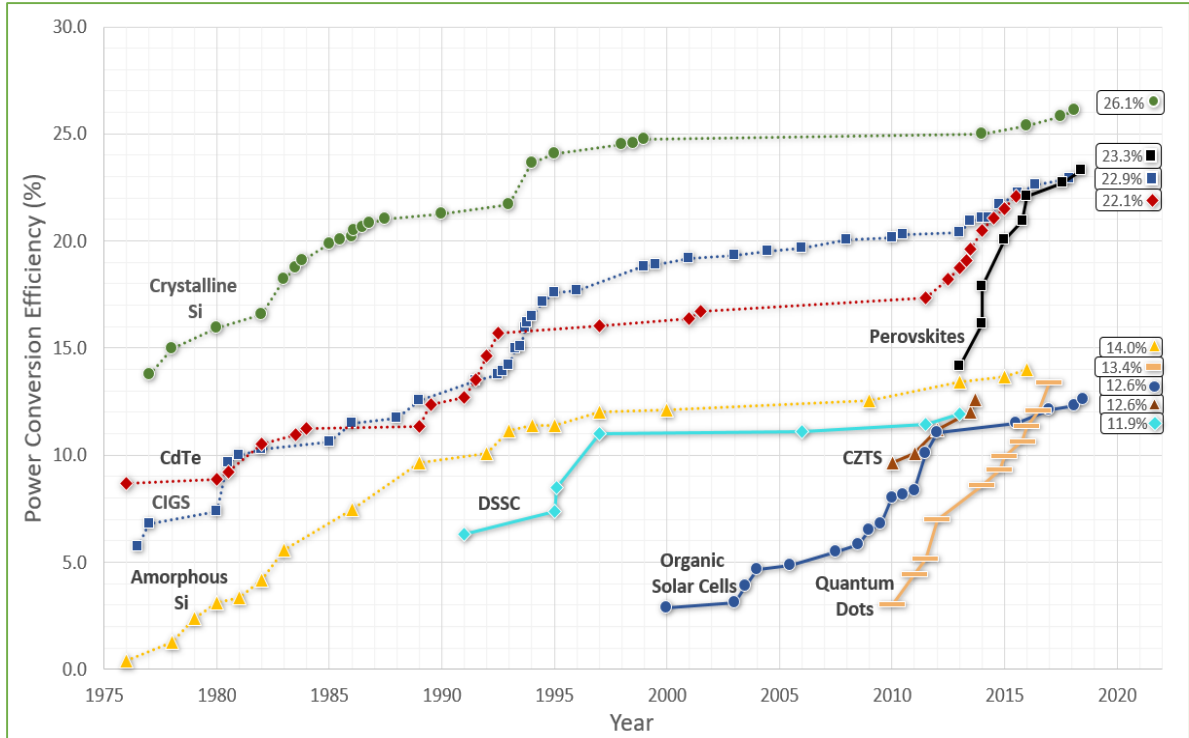


Figure 1.1: PCE for conventional photovoltaics (Best Research-Cell Efficiency Chart. (n.d.).

The first published perovskite solar cell was fabricated with methylammonium lead bromide ($\text{CH}_3\text{NH}_3\text{PbBr}_3$) as perovskite sensitizer and recorded 3.5% of power conversion efficiency (PCE) in 2009 (Tonui et al., 2018). Interestingly, the efficiency jumped to >15% after seven years later by making the perovskite material solid and cell design simpler with the use of methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) as perovskite material (Wu et al., 2014; Asghar et al., 2017). The high efficiency enabled the perovskite to compete with another conventional established technologies as shown in Figure 1.1. This dramatic increase in efficiency is due to the perovskite-based absorbers itself where it has larger capability to absorb photons than other conventional materials in making solar cells. In fact, it beats the industry-leading material silicon which it can absorb a larger spectrum of light (Mehmood et al., 2017).

Relatively, perovskite solar cells have two different configurations which are the meso-superstructured PSC and planar heterojunction PSC (Allesandro et al., 2016). In meso-superstructured device, the mesoporous layer typically made of metal oxide such as nano-crystalline titanium dioxide (TiO_2) and aluminium oxide (Al_2O_3) as scaffold infiltrated with perovskite solar cell. In this research, the nanocomposites reduced graphene oxide (rGO) and titanium dioxide (TiO_2) nanoparticles were utilized as electron transport layers in meso-superstructured perovskite solar cell. It has been reported that graphene- TiO_2 nanocomposites has the benefits of high conductivity and better electrical contacts of graphene and graphene-like materials for electron transporting. Furthermore, the highest PCE reported graphene-PSC works so far was done by Nicholas which had shown remarkable PCE up to 15.6% (Nicholas, 2013). This shows that the integration of graphene into PSC can compete with other intrinsic PSC in term of power conversion efficiency.

Further study on the graphene-PSC integration by using reduced graphene oxide (rGO) that synthesized through improved Hummer's method and chemical reduction is conducted in this research. The hole transporting layers (HTM) used in the PSC is highly expensive due to synthesis complexity. The material of choices here is 2,2',7,7'-tetrakis-(N, N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-oMETAD) which has been well studied due to its popularity in solid state dye solar cells (DSCs). In addition, its tendency to be uncontrollably doped by O^2 which necessitate the development of alternatives. An application of nanocarbons such as graphite, carbon nanotubes, and graphene/polymer composites based hole transporters is one of alternative worth to further investigated.

Next, the synthesis, characterization and the application of titanium dioxide doped reduced graphene oxide (TiO_2/rGO) as mesoporous layer in the fabrication of perovskite solar cell were studied and discussed. The performance TiO_2/rGO thin film and TiO_2/rGO -

based perovskite is varied by the annealing temperature of titanium dioxide to enhance the electrical performances of perovskite solar cell.

1.2 Research Problem Statement

Resources for a clean and renewable energy is one of the challenges that our society have to face in order to allay with the rapidly increasing demand for the developing population and industrialization. The usage of non-renewable energy such as fossil fuels and others have contributed to rise of atmospheric temperature and high level emission of carbon dioxide (CO_2) that associated with the greenhouse effect (Khalaji et al., 2018). A lot of studies have been executed for solar energy harvesting that has been performed through photovoltaic devices. PSCs have been dominating research interest due to its impressive development in power conversion efficiency (PCE) that have reached 20% in over seven years of research as compared to other type of solar cell (Tonui et al., 2018). In spite of that, further improvement are imperative to optimize and enhance the PSC devices operation, stability and device performance. The aim is to construct photovoltaic device, an argonometal halide perovskite solar cell with $\text{CH}_3\text{NH}_3\text{PbI}_3$ as the absorber that coated upon the surface of mesoporous TiO_2/rGO .

Throughout the years, anatase TiO_2 was found to be the most common material to enhance photocatalytic properties of photoanodes in solar cell due to its long-term thermodynamic stability, low cost and relatively non-toxicity (Kang et al., 2019). However, the drawbacks are anatase TiO_2 tend to suffer from high recombination center of electrons and hole coupled with wide band gap which is 3.2 eV (Tan et al., 2013).

On the other hand, graphene has been widely used in application of optoelectronic and photon energy conversion due to its unique mechanical and electrical properties (Lundie et al., 2015; Chong et al., 2016). Some research was conducted and it is reported that rGO nanocomposites were an applicable additive for enhancing the charge collection properties in dye-sensitized solar cells (DSSCs), owing to its ability to reduce the charge-recombination pathways effectively and decrease the leakage current (Cho et al., 2016). More recently, Wang et al. reported that TiO₂/rGO composite based blocking layer is negatively effecting the energy barrier and series resistance between TiO₂ (Wang et al., 2014).

Therefore, it is believed that the induced of rGO in TiO₂ and its fabrication as TiO₂/rGO photoanodes in PSC utilizing the properties of graphene that have excellent electrical and optical properties merging with chemical stability in TiO₂ to increase PSC efficiency and to achieve good conductivity. Accordingly, the post annealing temperature dependence while synthesizing TiO₂-rGO solution and its performance as mesoporous layer in PSC is systematically studied in its surface morphologies, optical characteristic, chemical bonding analysis and current-voltage measurements.

1.3 Research Hypothesis

TiO₂ doped rGO that synthesized at different annealing temperature improve the performance of structural, optical, chemical bonding and electrical properties of TiO₂/rGO as fabricated in perovskite solar cell.

1.4 Research Gap

For research gap, there are two main findings of studies are discussed. First, it is studied from literature review that TiO_2 have three crystalline phase which are anatase, rutile and brookite. The phase changing often links to the annealing temperature used during synthesis. Previous work stated that TiO_2 will change its phase from anatase to rutile at annealing temperature of 700 °C and above (Fazli et al., 2016). Meanwhile the current study investigated annealing temperature from 450 °C to 650 °C with 100 °C increment that shown the presence of rutile phase in TiO_2 at 550 °C to 650 °C annealing temperature. This finding might surpassed the theory that only annealing temperature effecting the TiO_2 phase, might as well the surrounding atmosphere, the preparation methods or the type of chemicals used in preparing TiO_2 solution.

Secondly, in past few years, numerous perovskite fabrication has used mesoporous TiO_2 as electron transport material (ETM) with spiro-OMeTAD as HTM and $\text{CH}_3\text{NH}_3\text{PbI}_3$ as the absorber (Tonui et al., 2018). In the effort of finding the most reliable photovoltaic solar cells, research by research must be done to fully optimize the performances of solar cell. Then, the idea of doping the TiO_2 with rGO in conjunction with excellent properties of graphene has been introduced in DSSC as its photoanodes and has increased the efficiency of DSSC. In this wise, this research introduced the TiO_2 doped rGO in PSC configurations as its mesoporous layer with improvement in electrical properties of PSC.

1.5 Research Objectives

The aim of this research is to study the characterization of TiO_2 doped rGO (TiO_2/rGO) solution and its performance as thin mesoporous layer perovskite solar cell. In order to achieve the aim above, objectives of the research are as below:

- (i) To examine the effects of 450 °C, 550 °C and 650 °C annealing temperature on TiO_2 doped rGO by structural, optical, chemical bonding analysis and electrical.
- (ii) To fabricate $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based perovskite devices using spiro-OMeTAD as a hole transport layer and TiO_2 doped rGO as electron transport layer.

1.6 Scope of Research

This study focuses on modifying the electron transport layer in PSC. In this research, PSC is constructed with introduction of titanium dioxide doped reduced graphene oxide (TiO_2/rGO) layers as electron transport layer. The annealing temperature of titanium dioxide were varied at 450 °C, 550 °C and 650 °C. TiO_2 is prepared by using Titanium (IV) oxide nanopowder as precursor with addition of polyethylene glycol in its process. Meanwhile, for rGO solution, first the graphene oxide (GO) is prepared by using Improved Hummer's method, then the GO solution's obtained is chemically reduced to become rGO. Subsequently, the TiO_2 is doped with the rGO solution via nano-composite process to obtain the TiO_2/rGO mixture. Next, TiO_2/rGO is deposited by using spin coating technique for thin film characterization and fabricated as ETL to become perovskite solar cell.

Next, the performance analysis of TiO_2 -rGO thin film and perovskite solar cell has been carried out focusing on its surface morphology, optical, chemical bonding structure and electrical properties. Various method are used to analyse this characteristic which are

Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM) and X-Ray Diffraction (XRD) for surface morphology, Ultraviolet-visible spectroscopy (UV-Vis) for optical properties, X-ray Photoelectron Spectroscopy (XPS) for chemical bonding analysis and current-voltage (I-V) analysis for electrical properties.

1.7 Structure of Thesis

This thesis 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 titanium dioxide doped reduced graphene oxide (TiO_2/rGO) and perovskite 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 perovskite solar cell fundamental, the development of TiO_2/rGO as mesoporous layer in perovskite solar cell, preparation of every layer in perovskite solar cell are stated. This chapter also provides guidance and references for methodology in Chapter 3.

In Chapter 3, it focuses on the research methodology for synthesizing of every layer in perovskite solar cell, the deposition method by using spin coating and the annealing of each layer. Then, the characterization of the TiO_2/rGO and perovskite solar cell will be conducted. The steps and procedures are expressed with flow charts. Chapter 3 represents 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 are 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.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Generally, this chapter reviews the potential of TiO₂ doped rGO as electron transport material in PSC. First, the structure and properties of TiO₂, its synthesis methods and the effect of adding polymer in TiO₂ is discussed. Then, the development of rGO from graphite and graphene oxide are reviewed focusing on its synthesis methods, stating the goods and drawbacks of each method as well as with their performances in previous research. The discussion on doping process and past findings on advantages of TiO₂ doped with rGO following the next reviews. Lastly, the overall configuration of perovskite solar cell is discussed includes the PSC structures, configurations, working principles and charge transport buffer layers of PSC. The reviews on PSC mainly focusing on past performance of PSC with various electron transport material (ETM) and hole transport material (HTM) as TiO₂ doped rGO is rarely used as ETM in PSC therefore, the enhancement in PSC performances is expected.

2.2 Titanium Dioxide (TiO₂)

2.2.1 Introduction of TiO₂

Over the past few decades, TiO₂ or also known as titania has been studied extensively in the field of material science with regards to its wide range in application of photocatalysis, heterogeneous catalysis, sensor devices, in solar cell for the production of

hydrogen and electric energy, white pigment in paints, corrosion protective coating and optical layers (Coronado et al., 2008). The interest on TiO_2 studied have been motivated by the photo-catalyst properties of TiO_2 that have relatively high efficiency in water decomposition (Diebold, 2003; Tang et al., 2008), artificial photosynthesis (Kang et al., 2019) and degradation of organic species (Li et al., 2010; Chen et al., 2011).

In 1972, Fujishima and Honda discovered the production of hydrogen on TiO_2 photo-electrodes under ultraviolet illumination (Fujishima & Honda, 1972). After that, Frank and Bard first investigated the potentiality of using TiO_2 to decompose cyanide in water that increase research interest of TiO_2 in environmental applications (Frank & Bard, 1977). Accordingly, TiO_2 represent as effective photo-catalyst in water referring to its strong oxidation activity and hydrophilicity (Fujishima & Zhang, 2006).

On top of that, DSSC, a solar cell that based on dye-absorbed nanostructured TiO_2 film has shown excellent photo-conversion efficiency with a good long term stability as reported by Grätzel (Grätzel et al., 1991). In conjunction with that, the research affection in preparation and characterization of TiO_2 thin film has developed promptly because the performance of solar cell depends significantly on properties of TiO_2 thin film.

2.2.2 Structure of TiO_2

TiO_2 polymorphs exist in three distinct crystallographic forms which are anatase, brookite and rutile. Anatase and rutile shared the same crystalline structure that resembled to the tetragonal system meanwhile brookite has an orthorhombic structure (Lee et al., 2011; Gharavi et al., 2015). The three different crystalline phase in TiO_2 are assembled by titanium (Ti^{4+}) atoms that coordinated to six oxygen (O^{2-}) atoms forming TiO_6 octahedral structure

that linked with different corners and edges. Each octahedron in anatase and rutile is shared with four and two edges to form tetragonal structure meanwhile, each octahedron in brookite is shared with three edges to form orthorhombic structure (Lai et al., 2015). Figure 2.1 as depicted, shows the structure geometry of rutile, brookite and anatase phases in TiO_2 (Palaez et al., 2016).

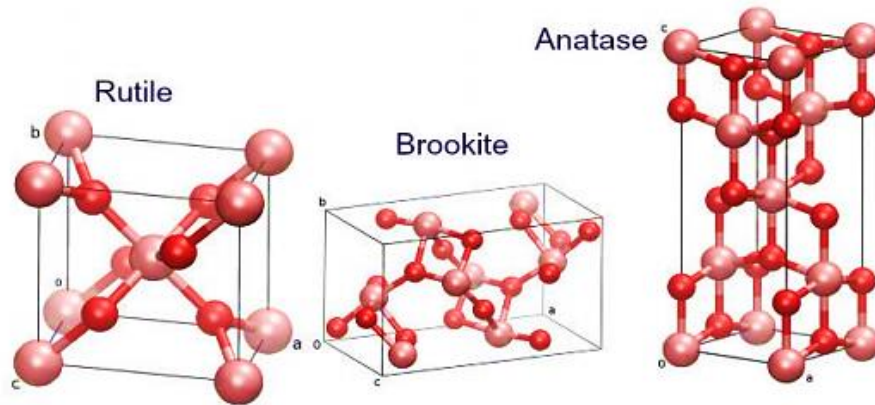


Figure 2.1: Crystal structure of TiO_2 phases (Palaez et al., 2016)

In addition, as a bulk material, rutile is thermodynamically most stable phase however, solution-phase preparation methods for TiO_2 generally favor for the anatase structure (Coronado et al., 2008). Moreover, anatase and brookite are in metastable phase and promptly reconstruct to rutile when heated (Paola et al., 2013).

Deposition methods and annealing temperature controls the physical properties of TiO_2 material. Annealing temperature can transform amorphous TiO_2 to anatase then to rutile as the temperature increases. In most cases, during deposition, TiO_2 thin films is amorphous and the phase change to anatase as the annealing temperature is in between 200 °C to 700 °C. Anatase TiO_2 may also change to rutile since it is metastable when the annealing temperature increase from 700 °C to 1000 °C (Fazli et al., 2016). Brookite may exist during both anatase and rutile phase as brookite is the by-product of the precipitation

process that carried out in acidic medium with low temperature. Brookite is the least studied TiO_2 properties due to its difficulty to be obtained in pure phase.

Aside from that, the effect of annealing contributes to improve the surface morphology and crystallinity of TiO_2 . Hasan and the team also reported that annealing of thin films make the grain size becomes larger, more porous, decrement in the transmittance of the film, increment in the value of refractive index and allowed indirect optical band gap (Hasan et al., 2008).

Table 2.1: Summary of TiO_2 with different phase

TiO₂ Phase	Crystalline Structure	Annealing Temperature (°C)	Phase Stability	Band Gap (eV)	Refractive Index (η_D)	Ref.
Anatase	Tetragonal	200-700	Metastable	3.20	2.491	Yu et al., 2016
Rutile	Tetragonal	700-1000	Most stable	3.02	2.903	Zhu et al., 1999
Brookite	Orthor- hombic	200-1000	Metastable	3.26	2.583	Fazli et al., 2016

Table 2.1 summarizes the differential in TiO_2 structure that lead to different properties along with the annealing temperature for each phase. Anatase is more preferred to be used in solar cell due to its larger band gap and low electron hole recombination rate even though rutile is more thermodynamically stable. Besides that, the refractive index for

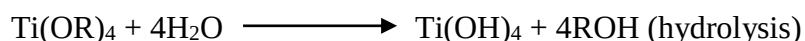
both anatase and rutile phase is relatively higher making the TiO₂ as an ideal candidate for generating photo electrons in solar cell (Pal et al., 2007).

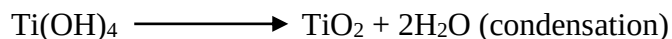
2.2.3 Synthesis Methods of TiO₂

The preparation or synthesis phase of TiO₂ nanopowder is very crucial as the size, morphology, the crystalline phase and the performance of TiO₂ is depending on it. Various synthesis method of TiO₂ have been developed over the last decade in order to obtain TiO₂ nanostructured with desired properties. Synthesis of anatase TiO₂ nanoparticles via solution routes in aqueous environment has been widely studied in variety of experimental conditions. There are five most commonly used methods which are the sol-gel technique, precipitation, microemulsion technique, hydrothermal and solvothermal (Gupta & Tripathi, 2011).

2.2.3.1 Sol-gel Technique

The sol-gel method is liquid process synthesis that based on inorganic polymerization reactions. There are mainly four steps in sol gel method which started with hydrolysis, polycondensation, drying and thermal decomposition. To begin, the hydrolysis of the precursors of the metal or non-metal alkoxides takes places and interact with water or alcohols. Then, addition of acid base to the water and alcohol supported in the hydrolysis of the precursor. The solvent is removed strictly after the condensation of the solution to form a gel occurred. Lastly, calcination is necessary to decompose the organic precursor (Behnajady et al., 2011; Deghan & Ansary, 2018).





Where R = alkyl group

While higher calcination temperature is required to decompose the organic precursor, it is crucial to control the solution composition, the pH of the solution and also the temperature as the size of the sol particles depending on it.

Hellers and co-workers have established several methods for production of TiO_2 thin films via sol-gel method. In their proposed methods, a titanium alkoxide as for example, titanium isopropoxide (TTIP) is hydrolyzed and treated with sulphuric acid (H_2SO_4) to produce a sodium-depleted layer. After that, the solution is coated onto a glass substrate and calcined at 500°C for approximately 20 to 30 minutes (Jackson et al., 1991; Heller et al., 1996). This method often resulting anatase TiO_2 crystallites of 3-6 nm in diameter and it is transparent (Zaban et al., 2000).

Other than that, titanium (IV) tetraisopropoxide also used as precursor with either ethanol or isopropanol as solvent and calcined at $300\text{--}700^\circ\text{C}$. It is found that the presence of isopropanol restrained anatase-rutile transformation by controlling the hydrolysis rate. In addition, the TiO_2 photocatalytic activities is strengthen with isopropanol solvent and have thermal stability in anatase crystalline phase (Chau et al., 2009).

The main advantages of sol-gel preparation method in terms of optical and electronic applications are ambient temperature of sol preparation and gel processing, product homogenally, low sintering temperature, mitigate multi-components in materials making, and great control over powder particle size, shape and size distribution (Ganguli & Mater, 1998). The application of mesoporous TiO_2 synthesized via sol-gel method can be used as

catalyst support, photoanodes in solar cell, adsorbent and as a ceramic membrane top layer (Parala et al., 2002; Li et al., 2003).

2.2.3.2 Precipitation Method

There are mainly two reasons for the formation of the precipitate from a homogeneous liquid phase which are the physical transformation and chemical process. The physical transformation referring to the temperature changes, pH, solvent evaporation and reactant concentration meanwhile, the chemical process are the addition of bases or acid and the usage of complex forming agents (Gupta & Tripathi, 2011).

In general, the formation of new solid phase in liquid medium produced two elementary processes that developed either simultaneously or sequentially. The first one is the nucleation which referring to the formation of the elementary particles on the new phase under a stable precipitation conditions. The second elementary process is the growth or agglomeration of the particles (Schwarz, 1995).

The release of anions and cations is controlled by the kinetics of nucleation and particle growth. It is important to control the factors that determine the precipitation process such as the concentration of the reactants and pH in order to obtain nanoparticles with narrow size distribution (Burda et al., 2005). Besides that, it is also studied that for a better metal dispersion, lower processing temperatures is more favorable compared to high processing temperature (Davis et al., 1992).

Firstly prepared TiO₂ nanoparticles by precipitation is done by Namin and co-workers by using aqueous titanium tetrachloride (TiCl₄) solution with ammonium hydroxide (NH₃) as precipitation agent. The TiO₂ gel is let to crystallize under refluxing and

continuously stirring for 6 hours at 90 °C and then dried overnight in an oven with 100 °C temperature. The resultant solid is then annealed at 300 °C to 900 °C. Both anatase and rutile phases of TiO₂ is obtained as the calcination temperature increased (Namin et al., 2008). After that, chemical precipitation method has been used to synthesis doped-TiO₂ (Wu et al., 2007). It is reviewed that doped-TiO₂ nanoparticles able to show great photocatalytic activity under visible light irradiation (Sato et al., 2006; Kostedt et al., 2008).

To conclude, precipitation method is an easy and convenient approach to synthesize TiO₂ nanoparticles from aqueous solutions as well as the sol-gel method. Furthermore, the precipitation method is now studied to minimize the production cost for commercial use while conserving the high photoactive in TiO₂.

2.2.3.3 Microemulsion Technique

Researches define microemulsion technique as micro-domains of one or both liquid that stabilized by an interfacial film of any surfactant. Microemulsion is thermodynamically stable and the solution of two immiscible liquids is optically isotropic. Besides providing a micro-heterogeneous medium for generation of nanoparticles, microemulsion restrain the formation of the particle via reactant distribution in the droplets and inter-droplet dynamic exchange of reactants. Particle nucleation, particle growth and agglomeration is limited due to cage-like effect of microcavities (Leung et al., 1988; Liu et al., 2008).

There have been limited details on controlled TiO₂ synthesis from microemulsion although convincing early studies is broadcasted (Zhang et al., 2002; Lim et al., 2004). In general, Deorsola and co-workers reported that hydrolysis of titanium alkoxides in

microemulsion based sol-gel method produced an uncontrolled aggregation and flocculation aside from synthesis at very low concentration (Chong et al., 2006; Deorsola et al., 2009).

In addition, Chhabra and the team has introduced microemulsion-mediated process for TiO_2 synthesis with ultrafine particle (Chhabra et al., 2001). In their work, water-in-oil microemulsion have been used as reactor to precipitate the titanium (IV) hydroxide that act as precursor. They conclude that the particle size increases when the calcination temperature decreases. Apart from that, both anatase and rutile phase of TiO_2 can be obtained by microemulsion with hydrothermal treatment at 120 °C (Wu et al., 1999). It is somehow interesting to have two different TiO_2 polymorph by using same temperature method.

2.2.3.4 Hydrothermal Method

Hydrothermal synthesis defined as the engagement of water as a catalyst and as a component of solid phases at temperature more than 100 °C and at pressure more than few bars (Somiya et al., 2000). This method produces mono-dispersed and highly homogenous nanoparticles and generally used in ceramic industries to process nano-hybrid and nanocomposites material (Byrappa et al., 2007; Chen et al., 2007).

The synthesis of TiO_2 via hydrothermal method is often conducted in a small autoclaves of Morey type that also provided with Teflon liners. Pure and homogenous TiO_2 nanoparticles can be achieved with aid of Teflon liners. The selected temperature and pressure for TiO_2 synthesis are not more than 200 °C and less than 100 bars.

There are a few preliminary studies conducted for hydrothermal method. First, synthesis of TiO_2 particles in ethanol-water solution with mixed anatase and rutile phase as precursor (Yan et al., 2010). Yan and the team conclude that the shape and phase structures

of TiO_2 is depending on ratio of the water-ethanol used. Besides that, synthesis of mesoporous TiO_2 by hydrothermal method with cetyltrimethyl ammonium bromide (CTAB) as precursor that prepared by Zhou and the team (Zhou et al., 2008). Their findings stated that as claimed method exhibited good catalytic activity for degradation of methyl orange. Next, microwave assisted hydrothermal method is introduced to synthesis nitrogen doped TiO_2 nanoparticles. Excellent heating performance of microwave able to gain rapid synthesis in comparison to conventional method and higher photocatalytic activities is obtained (Zhang et al., 2017).

2.2.3.5 Solvothermal Method

The solvothermal method can be defined as the chemical reaction or chemical transformation in organic solvents during hypercritical temperature and pressure (Kim et al., 2003). The type of organic solvents used such as methanol, butanol and toluene differs the solvothermal method from hydrothermal method as hydrothermal method used water as solvents (Wang et al., 2001; Fujishiro et al., 2003). The properties of TiO_2 such as particle size, crystalline phase and the surface configuration can be controlled via reaction temperature, pressure, solvent properties and aging time (Carp et al., 2004). As compared to hydrothermal method, the output from solvothermal method is free from foreign anions due to the usage of organic solvents in this method (Chen et al., 2010).

Apart from sol-gel method, solvothermal method is commonly used among researchers. First employed solvothermal method by synthesizing colloidal solutions with TiO_2 nanoparticles resulting smaller and better uniformity TiO_2 nanoparticles (Lee et al., 2001). Next, 9-15 nm crystallite size of TiO_2 nanoparticles is obtained via solvothermal

method by controlling the concentration of titanium (IV) butoxide, the holding time as well as the reaction temperature. The crystallite size of TiO_2 is increasing along with the increment in temperature and holding time (Kongsuebchart et al., 2006).

In addition, different nanoforms of TiO_2 such as nanorods, nanowires and nanotubes in pure anatase phase are synthesized using solvothermal route. Different reaction time and different type of solvent have been used during synthesized that controlled the shape, size and optical properties of TiO_2 (Das et al., 2008). Phase transition of TiO_2 from anatase to rutile also occurred when TiO_2 is doped with nitrogen in solvothermal (Liu et al., 2009).

To conclude, this method contributes to excellent chemical homogeneity and produces uncommon metastable structure of TiO_2 at low reaction temperature aside from recording higher photocatalytic activities compared to TiO_2 commercial product (Lee et al., 2001).

2.2.3.6 Summary of Synthesis Method for TiO_2

Table 2.2: Synthesis method of TiO_2 with resultant phases

Synthesis Method	Temperature	Phases Formed				Ref.
		Amorphous	Anatase	Rutile	Anatase + Rutile	
Sol-gel (TTIP + H_2SO_4)	200 °C	•	•			Zaban et al., 2000

Table 2.2 continued

Synthesis Method	Temperature	Phases Formed				Ref.
		Amorphous	Anatase	Rutile	Anatase + Rutile	
Precipitation (TiCl ₄ + NH ₃)	300 °C		●	●		Namin et al., 2008
Micro- emulsion (TiO ₂ micro- Emulsion)	360 °C		●	●		Wu et al., 1999
Hydro-thermal (TiO ₂ + ethanol-water)	500 °C		●	●	●	Yan et al., 2010
Solvo-Thermal (TiO ₂ + nitrogen)	600 °C		●	●	●	Liu et al., 2009

2.2.4 Addition of Polymer in TiO₂

Porosity in TiO₂ is often obtained via particle agglomeration, solvent evaporation or mediation of structure during synthesis and crystallization process (Brezesinski et al., 2009). However, the high porosity realization in TiO₂ is still in constrained due to inadequate studies and relevant process. Even though some synthesis methods have achieved preferable porosity but the purity as well as the ambiguity in the reproducibility and stability of porosity

is still uncertain (Liu et al., 2011; Ye et al., 2011). Therefore, it is crucial to encounter synthesis process that leads to architecture of excellent porosity along with porous connectivity (Zhang et al., 2013).

Recently, water based polymer, the polyethylene glycol (PEG) has been widely used in synthesis of metal oxide owing to its strong reducing power (Wei et al., 2006) and high boiling point which is up to 197 °C (Pol et al., 2007). Jiang and co-workers have synthesized TiO₂, SiO₂, Al₂O₃ and PbO₂ with PEG to obtain nanoporous particles (Jiang et al., 2004).

PEG is reported to have excellent properties as a polymer such as graft modification on the surface of nanoparticles in order to prevent agglomeration, renders nanoparticles resistant to protein absorption and enhancing bio-compatibility of nanoparticles (Mano et al., 2012; Sanaz et al., 2014). Other than that, the abilities of PEG to enhance photocatalytic activities is diagnosed considering the effect of porosity and larger specific surface area (Chang et al., 2013; Wang et al., 2013). Imao and the team conclude that as the PEG content in the solution increases, the particles size is decreasing and this leads to higher performance in solar cell (Imao et al., 2006).

2.3 Reduced Graphene Oxide (rGO)

2.3.1 Introduction of rGO

Graphene is a novel two-dimensional carbon material that have admirable electrical, thermal, mechanical and optical properties. These abilities of graphene makes it suitable for energy reconstruction and storage (Chen et al., 2012). Meanwhile, reduced graphene oxide (rGO) 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 (Pei & Cheng, 2012). The reduction of graphene oxide able to produce graphene-like material both in structure and properties.

Researchers defined graphene oxide (GO) as a random distribution of oxidized areas with oxygen-containing functional groups, combined with non-oxidized regions whereas most of the carbon atoms preserve sp^2 hybridization (Marcano et al., 2010). GO has layered structure similar to graphite with numerous functional groups such as, epoxy, carbonyl, carboxylic acid and lactol group that covalently bounded to its basal plane and edges (Zhu et al., 2010; Hansora et al., 2015).

Due to the presence of oxygen-containing functional groups in graphene oxide, reduction of graphene oxide is conducted in order to remove the oxygen containing group that bonded to graphene while restoring the conjugated network of the graphitic lattice. This modification is believed to enhance electrical conductivity and other properties of graphene (He & Fang, 2016).

In view of rGO as intermediate state between graphene oxide and graphene, rGO is obtained via two synthesis process. The first one is synthesis of graphite oxide that produced graphene oxide and the second one is the reduction process of graphene oxide to obtain rGO.

2.3.2 Synthesis Methods of GO

Over the past 150 years, there is a few methods that have been proposed to synthesis graphene oxide. The methods are Brodie's method, Staudenmaier's method, Offeman's method, Hummer's method, Modified Hummer's method and Improved Hummer's Method.

Among these methods, the most common method that widely used for graphite oxidation is Brodie, Offeman and Hummer's method (Wu et al., 2009).

On 1859, Brodie's method is proposed, which stand as pioneering work on the synthesis of graphene oxide. In this method, one equal weight of graphite is mixed with three equal weights of potassium chlorate (KClO_3) and reacted in fuming nitric acid (HNO_3) at 60 °C for 4 days (Botas et al., 2013). After that, Staudenmaier improved the Brodie's method by replacing approximately two thirds of fuming nitric acid (HNO_3) with concentrated sulfuric acid (H_2SO_4), and adding some potassium chlorate (KClO_3). Thus, the presence of concentrated sulfuric acid (H_2SO_4) enable the overall reaction in a single vessels which make the synthesis method become simpler (Marcano et al., 2010).

In conjunction, Offeman's method and Hummer's method is invented in 1958. In this method, one equal weight of graphite powders is introduced to concentrated sulfuric acid (H_2SO_4) solution containing three equal weights of potassium permanganate (KMnO_4) and 0.5 equal weight of sodium nitrate (NaNO_3) (Alazmi et al., 2006).

The Hummer's method, has three important advantages compared to previous techniques. First, the reaction is completed within few hours while previous method take at least days. Next, the oxidation agent for Brodie's method, potassium chlorate (KClO_3) is replaced with potassium permanganate (KMnO_4) to improve the safety of the reaction due to the presence of chlorine dioxide in potassium chlorate lead to explosive gas evolution. Third, the usage of sodium nitrate (NaNO_3), instead of fuming nitric acid (HNO_3) eliminates the formation of acid fog during reaction (Cao & Zhang, 2015).

Hummer's method has the most intensive attention because of its high efficiency and satisfying reaction safety. Then, the Hummer's method is improved by replacing sodium

nitrate (NaNO_3) with phosphoric acid (H_3PO_4), increasing the amount of potassium permanganate (KMnO_4) and performing the reaction based on volume ratio 9:1 for the mixture of H_2SO_4 : H_3PO_4 .

Other than that, Improved Hummer's method provides greater amount of hydrophilic oxidized graphene material compared to Hummer's method and Modified Hummer's method with additional potassium permanganate (KMnO_4). This proved that Improved Hummer's method is more oxidized than other Hummer's method. In addition, this modification also successfully increase the reaction yield, reducing toxic gas evolution and have a simpler protocol (Shahriary & Athawale, 2014).

2.3.2.1 Summary for Synthesis Method of GO

Table 2.3: Summary for synthesis method of GO

Synthesis Method	Oxidation Agent	Advantages	Disadvantages
Brodie	KClO_3 and NaNO_2	Favors the formation of conjugated epoxy and hydroxyl groups that leads to incorporation of oxygen-in-plane.	Explosive evolution of chlorine dioxide (ClO_2)

Table 2.3 continued

Synthesis Method	Oxidation Agent	Advantages	Disadvantages
Hummer's	KMnO ₄ , H ₂ SO ₄ , and NaNO ₃	Reaction completed within few hours and the usage of KmNO ₄ improve reaction safety.	Oxidation procedure releases toxic gases such as NO ₂ and N ₂ O ₄
Improved Hummer's	KmNO ₄ , H ₂ SO ₄ and H ₃ PO ₄	Increase reaction yield, simpler protocol and reduce toxic gas evaluation during preparation.	-

2.3.3 Synthesis Method of rGO

Generally, rGO is a product of reduction from graphene oxide. Reduction is conducted in the effort to partly restore the structures and properties of graphene whereby the final properties of rGO is depending on the type of reduction method. In present day, multiple reduction strategies have been proposed such as chemical reduction, thermal reduction and multi-step reduction. Chemical reduction can be divided to chemical reagent reduction, photocatalyst reduction and salvothermal reduction. As for thermal reduction, there are two proposed methods which are thermal annealing and microwave reduction. Next is the multi-step reduction, which combine chemical reduction and thermal annealing (Pei & Cheng, 2012; He & Fang, 2016).

2.3.3.1 Chemical Reduction

Chemical reduction defined as the chemical reaction of chemical reagent with GO. Reduction is normally conducted by moderate heating in room temperature. Due to this, the demand in equipment neither the surrounding to carry out chemical reduction is not as critical as other type of reduction. Thus, chemical reduction is cheaper and easily available for mass production of graphene. Stankovich and co-workers have discovered the potential of hydrazine to chemically reduced graphene oxide (Stankovich et al., 2007). These discoveries pioneer the studies in mass production of graphene and owing to that, hydrazine has been accepted as a good chemical reagent to reduce graphene oxide (Mattevi et al., 2009; Fernandez et al., 2010).

Reduction by hydrazine and its derivative such as hydrazine hydrate, can be prepared by adding the liquid reagents to the GO solution. Hydrophobicity of rGO is increasing as hydrazine reduction produced agglomerated graphene-based nanosheets. In case of drying or calcination, the electrically conductive rGO black powder with carbon to atomic ratio around 10 can be achieved (Stankovich et al., 2008). The highest conductivity reported by rGO film produced by hydrazine reduction is 99.6 S/cm with carbon to oxygen atomic ratio around 12.5 (Wang et al., 2008).

Most recent, sodium borohydride (NaBH_4) is found out to be more effective than hydrazine as a reductant agent of GO (Shin et al., 2017). Sodium borohydride (NaBH_4) is slowly hydrolyzed by water. Then, its use is kinetically slow enough that the freshly-formed solution functions effectively to reduce graphene oxide. Though sodium borohydride (NaBH_4) is most effective at reducing C = O species, the drawback is the moderate efficiency

in the reduction of epoxy groups and carboxylic acids, yet the alcohol groups remain after reduction (Moon et al., 2010).

2.3.3.2 Thermal Reduction

Reduction of GO by heat treatment is called thermal annealing reduction. Usually, rapid heating at temperature below 2000 °C per minutes is performed to exfoliate graphite oxide to achieve graphene (Schniepp et al., 2006; Wu et al., 2009). After that, the rGO is exfoliated in sudden expansion of carbon oxide and carbon dioxide gases that derived in between graphene sheets during the rapid heating procedure. Apart from that, the oxygen-containing groups that attached on carbon plane of GO is decomposed into gases as the rapid heating temperature increases (McAllister et al., 2007).

Other than that, rapid heating strategies also decreased the amount of functionalized graphene sheets by decomposing oxygen-containing groups during increment in temperature. This ability of thermal treatment makes it as a good approached to produce bulk quantity of graphene. However, this technique also has some drawbacks which are producing small size and wrinkled graphene sheets (Schniepp et al., 2006). This is mainly because oxygen-containing groups also removes carbon atom from the carbon plane during decomposition which splits the graphene sheets into small pieces and result in the distortion of the carbon plane. Plus, the carbon dioxide released from thermal exfoliation also caused structural damage to graphene sheets (Kudin et al., 2007).

In addition, thermal annealing is often conducted in vacuum condition, in an inert or reducing atmosphere (Becerril et al., 2008) This is due to the presence of oxygen gas is

strictly prohibited because the presence of oxygen increased along with the high temperature (Wang et al., 2008).

To conclude, even though high temperature annealing is efficient to reduce GO, there are still some drawbacks. First, large energy is consumed during high temperature annealing. Then, the heating process must be very slow to avoid the expansion of the structure if the aim of the process is to obtain an assembled GO which is very time consuming. If the rapid heating is used, the structure of rGO may explode. Lastly, high temperature means that this reduction method cannot be used for graphene oxide thin films on substrates with a low melting point, such as glass (Gilje et al., 2007).

2.3.3.3 Multi-Step Reduction

Multi-step reduction is recommended to enhance the reduction of graphene oxide. Eda and co-workers reported that the annealing temperature needed to require an excellent reduction of graphene oxide film is decreased by using pre-reduction of hydrazine vapor (Eda et al., 2008). Hydrazine reduction that combined with low temperature thermal annealing at 200 °C able to produce a better conductivity of rGO thin film as compared to the rGO thin film that obtained from thermal annealing only (Chen et al., 2008; Si & Samulski, 2008).

By considering that majority of the effect in the reagents of chemical reactions is selective, the usage of only one reducing agents cannot eliminates all oxygen-containing functional groups. Gao and the team have introduced a three steps reduction process that started with deoxygenating with sodium borohydride (NaBH_4), dehydration with concentrated sulfuric acid (H_2SO_4) and thermal annealing (Gao et al., 2009). The presence

of NaBH₄ able to remove most of the alcohol group including ketone, ester and lactone. Meanwhile, concentrated H₂SO₄ dehydrated the remaining alcohol groups to form alkene bond from conjugated sp² carbon network (Zhou et al., 2009).

Multi-step reduction able to record the highest value of carbon to oxygen atomic ratio as compared to other type of reduction. However, the electrical conductivity of reduced graphene oxide film reported is still lower than thermal annealing in Argon (Ar) atmosphere at the same temperature (Wang et al., 2008). Multi-step reduction also not prefer by some researchers as the annealing atmosphere required is very high also time consuming whereas two types of reduction is combined to produce rGO.

2.3.3.4 Summary for Synthesis Method of rGO

Table 2.4: Summary for synthesis method of rGO

Reduction Method	Characterization	Advantages	Disadvantages
Chemical Reduction - Hydrazine hydrate	Moderate heating at room temperature.	Cheaper and easily available for mass production of graphene.	Produce aggregation of rGO sheets.
Thermal Reduction - Thermal annealing in Ar/H ₂	Rapid heating (>2000 °C/min) to exfoliate graphite oxide.	Have dual effect that can produce bulk quantity of graphene.	High temperature of annealing consume large energy.

Table 2.4 continued

Reduction Method	Characterization	Advantages	Disadvantages
Multistep Reduction			
- NaBH ₄ solution	Combination of chemical reduction and thermal annealing.	Produce rGO film with better carbon to atomic ratio.	Electrical
- Concentrated H ₂ SO ₄			conductivity of rGO film lower
- Thermal annealing at 1100 °C in Ar/H ₂			than direct thermal annealing.

2.4 Titanium Dioxide (TiO₂) Doped Reduced Graphene Oxide (rGO)

Anatase crystalline phase of TiO₂ is well known with their capabilities in photocatalytic activities. Anatase TiO₂ is favorable in solar cell fabrication due to its strong redox ability and excellent resistance to photocorrosion (Hasan et al., 2015). However, the wide band gap properties in anatase TiO₂ is coupled with high recombination center of electrons and holes (Tan et al., 2013). In addition, the electron and hole pairs produced by TiO₂ have audacity to withstand rapid recombination, which lead to deactivation of photocatalyst (Song et al., 2011).

Recent years of research suggested that doping of TiO₂ is a promising solution to enhance the photocatalytic abilities of TiO₂. This is referring to the changes at internal structure of TiO₂ crystallinity and expansion of the absorption spectrum (He et al., 2011; Fan

et al., 2012). The doping of TiO₂ is claimed to narrowing the band gap while expanding the absorption spectrum to visible region due to hybridization between 2p state and O-2p state of dopants that culminates in photocatalytic enhancement of TiO₂ (Zhou et al., 2013).

Yun and co-workers reviewed that recombination process in TiO₂ can be reduced via metal doping as the centers of metal have the potential as electron trapping (Yun et al., 2012).

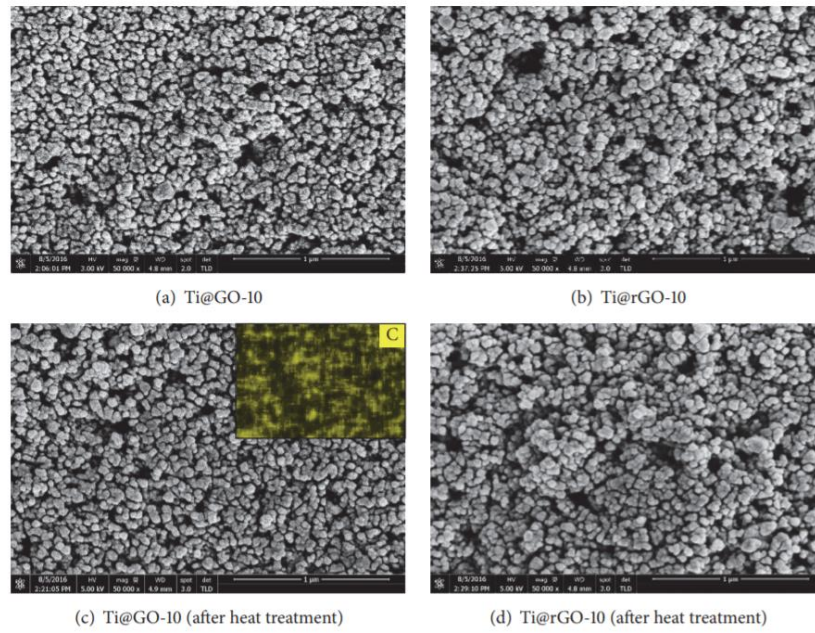


Figure 2.2: Porous structure of GO /TiO₂ before and after heat treatment for Dye Synthesized Solar Cell Application (Kanta et. al., 2017)

Graphene is one type of metal that have raised research interest owing to its high conductivity and large surface area. Graphene also widely used in the field of photo-catalyst due to its rare structure (Shu et al., 2013; Tang et al., 2013). TiO₂ doped with rGO able to decrease the band gap of TiO₂ due to formation of Ti-O-C bond and hybridization of C 2p² orbitals and O 2p⁴ orbitals that produces a new valence bond (Li et al., 2013). To conclude, doping of TiO₂ with rGO increase its adsorption performance in visible area that leads to increment in photocatalytic efficiency of TiO₂.

In this study, the heat treatment (annealing) of TiO₂ doped rGO is of interest because this approach could be suitable with the DSSC application, taking into account the fact that the TiO₂ coated FTO usually underwent heat treatment (or annealing) during the fabrication process in order to get rid of some organic residual. In relation to this study, it can be expected that the GO phase in the GO/TiO₂ composites could be in situ reduced during annealing. In fact, better photovoltaic performance of the heat treatment GO/TiO₂ based photoelectrode has been demonstrated by several researchers (Wang et. al., 2012, Kusumawati et. al., 2014, Cheng and Stadler, 2015).

It has been shown that the heat treatment of GO/TiO₂ based photoanode resulted the porous structure as shown in Figure 2.2. It is shown that the porous structure consisting of interconnected particulate structure of the titania was retained.

2.5 Perovskite Solar Cell

2.5.1 Perovskite Solar Cell Overview

In the history of solar cell, there have been numerous of photovoltaic technologies that evolved rapidly in the search of high efficiency, organic and low cost solar cells. Nowadays, there are three generation of photovoltaic technologies evolution as shown in Figure 2.3 (Kumar et al., 2015). The first generation of solar cell is silicon that control the photovoltaic market for over half of century. However, the high efficiency portrayed by silicon solar cell comes with high processing cost that limiting its availability (Kibria et al., 2014). The second generation of solar cell in the inorganic thin film compound such as CdTe, CIGS and polycrystalline silicon (Si). The fabrication of this solar cells usually required vacuum vapor deposition that depleted high energy. Meanwhile, the third generation solar

cell is the organic solution processable thin film solar cell constructed to enhance efficiency while having low production cost such as DSSC, polymer based and PSC (Kumar et al., 2015). Perovskite has gained research interest due to its rapid performance in efficiency in just a few years of discovery.

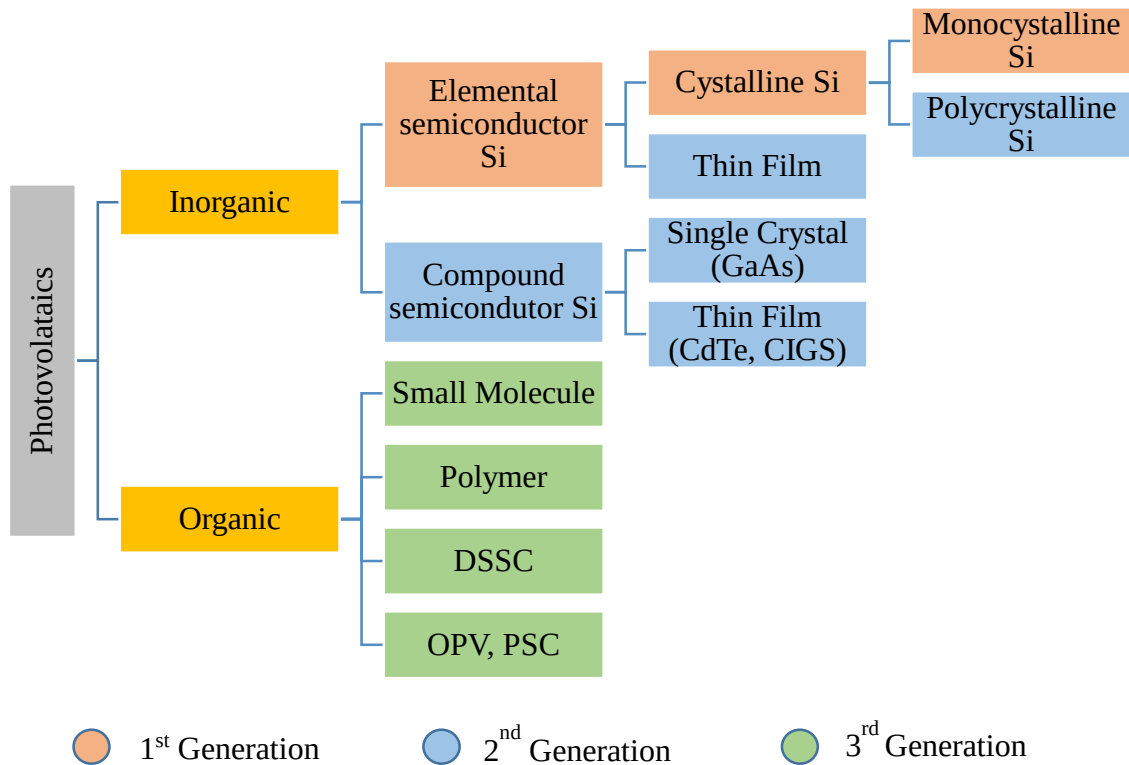


Figure 2.3: Generation of photovoltaics (Kumar et al., 2015)

The “perovskite solar cell” name is inspired from the fact that perovskite structure light absorber is employed for photovoltaic activities (Asghar et al., 2017). Perovskite material is first popularized in solar cell fabrication by Miyasaka and co-workers as a result of their interest in potentiality of perovskite as an electron collector in mesoporous TiO₂ layer in dye sensitized solar cell (DSSC). The first recorded efficiency of perovskite is 2.2% in 2006 with CH₃NH₃PbBr₃ then the efficiency increased to 3.8% in 2009 even though the

stability of the devices is still unstable. (Kojima et al., 2006; Miyasaka et al., 2009). In addition, the perovskite reported to have enhancement in stability and durability as the liquid corrosive electrolyte is employed. After that, $\text{CH}_3\text{NH}_3\text{PbI}_3$ is introduced as absorber as it is claimed to have better performance than N719 ruthenium dye used in DSSC (Gratzel et al., 2012).

Hole transport material (HTM) is introduced to perovskite in the effort to bypass the corrosion of liquid electrolyte. 9.7% of PCE is achieved by using spiro-OMeTAD as HTM owing to the properties of spiro-OMeTAD as an excellent solid state electrolyte (Kim et al., 2012). High efficiency is obtained due to the excitement of perovskite absorber to the mesoporous TiO_2 film and spiro-OMeTAD (Lee et al., 2012).

Next is the electron transport material (ETM) in perovskite. Most commonly used as inorganic ETM is TiO_2 and zinc oxide (ZnO) alongside the organic HTM in the preparation of organic-inorganic PSC. TiO_2 is more favorable due to its low temperature solution preparation, long electron lifetimes and encouraging electron injection rates from perovskite absorber to mesoporous TiO_2 (Liu et al., 2016). Even so, the conductivity of PSC with TiO_2 is still low in performances and rGO incorporated with TiO_2 is believed to overcome these drawbacks and enhanced the PCE.

2.5.2 Perovskite Solar Cell Structure

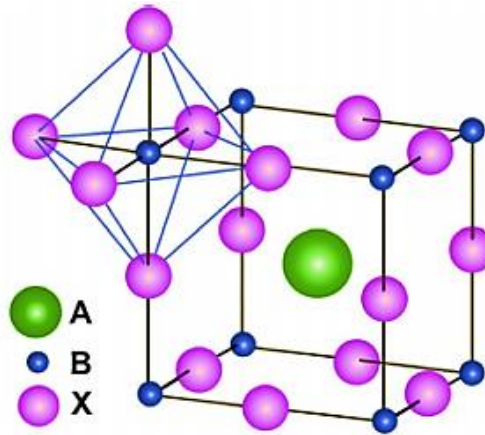


Figure 2.4: Perovskite ABX_3 structure with BX_6 octahedral (Mehmood et al., 2017)

The general formula of perovskite solar cell is ABX_3 with A as larger cation, B as smaller metal cation and X as halide anion. Figure 2.4 represents the crystal structure of perovskite retrieved from Mehmood and co-workers in 2017. Another octahedral unit of BX_6 is formed with three dimensional structures linked at each corners. The coordinated space in the octahedral unit is filled with large cation A that produced the three dimensional structure. It is important to control the size of cation A as its hold the formation of close packed perovskite structure (Safdari et al., 2015).

In addition, the large cation A is usually divalent metal ions element that belongs to group I and II in periodic table while the small cation B is the transition metal prescribed to methylammonium, ethylammonium and formamidinium and the anion X is halogen ion such as such as iodide, chloride and bromide (Green et al., 2014; Kajal et al., 2018).

Equally, the perovskite structures and arrangement is classified on its geometric tolerance factor (t) as shown in Equation 2.1. The tolerance factor often used to determine the stability of PSC (Li et al., 2008). The t is the ratio of A-X and B-X bond lengths in

idealized solid-sphere model where R_A , R_B and R_X are the efficient of ionic radii of A, B and X respectively.

$$t = \frac{(R_A + R_X)}{\sqrt{2} (R_B + R_X)}$$

For perovskite oxide with metal cations transition, the perfect cubic perovskite is predicted when t lies in narrow range of 0.89-1 and if $t=1$, the structure is orthorhombic or tetragonal (Mosconi et al., 2013). The symmetrical of PSC is lessen for $t < 1$, which effecting the electronic characteristic of PSC (Park, 2015).

2.5.3 Perovskite Solar Cell Configuration

There are two possible configurations purposed for perovskite solar cell which are *n-i-p* junction type (ETM/perovskite absorber/HTM) or *p-i-n* (HTM/perovskite absorber/ETM) to balance the charge transport properties of PSC (Mehmood et al., 2017). In the family of thin film solar cell, the most important factor to gain high efficiency light to electrical conversion process is the preparation method and the architecture of the devices. Mesoscopic nanostructure and planar structure are two main devices configuration for PSC (Tonui et al., 2018).

2.5.3.1 Mesoporous Configuration

The most common configuration of PSC based with mesoporous TiO_2 scaffold shown in Figure 2.5 consist of organic-inorganic halide perovskite absorber with high crystallinity, a mesoporous TiO_2 ETM and a spiro-OMeTAD HTM that sandwiched in between transparent conducting substrate (TCO) and a metal contact. PCE of 3.8% is

achieved when perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanocrystal filled up the inner porosity of mesoporous TiO_2 layer to improve the absorption of light in liquid solar cells (Kojima et al., 2009).

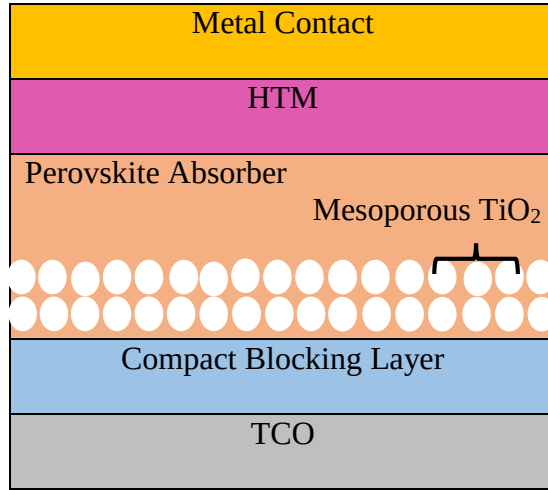


Figure 2.5: Schematic of mesoporous structure

Moreover, the separation of charge by electron injection from perovskite to TiO_2 exist in mesoporous configuration (Kim et al., 2012). It is also reported that the charge carrier in mesoporous configuration has high recombination rate. Therefore, mesoporous PSC with low performance is attributed to short diffusion length that lowering the recombination resistance with acceleration in charge recombination (Jung & Park, 2014). The charge recombination rate can be lessen with aid of novel nanomaterial such as 3D- TiO_2 , TiO_2 /graphene nanocomposites or ZnO nanorods (Han et al., 2014; Wang et al., 2014).

The presence of mesoporous layer in mesoporous architecture allowed fast extraction of photoinduced electrons from perovskite, limiting the length of electron transport and efficient light absorbing is not necessarily with high crystal quality (Xiao et al., 2015). To add, the charge collection is improved in mesoporous layer as the carrier transport distance

is decreased with no current leakage between HTM and perovskite and photon absorption is increased due to light scattering medium (Tonui et al., 2018).

To conclude, the photovoltaic performance of mesoporous PSC architecture has increased from 3.8% to 19% in just five years through careful optimization of the selective TCO-TiO₂ interfaces (Kojima et al., 2009; Zhao et al., 2014). Regardless, the studies in finding most stable mesoporous configuration to obtain higher PCE is still in matter of discussion.

2.5.3.2 Planar Configuration

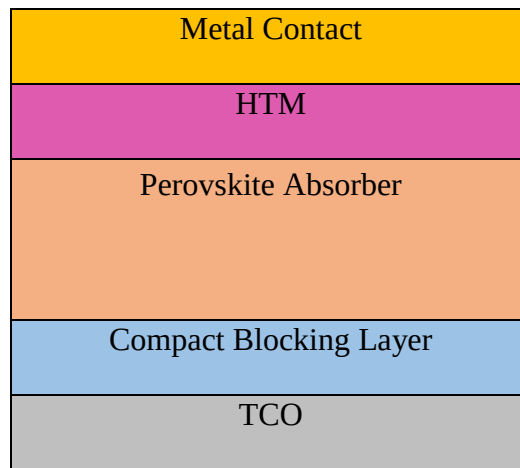


Figure 2.6: Schematic of planar structure

The planar architecture has more simple design as the thin film layer of perovskite is deposited on compact TiO₂ rather than on mesoporous TiO₂ scaffold, contacting the perovskite directly to the n-type blocking layer as shown in Figure 2.6. This type of architecture is favorable due to better performance in working mechanism behind the charge transport and separation in the perovskite material (Mesquita et al., 2018). Likewise, the PSC

structure without the mesoporous layer is particularly interesting as the issue between perovskite and HTM infiltration is eliminated. However, planar configuration also have some disadvantages such as often exhibits more severe current-voltage (I-V) hysteresis than mesoporous configuration (Zhao et al., 2014) and non-radiative electron hole recombination due to voltage lost in high density of trap states (Jeon et al., 2015). Blocking layer in planar configuration hold an important role. Thus, finding alternative compact layers for planar PSC have gained research interest. Planar PSC with ZnO as blocking layer have recorded 15.7% PCE with great reproducibility and 1.0 V for V_{oc} (Liu & Kelley, 2014). Meanwhile, 11.7% efficiency is obtained from CdSe nanoparticles with solution process at low temperature (Wang et al., 2014). The highest PCE of 20.7% is recorded when SnO₂ electron selective layers is deposited via combination of spin coating and chemical bath treatment (Anaraki et al., 2016).

In addition, spiro-OMeTAD is the most preferable HTM in planar architecture but poly(3-hexylthiophene-2,5-diyl) (P3HT) can also be used to reduce the work function of deposited metal that lead to improvement in efficiency. Unlike mesoporous architecture, the planar PSC going through various imperfection of PSC devices due to formation of low uniformity in perovskite films which usually lead to low device performances (Chuet et al., 2015).

2.5.4 Perovskite Working Principles

The success of perovskite as light absorber is solely depending in the long charge carrier diffusion length and high carrier mobility in the devices. The length of electron to hole diffusion can achieve around 1 μm which is sufficient enough for photo-generated

charges to reach the interfacial layers (Snaith et al., 2014). The charge transport channel in mesoporous PSC and planar PSC is depicted in Figure 2.7.

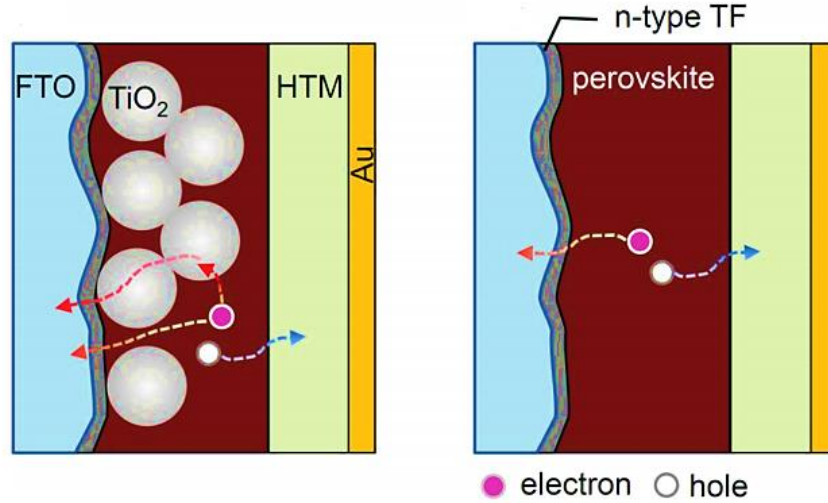


Figure 2.7: Charge transport channel in PSC (a) using mesoporous configuration (b) using planar architecture (Jung & Park, 2015)

In mesoporous configuration, the perovskite layer is deposited on mesoporous TiO_2 that responsible for creation of interpenetrating network between two phases that allow charge separation. Accordingly, the photo-generated electrons is transported to mesoporous TiO_2 to the cathode while the holes are transported from perovskite absorber to the HTM (Tonui et al., 2018; Mesquita et al., 2018).

Similarly, for the planar structure, the devices are fabricated using ETM and HTM where the creation of photo-generated charges can be moved to the electrode by the pressure of either external applied field or built in potential (Noh et al., 2013). To summarize, the PCE for both devices configuration is solidly dependent on the morphology performance as bad morphology of often enhancing the charge recombination which will lowering the efficiency of the devices.

2.5.5 Perovskite Charge Transport Buffer Layers

The processes of charge transport in PSC are dominated by the energy level alignment between the active electrode, the active layer and the crystallinity of the photoactive medium. The energy alignment can be controlled by purposing ultrathin charge transport material to be place in between active electrodes and active layers (Meng et al., 2015). Furthermore, the buffer layer in thin film solar cell are usually served to assist charge transport process and act as scaffold in the devices structure, avoid active layers from oxygen and humidity as well as aligned the energy mismatched between layers and electrodes (Tonui et al., 2018).

2.5.5.1 Hole Transport Material (HTM)

It is essential to have efficient holes collection in order to prevent charge recombination, thus assuring excellent solar cell device performances with improvement in stability. The exclusive crystallinity of perovskite ambivalent material able to create electrons and holes as well as transporting them for current generation (Popoola et al., 2018). The ideal HTM is defined with the following characteristics such as excellent hole mobility, good stability in UV and thermal, and perfect HOMO energy matches with the perovskites.

Numerous materials either from organic or inorganic source have been used as HTM to fabricate PSC with high efficiency. Nonetheless, the HTM from inorganic source is burden by limited choice of material available and obtained relatively low PCE as the result. Then, the more conductive organolead halide perovskite is used with the requirement to avoid direct contact between the perovskite and the metal anode. However, this approaches also have some drawbacks which is the increment in series resistance and decrement in the

fill factor (FF) of the PSC (Meyer et al., 2012). Therefore, organic-inorganic hole conductors is introduced to overcome the issue.

Currently, there are three categories of organic hole-conductors namely the small molecule hole-conductor with based compound such as spiro-OMeTAD, conductive polymer such P3HT and organometallic compound such as copper phthalocyanine (CuPc). It is proved that HTM deposited in insulating mesoporous buffer layer able to avoid migration of metal electrode as well as controlling the HTM thickness (Christians et al., 2013).

In PSC fabrication, quite a number of research groups employed spiro-OMeTAD as HTL to obtain good PCE and recently, 10% PCE is recorded in pioneer work of spiro-OMeTAD as HTM (Liu & Kelley, 2013) and ever since, above 12% PCE is achieved (Lee & Suk, 2015; Xu et al., 2015). Spiro-OMeTAD defined as a small amorphous organic molecule with low hole mobility and conductivity. Lithium bis (trifluoromethanesulfonyl)imide (Li-TFSI) is usually doped with spiro-OMeTAD to enhance the conductivity of PSC and improve holes transport via the oxidation of the spiro-OMeTAD molecule (Wang et al., 2015). The perfect match band gap with perovskite crystal, low temperature solution process as well as high melting point makes its suitable as HTL in PSC (Wang et al., 2015). However, spiro-OMeTAD is costly, poor crystallinity and expected to degrade under ambient environment (Shi et al., 2016).

2.5.5.2 Electron Transport Material (ETM)

Electron transport material is introduced into PSC to improve the collection of carrier in achieving better photovoltaic performance. Generally, the materials used can be classified

into metal oxide and organic ETM. It is crucial to deposit the metal-oxides at a relatively low temperature and annealing temperature controlled at 150 °C and below. Meanwhile, rigid PSC can withstand up to 500 °C for TiO₂ or Al₂O₃ ETMs (Green et al., 2014). TiO₂ and ZnO are the most common used inorganic ETM in conjunction with other HTM in the preparation process of organic-inorganic PSC.

TiO₂ is a semiconductor with large band gap of 3.20 eV for anatase crystalline phase and 3.02 eV for rutile crystalline phase. The conduction band is slightly lower than CH₃NH₃PbI₃ with 4.1 eV that guaranteeing direct electron injection from perovskite absorber to ETM. TiO₂ is also capable as excellent hole blocking layer owing to its low lying valance band edge (Liu et al., 2016).

12.3% of PCE is achieved as PSC is fabricated by using low temperature solution of mesoporous TiO₂ with CH₃NH₃PbI₃ absorber (Dkhissi et al., 2015). Meanwhile, Wang and co-workers fabricated PSC with TiO₂ nanotubes via electrochemical anodization at 20 V and less than 20 °C temperature recorded 8.31% PCE (Wang et al., 2015). Plasma assisted atomic layer deposition (Pl-ALD) of TiO₂ ETM also used to fabricate PSC with zero annealing. The Pl-ALD-TiO₂-ETM achieved 12.2% PCE with photocurrent above 20 mA cm⁻² (Kim et al., 2016).

Currently, TiO₂ is still favorable as high performing ETM due to not much studies have been conducted to improve the ETM in PSC. However, PSC with TiO₂ interlayer also have some drawbacks such as poor conductivity of the TiO₂ film and film degradation under UV light (Tonui et al., 2018).

2.6 Summary

To sum up, the available synthesis method for TiO_2 and rGO, the perovskite architecture as well as the performance of every charge buffer layer in PSC that linked to the devices efficiency is reviewed in this chapter. Based on previous studies, it can be conclude that mesoporous TiO_2 is more favorable as electron transport material in PSC due to its unique characteristic. The devices efficiency reported to improve with suitable combination of hole transport material and electron transport material in perovskite absorber. Furthermore, incorporation of rGO in TiO_2 as electron transport material is believed to enhance the devices conductivity and overcome the weaknesses in TiO_2 such as high recombination of electron and hole with wide band gap. In addition, the crystalline phase of TiO_2 also affecting its performance thus, the annealing temperature dependence is investigated in this research.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter focuses on the planning and the development of the research. This includes the chosen of suitable methods to prepare every layer in perovskite solar cell which consist of the preparation of compact TiO₂ layer, the preparation of mesoporous TiO₂/rGO layer, the preparation of perovskite layer, the preparation of hole transport layer and the deposition of every layer in perovskite solar cell. The highlight of this chapter is on the preparation of the mesoporous TiO₂/rGO layer as the modification part of this research occurs in that layer. Then, the characteristic such as surface morphology, optical properties and electrical properties of TiO₂/rGO solution and perovskite solar cell are analysed and determined. The information on the method of preparation, deposition, fabrication and characterization of TiO₂/rGO and perovskite is studied from various resources, journals, books and the internet. The step by step approach to fabricate perovskite solar cell is explained briefly in this chapter.

3.2 Designation of Perovskite Solar Cell

Figure 3.1 shown the devices structure of perovskite solar cell that generally consist of six different layers as reviewed in literature. The first layer is the glass substrate layer, then the compact TiO₂ layer. The third layer is the electron transport layer (ETL) which also called as mesoporous layer. Next is the perovskite absorber layer followed by the hole

transport layer (HTL) and last layer is the metal electrode layer. The preparation and deposition of each different layers will be further discussed in the next subtopics.

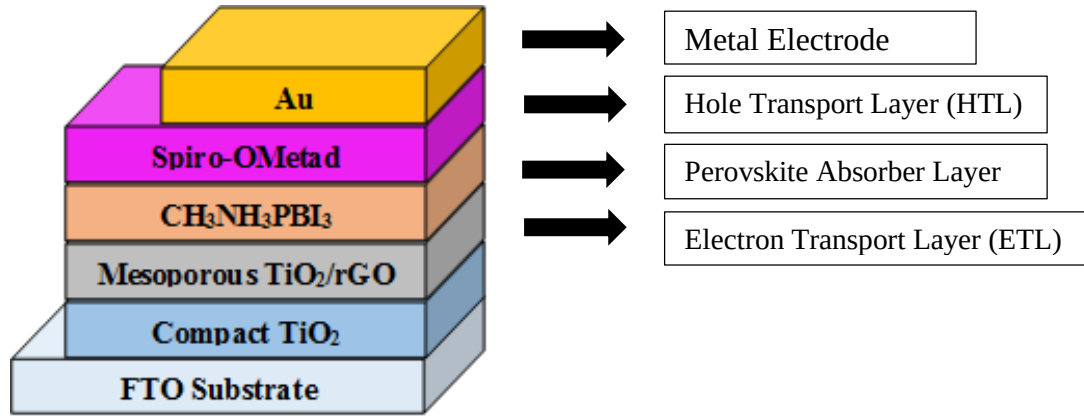


Figure 3.1: Cross sectional layer of perovskite solar cell

3.2.1 Glass Substrate Layer

Glass substrate layer was the first layer in fabrication of perovskite solar cell. This layer defines as glass substrate layer with transparent conducting oxide (TCO) cathode and there are two options of this TCO glass which were between fluorine doped tin oxide (FTO) glass or indium doped tin oxide (ITO) glass. FTO glass has been chosen to fabricate the perovskite solar cell due to its stability against heat and better conductivity as compared to ITO glass. In order to be used, the FTO glass must undergo cleaning process. The step for cleaning process started with immersing the FTO glass in liquid detergent (DECON 90) overnight. Next, FTO glass is sonicated in acetone, deionized water and 2-propanol each for 10 minutes respectively. The FTO glass was dried using blower and put inside UV ozone cleaner for 10 minutes. For safety and maintaining the cleanliness of the glass, the FTO glass is then placed inside small and tight container.

3.2.2 Compact TiO₂ Layer

For the preparation for compact TiO₂ layer, synthesis of 0.15 M of titanium dioxide (TiO₂) via sol-gel method was chosen due to performance of sol-gel method as reported in the literature (Harry et al., 2016). Titanium isopropoxide (Ti(OCH(CH₃)₂)₄) or also known as TTIP has been used as precursor along with absolute ethanol (C₂H₆O), acetic acid (CH₃CO₂H), Triton-X-100 and distilled water. 46.53 mL of ethanol was introduced to 2.22 mL of TTIP followed by 1.25 mL of acetic acid, 100 µL of distilled water and 50 µL of Triton-X-100. Then, the mixture was stirred at 600 rpm and heat at 60 °C for 2 hours and left overnight. Next is the deposition step for the TiO₂ layer.

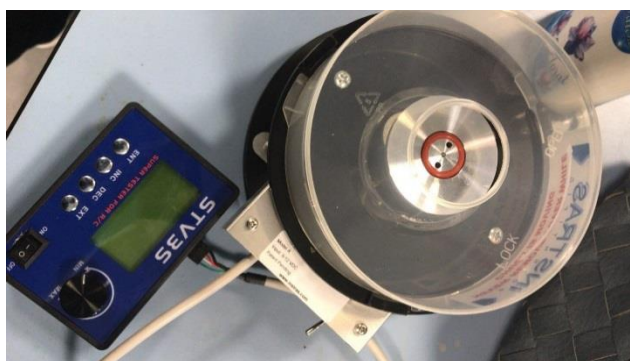


Figure 3.2: Vacuum spin coater

The prepared TiO₂ solution was stirred for 10 minutes in room temperature before being deposited. After that, spin coated the solution on top of the conductive side of FTO glass substrate at 300 rpm for 30 seconds by using vacuum spin coater then annealed on hot plate at 100 °C for 10 minutes and 450 °C for 2 hours. Figure 3.2 as attached is the image of vacuum spin coater that mainly used in all deposition in this research due to the uniformity

and its high consistency achieved by this method (Wu et al., 2013). Lastly, the deposited FTO glass with TiO_2 thin film is left to cool down at room temperature.

3.2.3 Electron Transport Layer (ETL)

In this research, titanium dioxide doped reduced graphene oxide (TiO_2/rGO) is introduced as the electron transport layer with different annealing temperature dependence. The preparation of the mesoporous TiO_2/rGO layer is divided to three main parts as shown in Figure 3.3. The first one was the preparation of graphene oxide solution that chemically reduced to become reduced graphene oxide solution. After that, the preparation of titanium dioxide solution before doping process of titanium dioxide and reduced graphene oxide takes place.

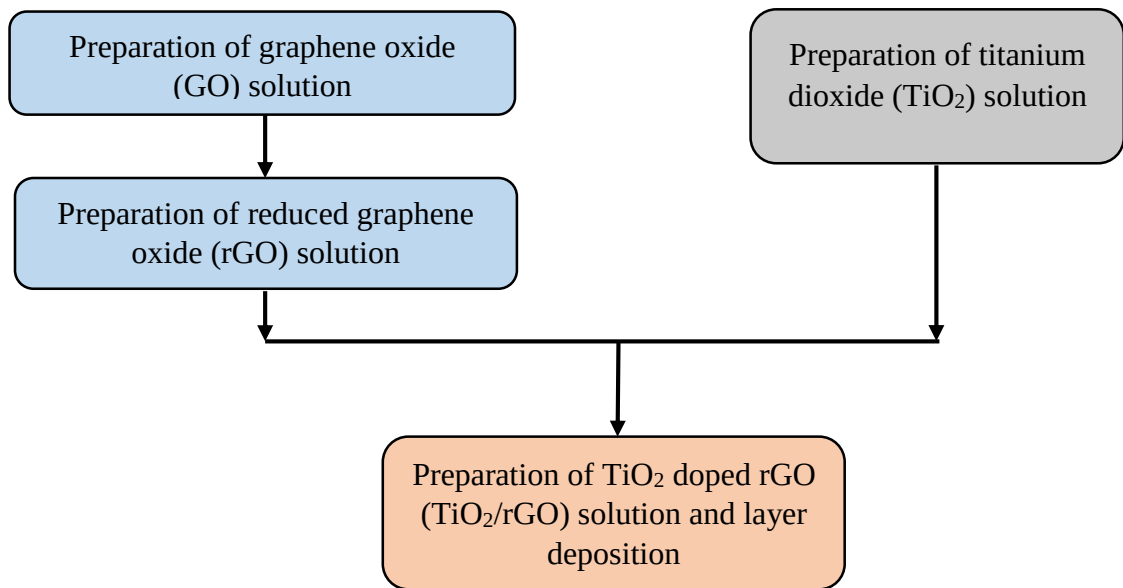


Figure 3.3: Process flow for the preparation of mesoporous TiO_2/rGO layer

3.2.3.1 Preparation of Graphene Oxide (GO) solution

As reviewed in literature, various synthesis method can be used to produce GO and in this research, GO was synthesized from a natural graphite powder by using Improved Hummer's method. An improved Hummer's method was widely used in preparing GO by eliminating the usage of Sodium Nitrate (NaNO_3) that can leads to the evolution of $\text{NO}_2/\text{N}_2\text{O}_4$ toxic gasses and simplifying the disposal of waste water because of the inexistence of Na^+ and NO_3^- ions (Chen et al., 2013). In addition, it was confirmed that the production of GO by improved Hummer method for the anode can improve the charge capacity of batteries (Alibeyli et al., 2014). Therefore, it is believed that the improved Hummer method is the best method to synthesize GO for solar cell application. In this work, the improved Hummer methods was utilized to synthesize the GO this.

The 3 g of graphite powders was added to a conical flask which contains 18g of potassium permanganate (KMnO_4) and stirred continuously by using glass rod for 60 seconds. In another beaker, 360 mL of sulfuric acid (H_2SO_4) was mixed with 40 mL of phosphoric acid (H_3PO_4) and also stirred continuously for 60 seconds. After that, the mixed solution, H_2SO_4 and H_3PO_4 were poured slowly into the conical flask which contained graphite powder and KMnO_4 earlier. The solution changed color to dark green at this stage.

Successively, the solution was then stirred and heated on hot plate at 80 rpm and 50 °C for 12 hours. The mixture was left to cool at room temperature for another 9 hours. Then, the solution was poured in the beaker that contains ice and 0.75 mL of hydrogen peroxide (H_2O_2) was added. The solution was then stirred for 15 minutes under room temperature, turning the color of the solution from dark brown to dark purple.

Then, the mixture was centrifuged with deionized (DI) water at 6000 rpm for 30 minutes. The centrifuge process is repeated by using HCl at the same speed and time. The purpose of centrifuge process is to filter and washed the mixture and at the same time removing the impurities in the mixture such as metal ions. The resulting solid was dried by using an oven at 60 °C for 2 hours and 15 mL of DI water was added to obtain GO solution. Next, the GO solution is sonicated to remove amorphous carbon exist in the solution until it become clear with no visible particular matter seen. The sonication process was carried out at room temperature for 30 min. Finally, the GO solution is obtained. Overall process flow is illustrated in Figure 3.4.

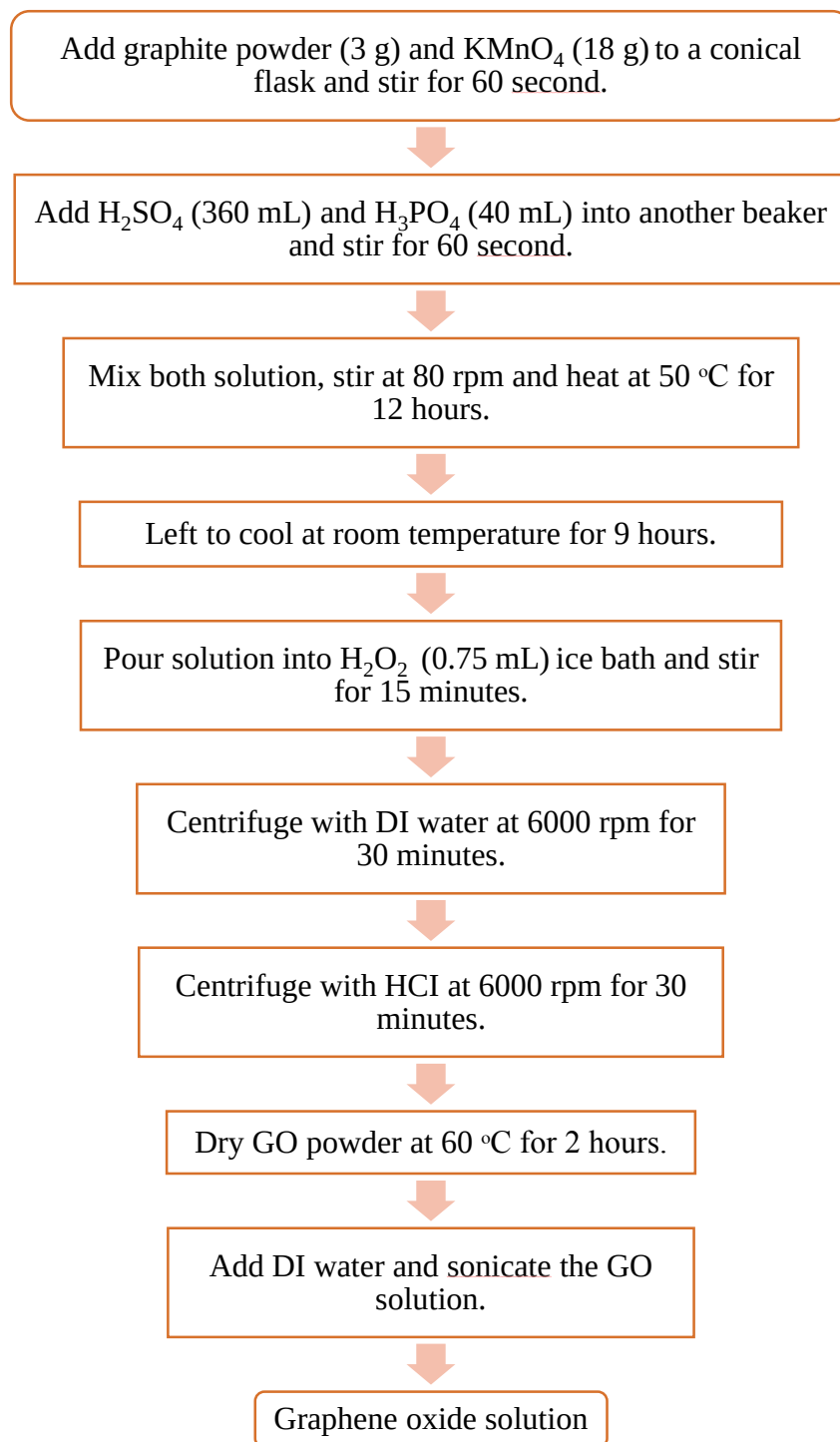


Figure 3.4: The Preparation Step of GO Solution

3.2.3.2 Preparation of Reduced Graphene Oxide (rGO) Solution

The GO solution that have synthesized earlier was used to prepare reduced graphene oxide (rGO) solution that chemically reduced by using hydrazine solution. Chemical reduction method is used due to ease preparation as compared to other methods in literature (Thakur et al., 2015). 1 mL of GO solution was added to 50 mL of deionized (DI) water then synthesized via reflux method in oil bath for equilibrium heat. Then, 17 μ L of hydrazine solution was added immediately to the mixture as soon as the stirring and the timer started. The solution was stirred on hot plate at 300 rpm and heated at 80 $^{\circ}$ C for 12 hours. As the result, black color liquid was form which represented as rGO. The solution was then filtered and left to dry at room temperature for 24 hours to obtain rGO powder. Lastly, 40 mL of dimethylformamide (DMF) was added to 0.5 g of rGO powder as a solvent that produce rGO solution. Figure 3.5 (a) attached shows the reflux method used while Figure 3.5 (b) shown the rGO solution that has been synthesized. The flow chart of the rGO solution preparation is shown in Figure 3.6.

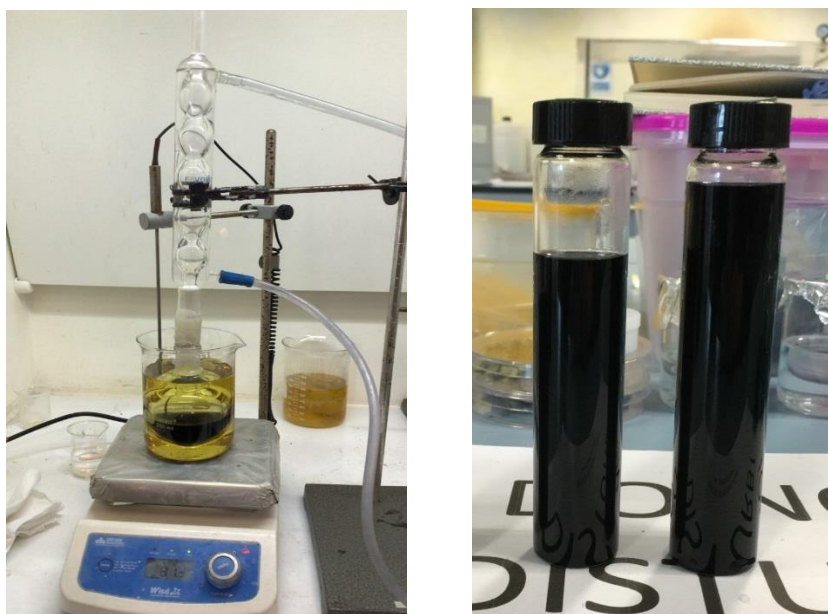


Figure 3.5: (a) Reflux method, (b) rGO solution

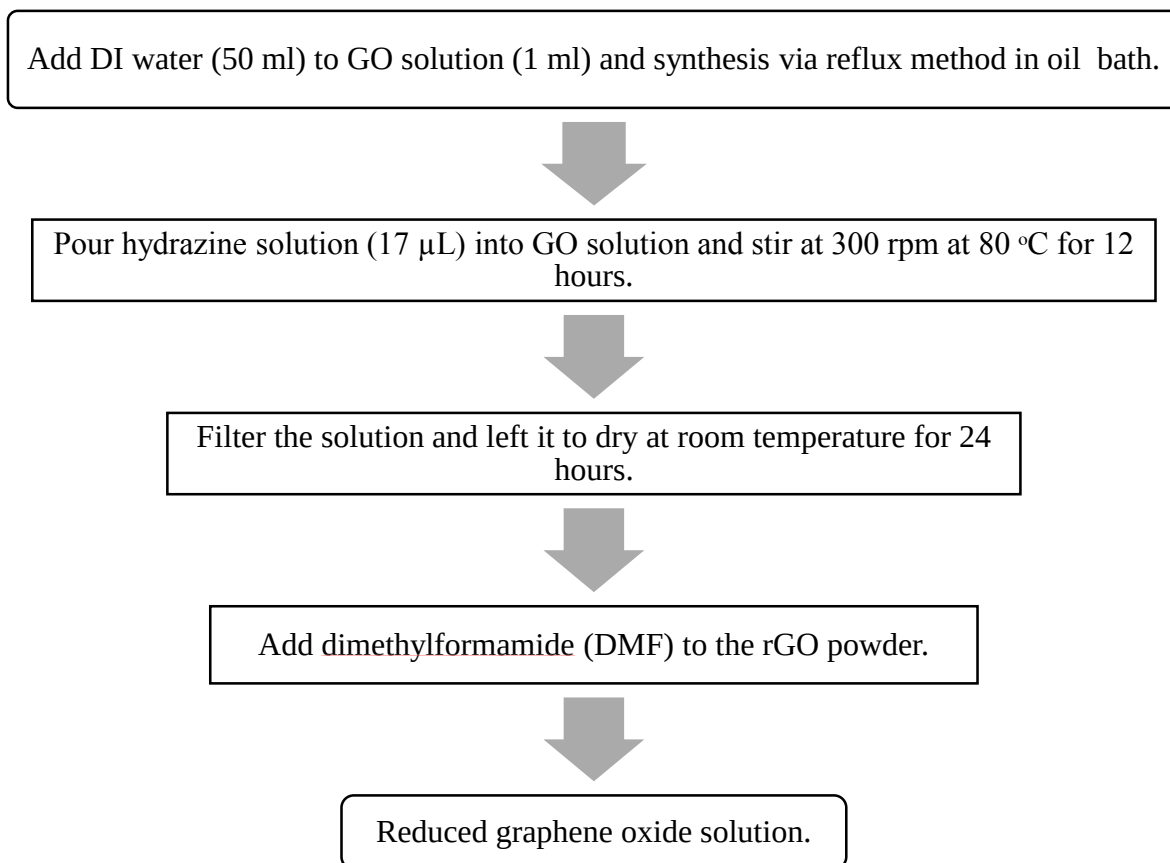


Figure 3.6: Flow Chart for Preparation of rGO Solution

3.2.3.3 Preparation of Titanium dioxide (TiO₂) Solution

Titanium dioxide (TiO₂) was prepared by using titanium (IV) oxide nanopowder as a precursor with introduction of polyethylene glycol in deionized water. Polyethylene glycol was used as a precursor because the ability of Titanium (IV) nanopowder to be solubilized in polyethylene glycol as discussed in previous research (Theivasanthi, 2017). In addition, polyethylene glycol is used to enhance the morphology of TiO₂ (Samari et al., 2009). In this research, three different annealing temperatures were used which are 450 °C, 550 °C and 650 °C. Figure 3.7 shows the graph for annealing process at 450 °C along with the furnace setting.

The rate of heating temperature used was set at 2.5 °C per minutes. The descriptions of each setting in furnace were elaborated in Table 3.1.

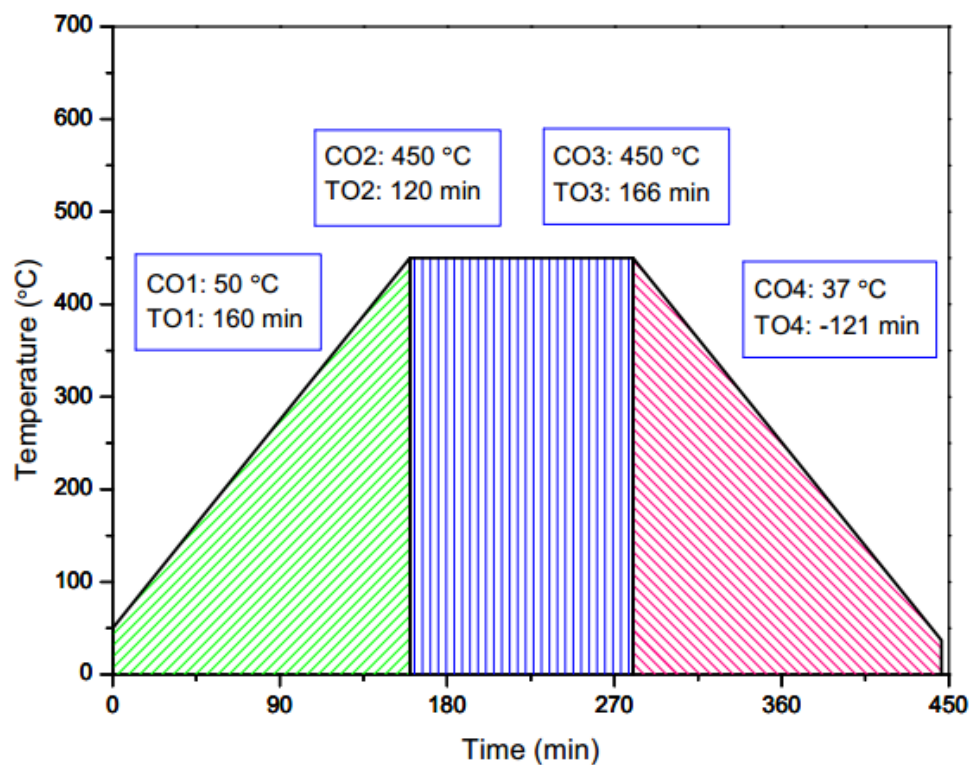


Figure 3.7: 450 °C annealing temperature graph

For TiO₂ solution preparation, 3 g of titanium (IV) oxide nanopowder was annealed at 450 °C for 2 hours respectively. Then, 6 mL of deionized water was added to 2 g of polyethylene glycol and stirred for 10 minutes in room temperature. Subsequently, 3 g of titanium (IV) oxide nanopowder that was annealed earlier is added to the solution followed by 5 mL of ethanol, 375 µL of acetic acid and 15 µL of Triton-X-100 as surfactant. After that, the solution was stirred and heated on hot plate at 300 rpm and 40 °C for 30 minutes. The steps were repeated with differs in annealing temperature (550 °C and 650 °C) until three different samples of TiO₂ solution were synthesized.

Table 3.1: Descriptions of furnace each setting

Furnace Setting	Description
CO1	Initial temperature of furnace
TO1	160 minutes from CO1 to CO2 heating rate at 2.5 °C
CO2	Temperature in first inflexion (target temperature in this section and initial temperature in the next segment)
TO2	120 minutes from CO2 to CO3 to remain the temperature
CO3	Temperature in second inflexion (target temperature in this section and initial temperature in next segment)
TO3	166 minutes from CO3 to CO4, heating rate at 2.5 °C
CO4	Temperature in third inflexion (target temperature in this section and initial temperature in next segment)
TO4	Program finished and cool naturally

3.2.3.4 Preparation of TiO₂ doped rGO Solution and Layer Deposition

The last process for preparation of TiO₂/rGO was the doping process. 0.8 mL of prepared rGO solution was added to 10 mL of prepared TiO₂ solution. 0.8 ml was chosen due to its best performance in photocatalytic activities when doped with 10 ml of TiO₂ (Tang et al., 2018). After that, the solution was stirred at 500 rpm and heated at 40 °C for 2 hours and left overnight to suppress the bubble in the solution. This process resulting a thick and concentrated TiO₂/rGO solution as shown in Figure 3.8.

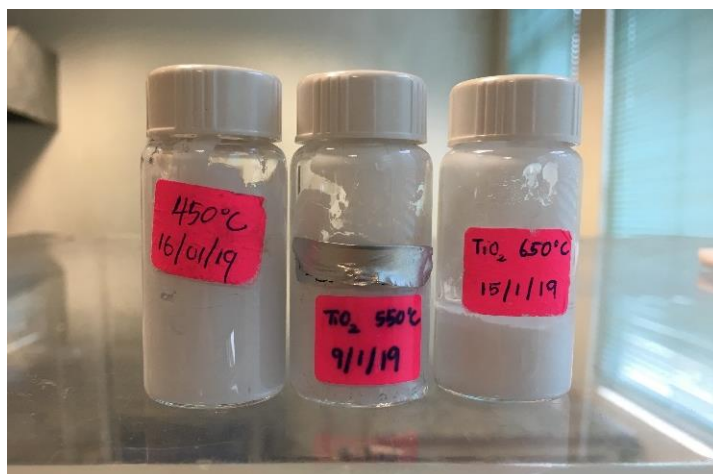


Figure 3.8: 450 °C, 550 °C and 650 °C TiO₂/rGO samples

Mesoporous TiO₂/rGO layer was the third layer in perovskite solar cell fabrication. The TiO₂/rGO solution was deposited on top of the compact TiO₂ layer that has been prepared and annealed earlier. Spin coating technique has been used for the deposition whereas the solution was spin coated at 300 rpm for 30 seconds. After that, the deposited FTO substrate was annealed on hot plate at 100 °C for 10 minutes and left to cool down at room temperature. All of the procedure was carried out in ordinary air condition.

3.2.4 Perovskite Layer

For the preparation of the perovskite layer, methylammonium lead iodide (CH₃NH₃PbI₃) was chosen as the perovskite material. The method used to prepare the perovskite layer was adapted from the previous research (Al-She'irey et al., 2016). Firstly, 0.494 g of methylammonium iodide (CH₃NH₃I) was introduced to 1.447 g of lead (II) iodide (PbI₂). After that, 1375 µL of γ -butyrolactone analytical standard was added into the solution followed by 1125 µL of dimethylformamide (DMF) with desired molar ratio at 1:1:1. Next, the solution was stirred at 300 rpm and heated at 60 °C for 1 hour. As PbI₂ was very sensitive

to light and the solution was very sensitive to humidity, the procedure was conducted in a glove box with very minimal light used in the experimental area.

The solution of the perovskite phase was then introduced on top of the mesoporous TiO₂/rGO layer via spin coating method at 2000 rpm for 45 seconds and annealed from room temperature to 100 °C for 15 min. Then, left the deposited FTO substrate to cool down at room temperature.

3.2.5 Hole Transport Layer (HTL)

In this research, the hole transport layer used was the 2,2',7,7'-tetrakis-(N, N-di-p-methoxyphenylamine)-9,9'-spirobifluorene or also known as spiro-OMeTAD. Spiro-OMETAD was used as a transport layer because its stability and efficiency even after exposed about 840 hours of air exposure as discussed in previous research (Jung et. al., 2015). For the first step, 0.52 g of lithium bis(trifluoromethylsulfonyl) imide (Li-TFSI) was mixed with 1 mL of acetonitrile. In another beaker, 144 µL of 4-tert-butylpyridine was added into 87.5 µL of Li-TFSI that was prepared earlier. Then, 0.3615 g of spiro-OMeTAD in 5 ml of chlorobenzene was mixed in the solution. After that, the solution was stirred at 300 rpm and heated at 40 °C for 12 hours. All of the procedure was carried out in a glove box with argon gas.

As for the deposition, the same deposition method was used which is the spin coating technique. The prepared spiro-OMeTAD solution was spin coated at 4000 rpm for 60 second then left to dry overnight in desiccator.

3.2.6 Metal Electrode

The metal electrode used in perovskite fabrication was the gold (Au) metal contacts. The Au was coated by using gold sputtering machine with aid of homemade mask as shown in Figure 3.9 (a) while the result after Au coating is shown in Figure 3.8 (b). The gold sputtering time was set up to 180 seconds to maximize the thickness of Au coated on top of the deposited FTO substrate.

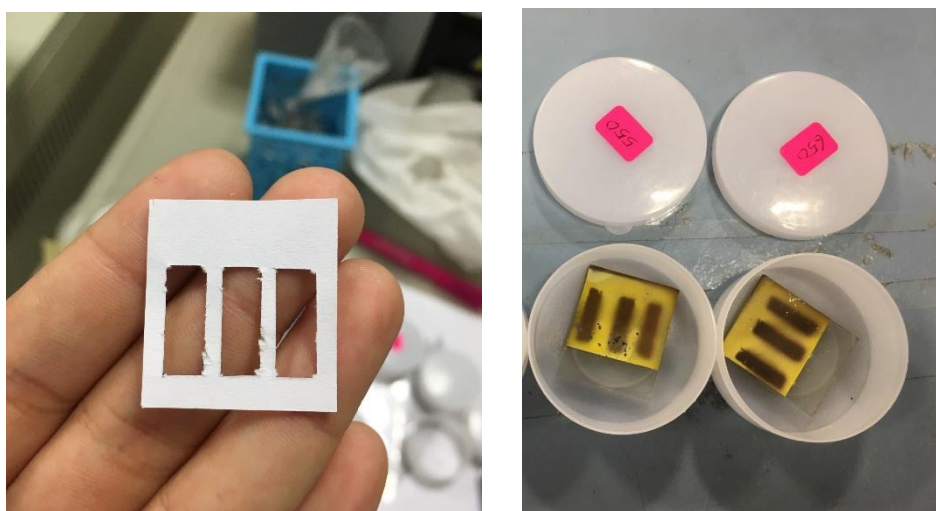


Figure 3.9: (a) Homemade mask (b) Perovskite solar cell after Au coating

3.2.7 Summary of Perovskite Solar Cell Fabrication

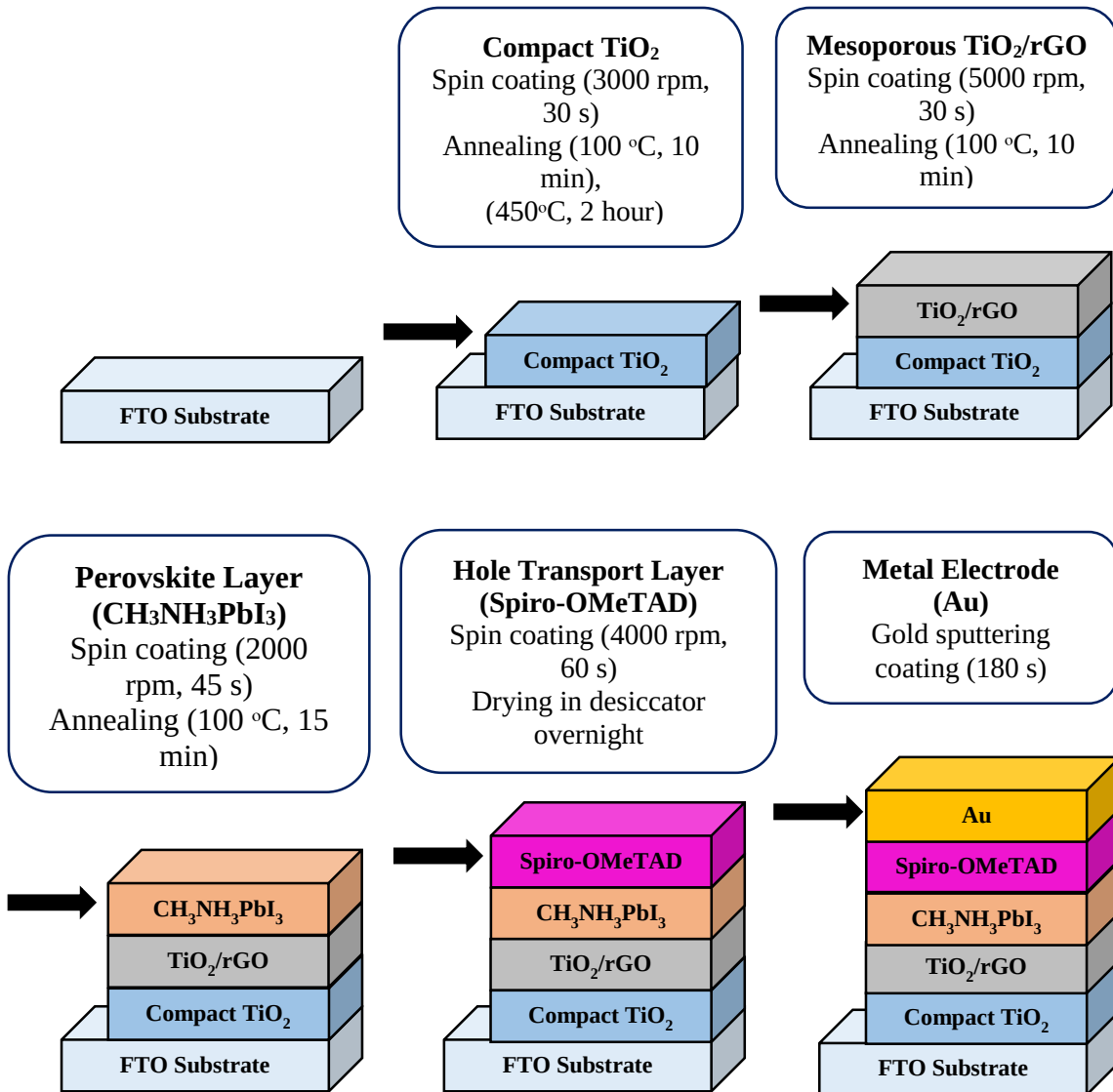


Figure 3.10: Schematic Illustration for Perovskite Solar Cell Fabrication

3.3 Characterization of TiO₂ doped rGO (TiO₂/rGO) and Perovskite Solar Cell

In order to characterize TiO₂/rGO solution, the solution was deposited on an ordinary glass substrates to become TiO₂/rGO thin film while characterization for perovskite solar cell was conducted on a full grown solar cell. The TiO₂/rGO and PSC were analyzed into three different morphologies. Firstly is the surface morphology for TiO₂/rGO thin film was characterized. The characterization conducted were the Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and X-ray Powder Diffraction (XRD).

Next, the optical characterization of TiO₂/rGO thin film was carried out. Ultraviolet-visible spectroscopy (UV-Vis) was used to measure the absorbance wavelength of TiO₂/rGO and from that, band gap for each of TiO₂/rGO samples were obtained. Then, X-ray Photoelectron Spectroscopy (XPS) were used to characterize the chemical bonding structure of TiO₂/rGO samples. The last characterization was the electrical properties of perovskite solar cell which characterized by using I-V characteristic. The current-voltage measurement of perovskite solar cell was examined by Keithley (Model 2450) source measurement unit.

3.3.1 Surface Morphological Characterization

First surface characterization conducted for TiO₂/rGO thin film was the Scanning Electron Microscopy (SEM, Hitachi TM3030 Tabletop Microscope). The acceleration voltage used was from 0.5 kV to 30 kV. The light microscopes normally used visible light for imaging, while the electron microscope as for example the SEM, used electron for imaging. SEM will produce the images of TiO₂/rGO by scanning the beam in a raster-like pattern and electrons is reflected near the surface region of the TiO₂/rGO thin film. The

surface uniformity and porosity of TiO₂/rGO thin film can be seen from the images obtained from the SEM.

Next, the Atomic Force Microscope (AFM, XE-100 Park System) characterization. The AFM was designed to measure local properties of the sample, such as friction, height, magnetism by using a probe. The images of TiO₂/rGO is required by raster-scans the probe over a small area of the TiO₂/rGO, measuring the local property simultaneously. The surface topology and surface roughness of TiO₂/rGO thin film can be investigated.

After that, the PANalytical X'PERT PRO MRD PW 3040/60 is used to determine the X-Ray Diffraction (XRD). The scanning rate employed was 0.033 °s⁻¹ in 2 Θ range from 20 ° to 80 ° with Cu-K α radiation ($\lambda=1.5406 \text{ \AA}$). The characterization of structural properties for TiO₂/rGO thin film was carried out by using this machine. XRD are mainly used to identify the crystalline phase of various materials and the quantitative phase analysis for identification of material, in this case the TiO₂/rGO materials. XRD used X-ray that scattered by the atoms of a crystal to produces an interference effect that give information on the structure of the crystal via diffraction pattern. The TiO₂ phase and the TiO₂ crystallinity is determined from XRD spectra.

In addition, the interplanar spacing between atoms (d-spacing) for TiO₂/rGO thin films at different annealing temperature was calculated from the XRD peaks by using Bragg's law as shown in Equation 3.1.

$$n\lambda = 2d \sin \Theta \quad (3.1)$$

Where n is the order of diffraction peak at the value of 1, λ is the wavelength of Cu-K α radiation at 1.5406 $\text{\AA}$ and Θ is the scattering angle.

Then the average crystalline size of each TiO₂/rGO thin film samples were obtained by using Debye-Scherrer formula as depicted in Equation 3.2.

$$d = \frac{k\lambda}{\beta \cos \theta} \quad (3.2)$$

Where,

d = average crystalline size (nm)

k = Scherrer constant (0.9 assuming the particles are in spherical crystallite)

λ = wavelength of Cu-K α radiation (1.5406 Å)

β = full width at half maximum (FWHM) intensity at (101) peak in radians

θ = XRD peak position, $2\theta/2$

3.3.2 Optical Characterization

The optical characterization of TiO₂/rGO was obtained by using Ultraviolet-visible Spectroscopy (UV-Vis, Shimadzu UV-1800). The UV-Vis measured absorption of light across the ultraviolet and visible light wavelengths through TiO₂/rGO solution. The TiO₂/rGO solution used was a very clear solution with addition of more solvent so that the light can passed through it. The absorbance wavelength of TiO₂/rGO were measured from 200 nm to 800 nm wavelength.

Based on absorbance spectra, the band gap for TiO₂/rGO solution can be obtained by applying the Kubelka-Munk (K-M) expression as shown in Equation 3.3.

$$\alpha h\nu = A(h\nu - E_g)^n \quad (3.3)$$

Where,

α = absorbance coefficient

A = constant (~ 1)

h = Plank's constant (4.136×10^{-15} eV)

ν = speed of light (3×10^8 ms⁻¹)

E_g = band gap energy

n = 2 for indirect allowed transition

3.3.3 Chemical Bonding Analysis

Chemical bonds of TiO₂/rGO solution is analyzed by using X-ray Photoelectron Spectroscopy (XPS). The characterization is conducted on the TiO₂/rGO thin film by using High Resolution Multi Technique X-Ray Spectrometer (Axis Ultra DLD XPS, Kratos). The X-ray sources applied is Al-K α at 1486.8 eV with line width at 0.85 eV. The XPS measured the elemental composition and the chemical state that exist within material. As X-rays are directed onto samples surface, the electrons in the core levels and in the valence band or conduction bands are excited. The measured data of XPS is presented as a graph intensity versus binding energy. In this research, the XPS were used to determine chemical composition and bonding state of TiO₂/rGO thin film. XPS spectra of Ti2p, C1s and O1s were viewed by using CasaXPS software.

3.3.4 Electrical Characterization

For electrical characterization of perovskite solar cell, the solar cell were tested right after the deposition of Au contact. The electrical characteristic were measured by using Keithley (Model 2450) source measurement unit with 2 probes testing as shown in Figure 3.11. The light sources for electrical testing was from Nickel Cool Beam Lamp (230 V, 150 W). The KickStart software was used to display the current and the voltage graph whereas the start voltage was set at 0 V and stop voltage at 1 V. The measured data from Keithley is presented as current-voltage graph.



Figure 3.11: Keithley Sourcemeter

From the current-voltage graph, the electrical properties of TiO_2/rGO perovskite solar cell such as resistance, conductance, resistivity and conductivity are acquired. Equation 3.4 and Equation 3.5 shown the formulas for resistance and conductance calculation respectively.

$$R = \frac{V}{I} \quad (3.4)$$

$$G = \frac{I}{V} = \frac{1}{R} \quad (3.5)$$

Then, the resistivity of TiO₂/rGO perovskite solar cell is calculated by using Equation 3.6 as follows:

$$\sigma = k \frac{V}{I} \quad (3.6)$$

Where k is the cell constant. The cell constant indicates the ratio of the distance (d) between the electrodes to the area (a) of the electrodes. As for this case,

$$k = \left(\frac{d}{a} \right) \quad (3.7)$$

$$= \frac{2.5}{2 \times 1.5}$$

$$= 0.833 \text{ cm}^{-1}$$

Lastly, the conductivity of TiO₂/rGO perovskite solar cell is obtained from the resistivity by using formula as shown in Equation 3.8.

$$\rho = \frac{1}{\sigma} \quad (3.8)$$

CHAPTER 4

RESULT AND DISCUSSION

4.1 Overview

This chapter discusses and analyzes the performance of TiO₂/rGO and perovskite solar cell based on annealing temperature dependence in details. There were six different characterizations of the results obtained which were the Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM), X-Ray Diffraction (XRD), Ultraviolet-visible spectroscopy (UV-Vis), X-ray Photoelectron Spectroscopy (XPS) and lastly the current-voltage (I-V) analysis that were presented in graphic images, graphs and in the tables form.

4.2 Surface Morphology

4.2.1 Scanning Electron Microscopy (SEM)

Figure 4.1 and Figure 4.2 show the SEM images of TiO₂/rGO that was varied at different annealing temperature as mentioned in Chapter 3. The magnification of the SEM images are 1k for Figure 4.1 and 5k for Figure 4.2 with the same scan rate at 20 $\mu\text{m/s}$. From Figure 4.1, it can be observed that 650 °C TiO₂/rGO have better porosity and larger grain size as compared to 550 °C TiO₂/rGO. In solar cell application, porosity is important as the structure is more porous, it have higher ability to absorb sunlight (Sahari et al., 2017). Therefore, these images providing early confirmation that annealing temperature do have effect on surface morphology of TiO₂/rGO thin films.

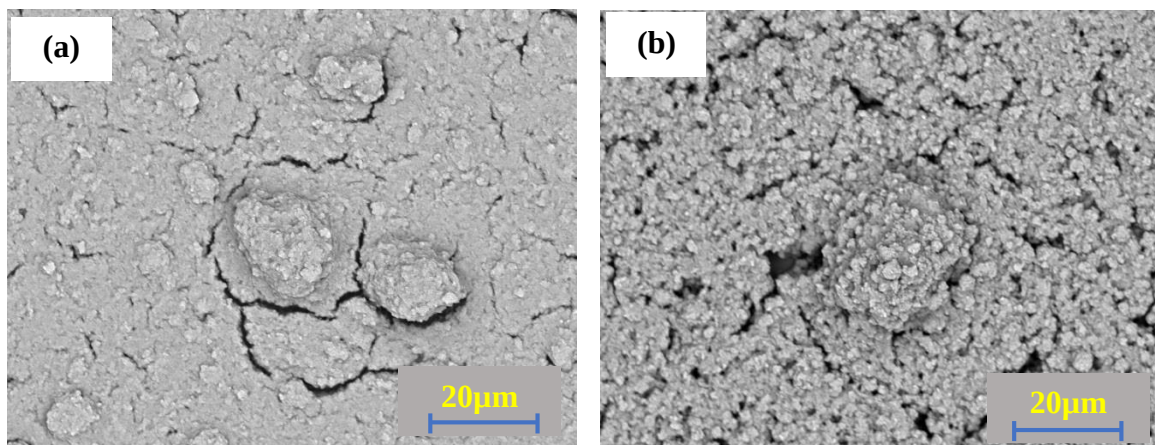


Figure 4.1: SEM images at 1k magnification for (a) 550 °C TiO₂/rGO and (b) 650 °C TiO₂/rGO

In addition, Figure 4.2 displayed more magnified SEM images of TiO₂/rGO at 5k magnification. Referring to Figure 4.2 (a), the porous structure of TiO₂/rGO particles were less seen as compared to Figure 4.2 (c). The Figure 4.2 (c) is consistent with the finding of the previous researchers (in Figure 2.2) that compared the heat treatment of GO/ TiO₂ based photoanode that shows the interconnection of particulate structure of the titania (Kanta, et. al., 2017). It is believed that decomposition of polymer in PEG contributed to more porous structure in TiO₂/rGO with small pore size as reported in previous study (Balaganapathi et al., 2017). Other than that, it can also be seen that the grain size of TiO₂/rGO particles become larger and were well-connected with each other. The increment in grain size as the annealing temperature increases agreed the previous study done by (Ahmad et al., 2010) and changes in crystallite size is due to densification effect from increasing in annealing temperature (Bakri et al., 2017).

In addition, Figure 4.2 (c) display more dispersed and uniform aggregation of TiO₂/rGO particles as compared to Figure 4.2 (a) and Figure 4.2 (b). The presence of rGO contributed to better agglomeration of TiO₂ nanoparticles as rGO usually crumpled as

exfoliation occurred (Wu et al., 2017) and it is supported by three-dimensionally assembled structure that can be observed from Figure 4.2 (a) to Figure 4.2 (c).

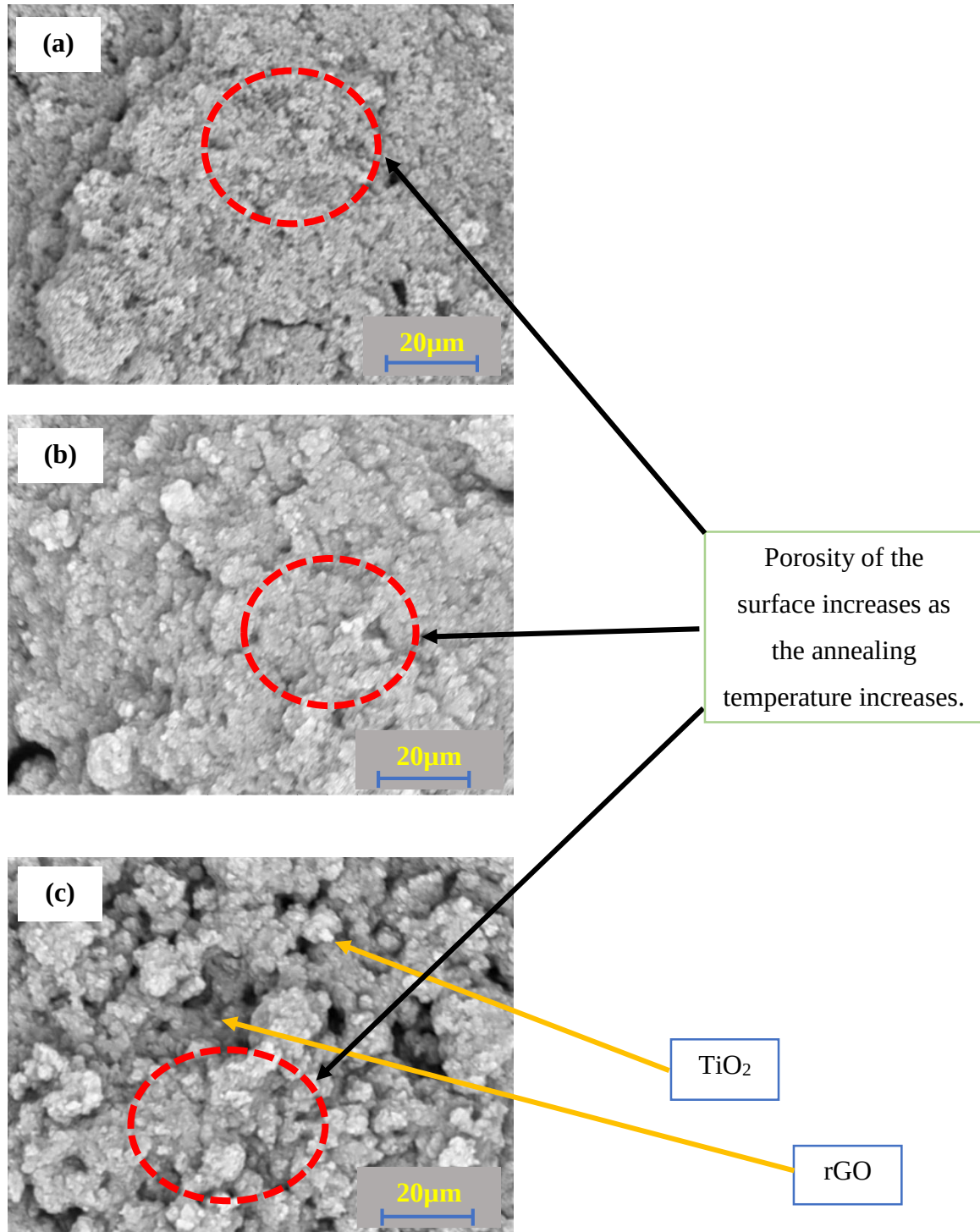


Figure 4.2: SEM images of TiO₂/rGO at different annealing temperatures (a) 450 °C TiO₂/rGO, (b) 550 °C TiO₂/rGO and (c) 650 °C TiO₂/rGO

From SEM results, it can be deduced that the evaporation rate of organic substance is affected by annealing temperature dependence (Liu et al., 2017). As the annealing temperature increases, the higher the evaporation rate. Thus, contributing to better porosity in TiO₂/rGO thin film. It is important to obtain a thin film with high porosity because as the thin film becomes more porous, the surface area of the film will increase accordingly. The increment in surface area assured absorbance of more perovskite material hence, the increment in the number of excited electrons (Lin et al., 2013). This is one important measures as TiO₂ performance in photocatalytic properties rely on the number of electron transfer (Fan et al., 2012).

4.2.2 Atomic Force Microscopy (AFM)

AFM measurement was performed in order to evaluate the surface roughness and morphology of the TiO₂/rGO films. Figure 4.3 display 3D AFM images of TiO₂/rGO corresponding to the annealing temperature dependence at 450 °C, 550 °C and 650 °C. As can be observed from the images, the large spherical features exist on the surface of deposited TiO₂/rGO films which believed to be the residue from the polymer that evaporated during annealing.

In addition, recrystallization of TiO₂/rGO also occurred due to increment in annealing temperature. From Figure 4.3 (a), less uniformity of particle distribution can be seen at 450 °C annealing temperature nonetheless, the grains tend to agglomerate as annealing temperature increases as reported by (Mathews et al., 2009). The doping of rGO significantly modified the surface structure of TiO₂, with loss of uniformity and increment

in surface roughness can be observed. This leads to formation of non-linear thin film due to heterogeneity of TiO_2 and rGO nanocomposites (Tsai et al., 2011).

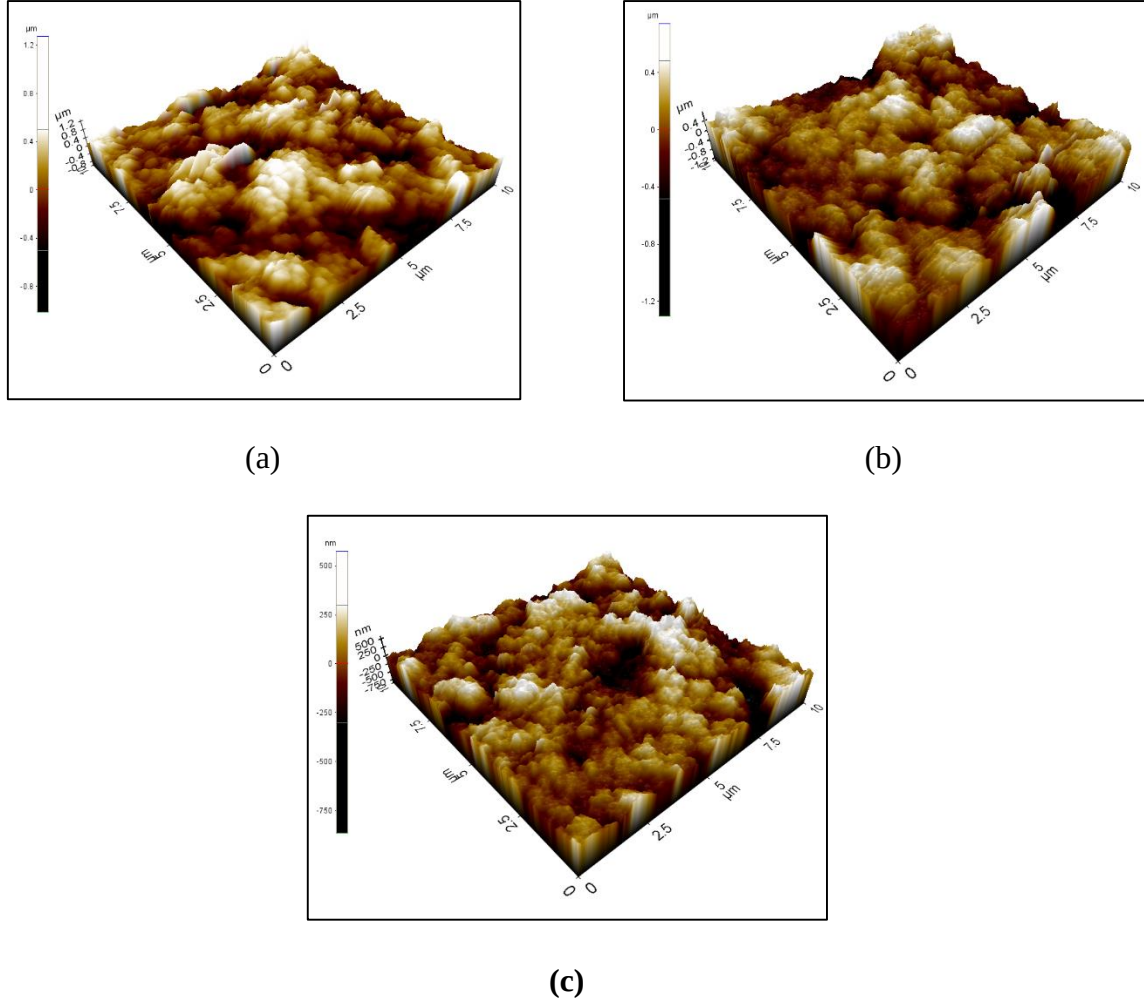


Figure 4.3: AFM images of TiO_2/rGO at different annealing temperatures (a) 450 °C TiO_2/rGO , (b) 550 °C TiO_2/rGO and (c) 650 °C TiO_2/rGO

Most commonly used parameter in AFM analysis to evaluate the surface roughness is the root mean square (RMS) analysis (Zhang et al., 2007). The RMS roughness analysis of TiO_2/rGO films were conducted for all the samples. Figure 4.3 (a), 450 °C TiO_2/rGO shown the RMS surface roughness at 21.5 nm. Next, the topology of TiO_2/rGO annealed at 550 °C is shown in Figure 4.3 (b) and recorded 23.42 nm surface roughness. Lastly, the surface roughness increased to 23.53 nm when the TiO_2/rGO is annealed at 650 °C. This

result matched the finding by Bakri et al., which stated that the increment in surface roughness referring to the increment in grain size as the annealing temperature increases and also the changes of thin film phases (Bakri et al., 2017).

4.2.3 X-ray Powder Diffraction (XRD)

XRD patterns of TiO₂/rGO nanocomposites which subjected to different annealing temperature were presented in Figure 4.4. The note A indicates TiO₂ in anatase phase while R means in rutile phase. The strong peaks in XRD patterns indicated the body-centered TiO₂ tetragonal at main (A101) diffraction peak at $2\theta = 25.3^\circ$ along with (A004) and (A200).

These peaks matched with the titanium anatase phase represented in International Centre of Diffraction Data (ICDD) standard with file no. 03-065-5714 (Awang & Talalah, 2019). The TiO₂ in rutile phase also detected by the main (R110) diffraction peak at $2\theta = 27.2^\circ$ along with (R101) which matched with the titanium rutile phase as stated in ICDD standard data with file no. 03-065-1118. (Ganesh et al., 2012).

It can be observed from Figure 4.4 (a) to Figure 4.4 (c) that the intensity of (A101) peaks become weaker as the annealing temperature increases, while the intensity of (R110) and (R101) peaks become sharper and stronger. This shows that the annealing temperature able to transform TiO₂ from anatase to rutile as the temperature increases when the rutile peaks are more dependent. (Nouri et al., 2016). In addition, the TiO₂/rGO annealed at 450 °C and 550 °C shown the (A105) peaks that was disappear in 650 °C TiO₂/rGO meanwhile the presence of (R111) only exist in 650 °C TiO₂/rGO.

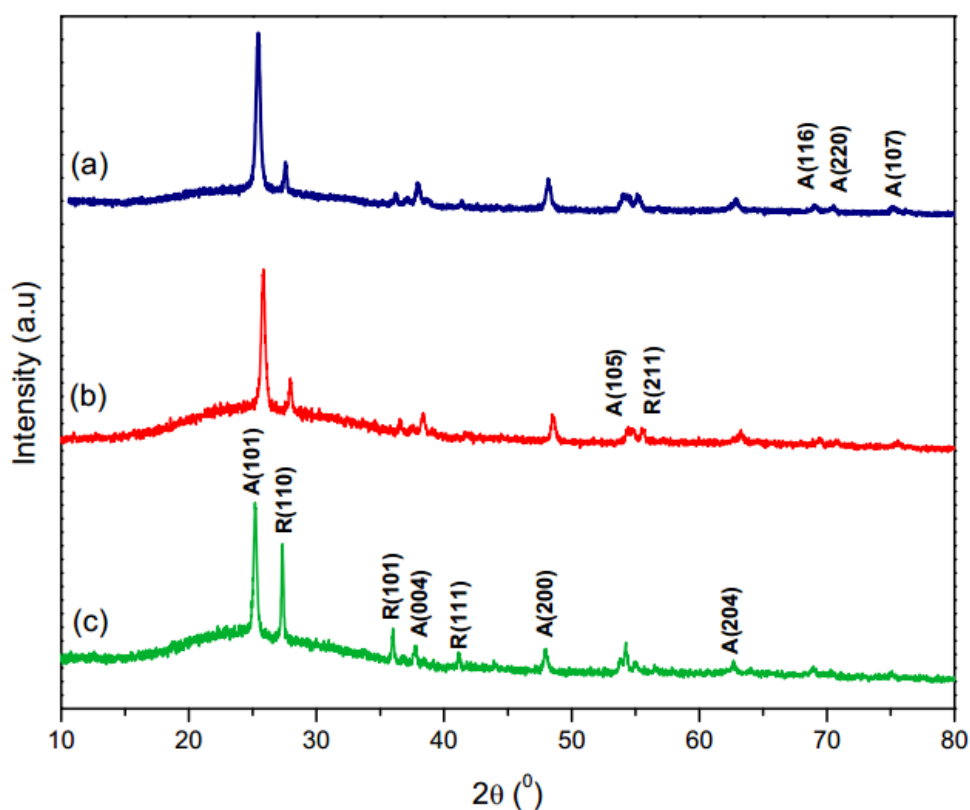


Figure 4.4: XRD patterns of TiO₂/rGO at different annealing temperatures (a) 450 °C TiO₂/rGO, (b) 550 °C TiO₂/rGO and (c) 650 °C TiO₂/rGO

Furthermore, Table 4.1 shown the analysis of XRD patterns which containing the interlayer spacing (d-spacing), full width at half maximum (FWHM) and the average crystalline size of TiO₂/rGO at different annealing temperature. As mentioned in Chapter 3, the d-spacing and the crystalline size were calculated via Bragg's law and Debye-Scherrer equation respectively. The d-spacing obtained were in the range of 3.44 Å to 3.52 Å which in agreement with previous work that stated anatase TiO₂ at (101) peak recorded d-spacing at 3.52 Å. (Theivasanthi & Alagar, 2013; Kite et al., 2019).

On the other hand, the average crystalline size corresponding to (101) anatase diffraction peak recorded 14.43 nm, 10.75 nm and 15.42 nm for 450 °C TiO₂/rGO, 550 °C

TiO₂/rGO and 650 °C TiO₂/rGO respectively. As 550 °C TiO₂/rGO have the smallest crystalline size, it implies that 550 °C TiO₂/rGO has the highest crystallinity and excellent repeatability compared to other samples (Low et al., 2017). Meanwhile, the 650 °C TiO₂/rGO has the largest crystalline size suggested that the increment in temperature induced grain growth getting along in phase transition from anatase to rutile phase (Balaganapathi et al., 2017).

Table 4.1: Analysis of XRD patterns

Samples	2θ (°)	d-spacing (Å)	FWHM	Average crystalline size (nm)
450 °C TiO₂/rGO	25.4484	3.4973	0.4324	14.34
550 °C TiO₂/rGO	25.8327	3.4461	0.4645	10.75
650 °C TiO₂/rGO	25.2261	3.5276	0.4119	15.42

From XRD analysis, it can be concluded that the spectrums of all samples showed high degree of crystallinity with small average particle sizes. The crystallinity in XRD spectrums also supporting the SEM observations that have been discussed earlier. Other than that, it also can be deduced the increment in annealing temperature also shows minimal effect on crystallinity. The 450 °C TiO₂/rGO exist in fully anatase crystallographic form meanwhile 650 °C TiO₂/rGO exist in anatase-rutile crystallographic form.

4.3 Optical Characterization

4.3.1 Ultraviolet-visible Spectroscopy (UV-Vis)

Figure 4.5 illustrates the UV-Vis spectra of TiO_2/rGO at different annealing temperature. The TiO_2/rGO spectra exhibits strong absorption peaks in the range of 310 nm to 330 nm. The strong absorption peaks is believed due incorporation of rGO that leads to the excitation of electrons from the valance band (O_{2p}) to the conduction band (Ti_{3d}) during light absorbing in ultra-violet region as discussed in previous research (Low et al., 2017; Kite et al., 2019). The TiO_2/rGO absorption spectra were illustrated by red shift absorption at 328 nm, 326 nm and 210 nm for TiO_2/rGO annealed at 450 °C, 550 °C and 650 °C respectively. In addition, the red shift attributed to the incorporation of rGO in TiO_2 which narrowing the optical band gap and lowering the energy thus, extrapolating the linear portion of the curve to zero and positioned it in visible region. These results agreed the experimental finding by some researchers (Park et al., 2011; Nouri et al., 2016; Low et al., 2017).

It can be observed that 550 °C TiO_2/rGO has the highest absorbance among all three samples meanwhile 650 °C TiO_2/rGO recorded lowest absorbance. These results are contradict with the finding in Section 4.21 whereby the porosity of structure increases with increasing temperatures. However, the AFM images reveal that the 650 °C has the rougher surface compare to others. Therefore, this phenomenon may be related to the lower absorbance of 650 °C compare to 550 °C. To investigate this phenomenon further, x-ray photoelectron spectroscopy analysis has been conducted and the results were discussed in Section 4.4. The low performance in absorbance by 650 °C TiO_2/rGO is due to the increasing of particle size which may contribute to the combination effect of particles and crystallinity (Liu et al., 2017). The increment in particles size agreed the finding in SEM characterization.

Meanwhile in visible region, 550 °C TiO₂/rGO showed the highest absorption which attributed to electron affinity within anatase and rutile phase, supporting the finding in XRD pattern.

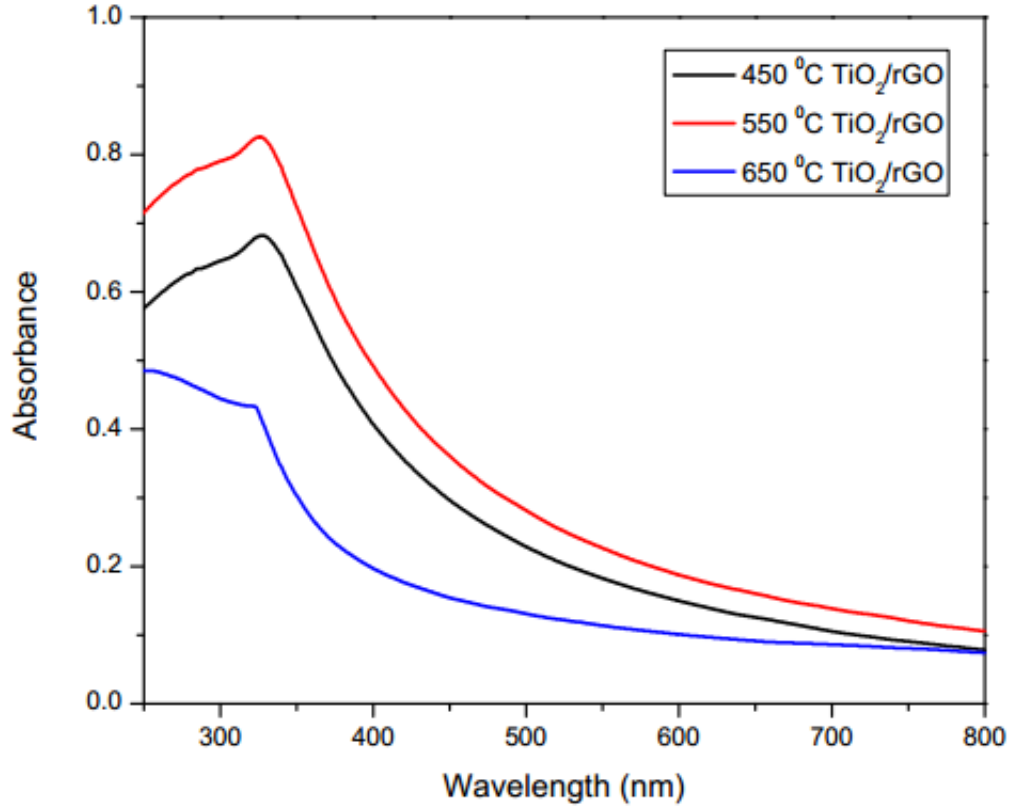


Figure 4.5: UV-Vis spectra of 450 °C TiO₂/rGO, 550 °C TiO₂/rGO and 650 °C TiO₂/rGO

In order to determine the band gap of the TiO₂/rGO thin films, the UV-Vis spectra must be transformed into Tauc plot by applying the Kubelka-Munk (K-M) equation as mentioned in Chapter 3. Figure 4.6 and Table 4.2 show the Tauc plot of TiO₂/rGO samples and its estimated optical band gap. The 550 °C TiO₂/rGO recorded the lowest band gap at 2.48 eV while the highest band gap at 2.97 eV belongs to 650 °C TiO₂/rGO.

The band gap obtained for 450 °C TiO₂/rGO and 550 °C TiO₂/rGO which are 2.50 eV and 2.48 eV are lower than the reported value in literature for anatase TiO₂ which is 3.2 eV.

eV. This result may implies that the formation of Ti-C and Ti-O-C bonds during doping process of TiO₂ and rGO. This result were identified by XPS analysis which will be discussed later. The formation of those bonds are expected to favor the photocatalytic properties of TiO₂/rGO and fastening the rate of electron transfer in perovskite solar cell. In contrast, 650 °C TiO₂/rGO have the highest band gap at 2.97 eV but still lower than as reviewed in literature which is 3.02 eV. This phenomenon might be the result of changes in film density and increase in grain size as discussed in SEM, XRD and AFM earlier.

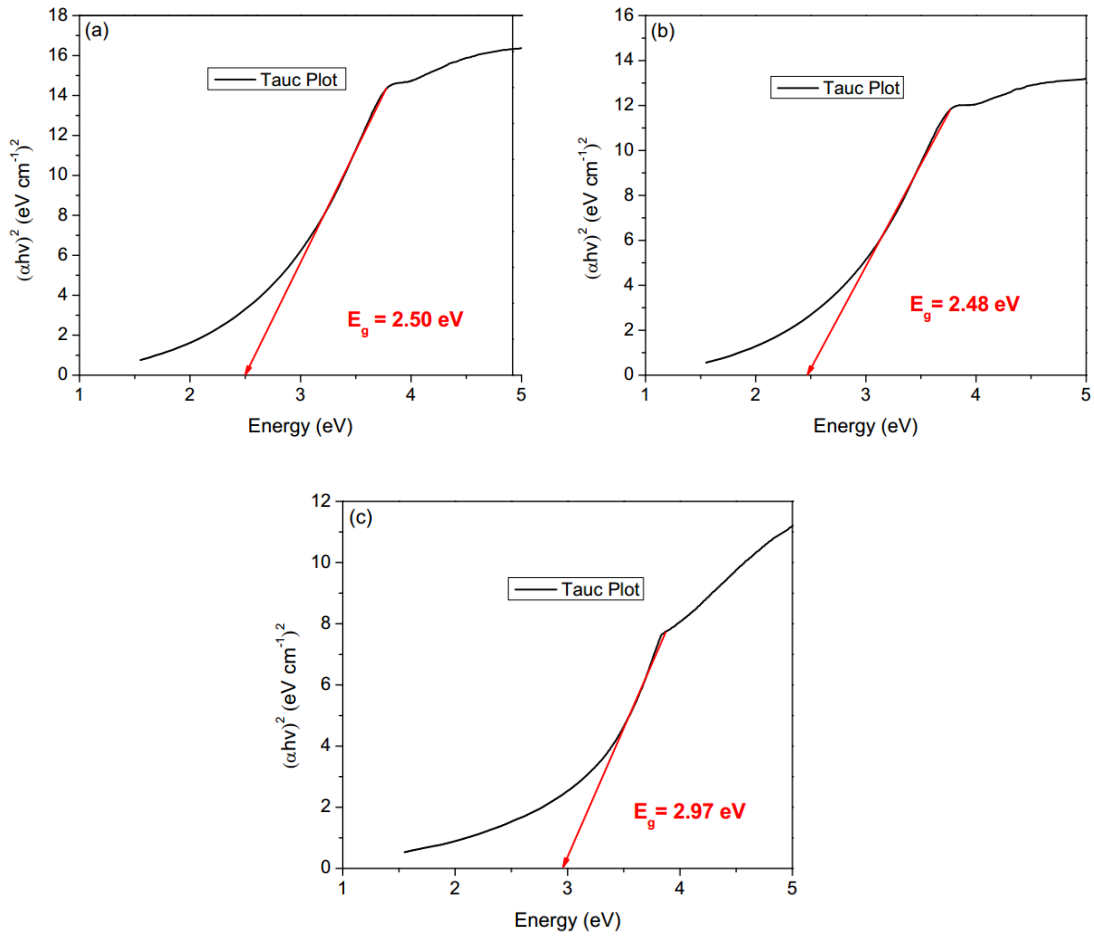


Figure 4.6: Tauc Plot of TiO₂/rGO at different annealing temperature (a) 450 °C TiO₂/rGO, (b) 550 °C TiO₂/rGO and (c) 650 °C TiO₂/rGO

Table 4.2: Energy band gap of TiO₂/rGO at different annealing temperature

Samples	Band Gap (eV)
450 °C TiO ₂ /rGO	2.50
550 °C TiO ₂ /rGO	2.48
650 °C TiO ₂ /rGO	2.97

4.4 Chemical Bonding Analysis

4.4.1 X-ray Photoelectron Spectroscopy (XPS)

The XPS data shown the chemical bonding structure of TiO₂/rGO at different annealing temperature. Then, from the narrow scan, Ti2p, C1s and O1s data were investigated. The results obtained from each bonding analysis is further discussed in the next subtopics.

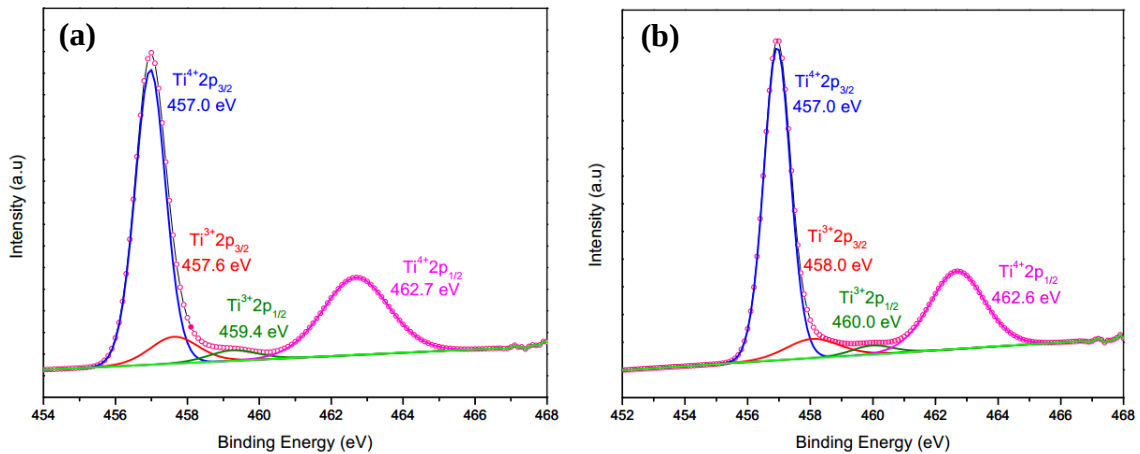
4.4.1.1 Ti2p XPS Data of TiO₂/rGO

Figure 4.7 illustrated the high resolution Ti2p data of XPS spectra for TiO₂/rGO at different annealing temperature. In this spectrum, two main peaks of Ti2p doublet corresponding to the core level binding energies of Ti2p_{3/2} and Ti2p_{1/2} arises from spin-orbital splitting. The splitting width in between Ti⁴⁺2p_{3/2} and Ti⁴⁺2p_{1/2} is around 5.6 eV which referring to common Ti⁴⁺ oxidation state in TiO₂ lattice which are dominant in all TiO₂/rGO samples (Zhang et al., 2017).

From Figure 4.7 (a) to Figure 4.7 (c), the Ti⁴⁺2p_{3/2} peaks for 450 °C TiO₂/rGO and 550 °C TiO₂/rGO were observed at 457.0 eV peak. However, after annealed at 650 °C the peaks slightly shifted to lower binding energy around 0.2 eV. Then, for Ti⁴⁺2p_{1/2} peaks, the

peaks also shifted towards lower binding energy as the annealing temperature increases from 462.7 eV for 450 °C TiO₂/rGO and 462.4 eV for 650 °C TiO₂/rGO. This implies that surface modification and chemical diffusion occurred during higher annealing temperature that lowered the binding energy as obtained in Figure 4.7.

Based on previous research, Ti ion in pure anatase phase recorded 457.9 eV and 463.8 eV for Ti2p_{3/2} and Ti2p_{1/2} peaks correspond to Ti⁴⁺ tetragonal structure in previous study (Song et al., 2005; Li et al., 2014). As compared to the finding of current work, the peaks is slightly shifted towards lower binding energy attributed to the presence of C element in rGO nanoparticles incorporated with TiO₂ lattice structure creating Ti-C bonds and/or Ti-O-C bonds (Liu et al., 2014; Low et al., 2017). The presence of these bonds also lowering the band gap of TiO₂/rGO which favoring its performances in electrical properties as discussed in Uv-Vis spectra.



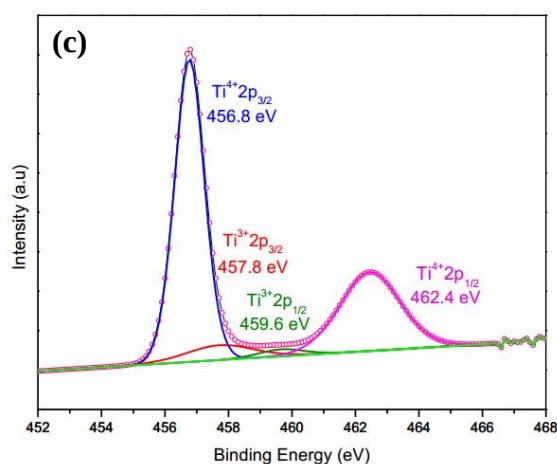


Figure 4.7: XPS spectra of Ti2p of (a) 450 °C TiO₂/rGO, (b) 550 °C TiO₂/rGO and (c) 650 °C TiO₂/rGO

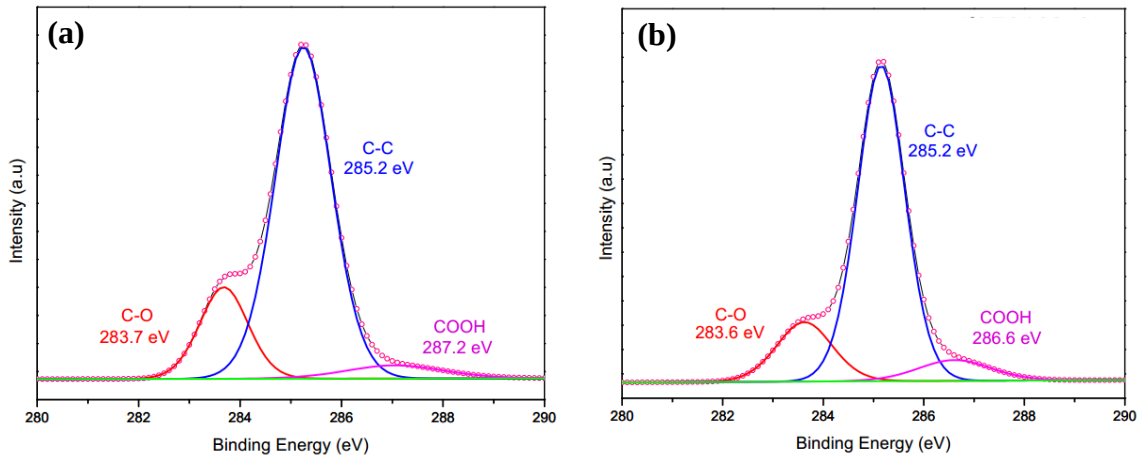
In addition, it is observed that the small amount of titanium suboxide species bonds appeared at 457.8 eV. This peak may correspond to the Ti³⁺ bonds which is similar with reported value by Liu and co-workers. From their previous work, it is stated that the lower the binding energy of Ti2p, the more titanium suboxide exists such as Ti³⁺ and Ti²⁺ (Liu et al., 2017). Another observation is the intensity of Ti³⁺ peaks are decreasing as the annealing temperature increasing. This finding suggested that the changes in TiO₂ crystallinity phase also affecting the elemental bonds in TiO₂.

4.4.1.2 C1s XPS Data of TiO₂/rGO

Figure 4.8 illustrated the high resolution C1s data of XPS for TiO₂/rGO peaks at different annealing temperature. It is observed that 450 °C TiO₂/rGO and 550 °C TiO₂/rGO have the same strongest peaks at 285.2 eV while at 650 °C TiO₂/rGO, the peak shifted slightly towards 285.0 eV. The peaks is the typical C-C peaks which mainly attributed to the graphitic sp² atoms. The reduced in binding energy of C-C peaks suggest that the Ti ion is

linked successfully in rGO structure which leads to weakening of C-C bonds at higher annealing temperature.

Next, the first shoulder peaks detected in XPS spectrum is belong to C-O bonds that attributed to the defect-containing sp^2 hybridized carbon (Tsai et al., 2011). The C-O bond peaks are at 283.7 eV, 283.6 eV and 283.5 eV for 450 °C TiO_2/rGO , 550 °C TiO_2/rGO and 650 °C TiO_2/rGO respectively. Other than the decrement in binding energy along with increment in annealing temperature, the intensity of C-O peaks also differs in between 450 °C TiO_2/rGO and 650 °C TiO_2/rGO with 550 °C TiO_2/rGO . It can be observed from Figure 4.8 that 550 °C TiO_2/rGO has lower intensity as compared to others. The decrease in intensity of C-O peaks referring to the O element that eliminated from Ti is bonded well with C element (Wang et al., 2011).



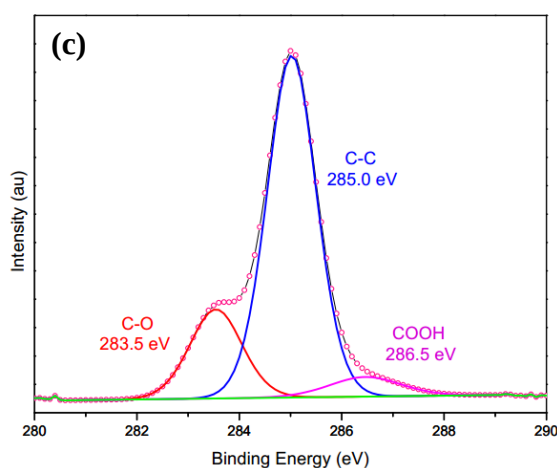


Figure 4.8: XPS spectra of C1s of (a) 450 °C TiO₂/rGO, (b) 550 °C TiO₂/rGO and (c) 650 °C TiO₂/rGO

In contrast, the second shoulder peaks of COOH bonds located at 286.6 eV for 550 °C TiO₂/rGO appeared to be wider in intensity as compared to 450 °C TiO₂/rGO and 650 °C TiO₂/rGO. This is in agreement of strengthening the carboxylic functional groups after the doping process of Ti ion which forming the Ti-O-C bond (Zhou et al., 2010). To add, the Ti-O-C structure which represented by intensity peak at 286.6 eV of 550 °C TiO₂/rGO also suggested that successful replacement of C atoms by Ti atoms through substitution approach of TiO₂ onto the rGO lattice structure in the doping process.

In conclusion, the C-C peaks, C-O peaks and the COOH peaks are shifted to the lower binding energies as the annealing temperature increases. This phenomenon suggested that the carbon networks of C-C, C-O and COOH are weak thus, enhancing the bonding of TiO₂ with rGO resulting formation of Ti-O-C bonds.

4.4.1.3 O1s XPS Data of TiO₂/rGO

The O1s spectrums of TiO₂/rGO with different annealing temperature is illustrated in Figure 4.9. There are four different peaks detected in Figure 4.9 (a) and 4.9 (b) while there

are five peaks appeared in Figure 4.9 (c). The O1s spectra for 450 °C TiO₂/rGO and 550 °C TiO₂/rGO were fitted into lattice oxygen, TiO₂, OH and H₂O. However, the presence of absorbed oxygen peaks only appeared in 650 °C TiO₂/rGO.

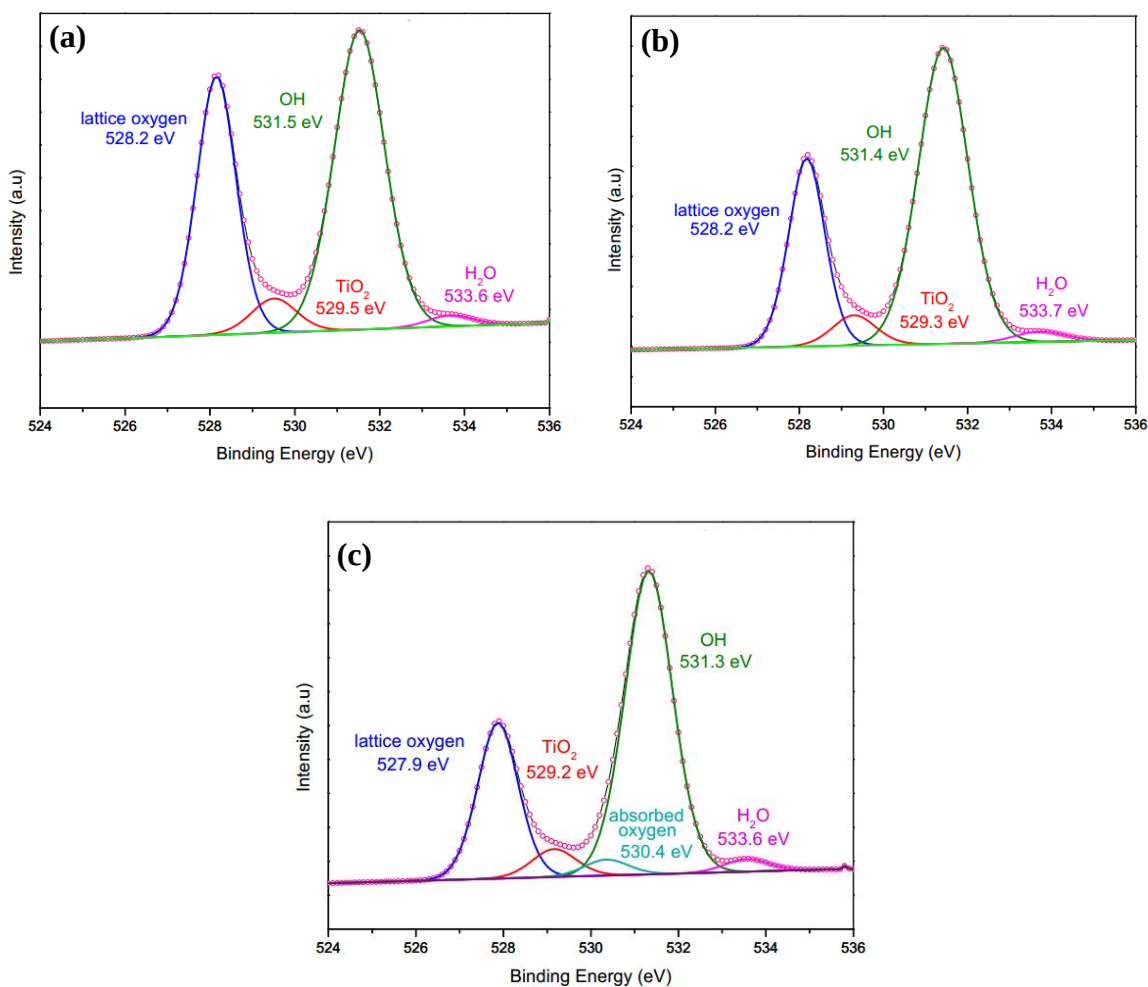


Figure 4.9: XPS spectra of O1s of (a) 450 °C TiO₂/rGO, (b) 550 °C TiO₂/rGO and (c) 650 °C TiO₂/rGO

The binding energy of lattice oxygen decreasing as the annealing temperature increasing at 528.2 eV for 450 °C TiO₂/rGO and 550 °C TiO₂/rGO and 527.9 eV for 650 °C TiO₂/rGO. The basicity of metal oxide commonly translated as its capability to provide electrons, according to the Lewis acid-base theory. Therefore, the decrement in binding

energy of lattice oxygen at 650°C annealing temperature of TiO₂/rGO successfully lowering the basicity of TiO₂/rGO.

Moreover, the presence of TiO₂ peaks, OH peaks and H₂O peaks in all three samples are the results from Ti ion implantation process which attributed to the interaction of C, O and Ti forming the Ti-O bonds and Ti-O-C bonds in TiO₂/rGO solutions (Tsai et al., 2011). The intensity of TiO₂ peaks is observed to be wider in 450 °C TiO₂/rGO whereby the binding energy for 450 °C TiO₂/rGO is also higher than the other at 529.5 eV. This due to the crystallinity phase of TiO₂ as 450 °C TiO₂/rGO is in anatase phase as compared to other samples that have the presence of rutile phase in it. This result is in agreement with XRD patterns that are discussed earlier.

In addition, the appearance of adsorbed oxygen peak at 530.4 eV in 650 °C TiO₂/rGO is related to the oxygen vacancies in TiO₂/rGO. As the adsorbed oxygen peak only exist in 650 °C TiO₂/rGO and none in 450 °C TiO₂/rGO and 550 °C TiO₂/rGO, this indicated that the increment in annealing temperature, increased the concentration of oxygen vacancies in TiO₂/rGO (Wang et al., 2017).

4.5 Electrical Properties of TiO₂/rGO PSC

The current-voltage performance of perovskite solar cell fabricated with TiO₂/rGO at different annealing temperature is illustrated in Figure 4.10. At voltage 0.6 V, the average current generated were 6.45 mA, 9.41 mA and 3.84 mA for 450 °C TiO₂/rGO, 550 °C TiO₂/rGO and 650 °C TiO₂/rGO respectively. From the results, it show that 550 °C TiO₂/rGO sample has the highest current corresponding to its performance in surface morphology and optical properties.

From the I-V graph, the resistance, conductance, resistivity and conductivity of TiO₂/rGO PSC at different annealing temperature is calculated. The values stated in Table 4.3 were calculated by using Equation 3.4 to Equation 3.8 as mentioned in Chapter 3. The result shows that 550 °C TiO₂/rGO gives the highest conductivity at 18.83×10^{-3} S/cm followed by 450 °C TiO₂/rGO at 12.91×10^{-3} S/cm and lastly 650 °C TiO₂/rGO at 7.683×10^{-3} S/cm. It is confirmed that the effect of rGO doping in TiO₂ increased the conductivity as previous work recorded only 9.62×10^{-3} S/cm for TiO₂ and 4.21×10^{-5} S/cm for rGO (Harry et al., 2016; Jaafar et al., 2018).

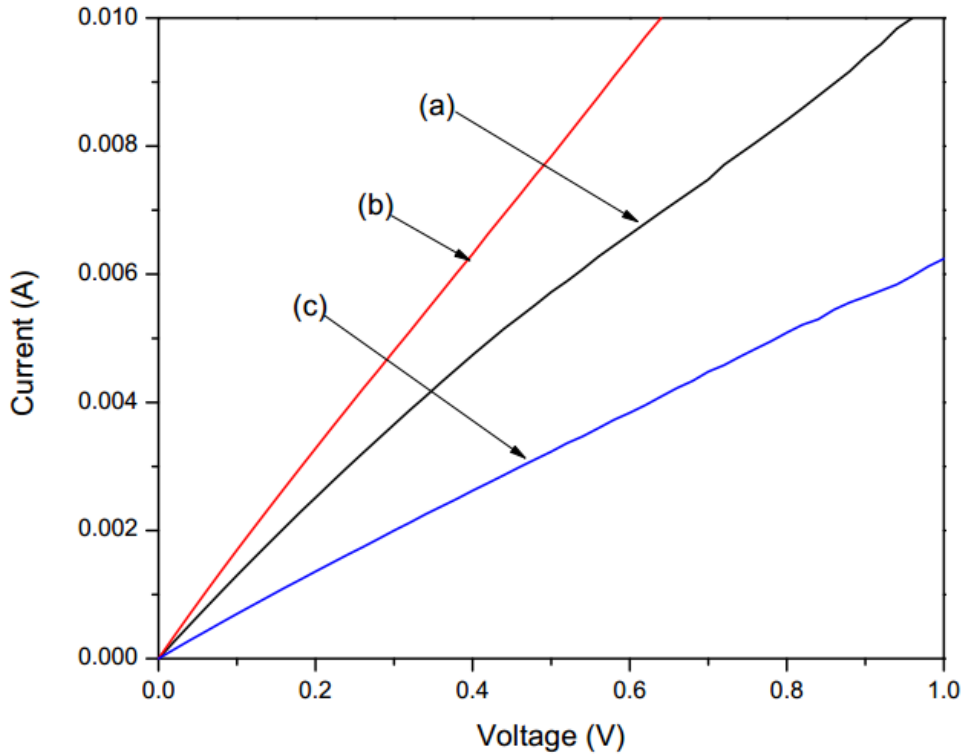


Figure 4.10: I-V characteristic TiO₂/rGO PSC at different annealing temperature (a) 450 °C TiO₂/rGO, (b) 550 °C TiO₂/rGO and (c) 650 °C TiO₂/rGO

Table 4.3: Electrical properties of TiO₂/rGO PSC at different annealing temperature

Samples	Current, (mA)	Resistance, (Ω)	Conductance, (10⁻² S)	Resistivity (Ω.cm)	Conductivity, (10⁻³ S/cm)
450 °C TiO ₂ /rGO	6.45	93.023	1.075	77.489	12.91
550 °C TiO ₂ /rGO	9.41	63.761	1.568	53.114	18.83
650 °C TiO ₂ /rGO	3.84	156.25	64	130.156	7.683

In addition, the decreasing of conductivity is believed to be affected by the changes in TiO₂ crystallinity phase as observed from 650 °C TiO₂/rGO PSC. As discussed in XRD pattern earlier, TiO₂ in rutile phase is detected in 650 °C which supported by increment in grain and crystallinity size as shown in AFM images and SEM morphology. As for 550 °C TiO₂/rGO, the electrical performance agreed previous work by (Fazli et al., 2016) that stated annealing temperature at 550 °C has better performance than TiO₂ that usually annealed at 450 °C due to its ongoing transition to rutile phase and from XRD pattern, it can be seen that 550 °C TiO₂/rGO exist in both anatase-rutile phase. The I-V graph and conductivity of 550 °C TiO₂/rGO supported by the UV-Vis with highest absorbance spectra and the lowest band gap as compared to other samples due to formation of Ti-O and Ti-O-C bonds that confirmed by XPS analysis.

Other than that, as TiO₂/rGO PSC fabricated with spiro-OMeTAD as hole transport material, the increment in conductivity also attributed to the suppressed charge recombination between TiO₂/rGO and spiro-OMeTAD (Niu et al., 2013). In addition, the

thick mesoporous TiO_2/rGO layer lower the possibility that the hole transferred to FTO electrode which favoring the electron transportation (Li et al., 2018). This leads to reducing the recombination of hole and transport carriers at the PSC interfaces. To sum up, the electrical performances obtained are in agreement with theoretical studies whereas the doping of rGO in TiO_2 with different annealing temperature and its fabrication in PSC will increase its photocatalytic performance in photovoltaics.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Overview

This thesis has presented the effect of TiO₂ doping with rGO towards focusing on its surface morphology, optical properties and chemical bonding analysis as thin films. Then, TiO₂ doped rGO is fabricated into perovskite solar cell as electron transport material thus, its performances in enhancing the electrical properties of perovskite is investigated. Therefore, this final chapter concludes the findings and also provides recommendation for future works in this field of study.

5.2 Conclusion of Research Finding

The study on the effect of TiO₂ doped rGO with annealing temperature dependence and its fabrication in perovskite solar cell as electron transport material have demonstrated remarkable findings and all objectives have been achieved. The following are list of research findings based on the objectives stated in Chapter 1.

- 1) Higher annealing temperature produces more porous TiO₂/rGO thin films as well as increment in crystallinity and grain size as observed from surface morphology of TiO₂/rGO in SEM images. The porosity of TiO₂/rGO thin films is importance as the photocatalytic performance of TiO₂ rely on it. This finding also in agreement with the surface roughness obtained from AFM images as the higher the annealing temperature, the higher the surface roughness of TiO₂/rGO thin films.

- 2) As the annealing temperature increased, the crystallinity phase of TiO_2 changed from anatase to rutile. From XRD patterns, it can be concluded that TiO_2 already started to change its phase from anatase to rutile at 550°C . In this research, 550°C TiO_2/rGO and 650°C TiO_2/rGO existed in anatase-rutile phase as intensity of rutile peaks is the highest in 650°C TiO_2/rGO . Interestingly, 550°C TiO_2/rGO is the most optimum samples in conjunction with its performances in optical and electrical properties which favoring the phase transition of TiO_2 .
- 3) The optical performances of TiO_2/rGO with different annealing temperature shown that 550°C TiO_2/rGO has the highest absorbance wavelength while 650°C TiO_2/rGO is the lowest. The band gap calculated also shown that 550°C TiO_2/rGO has the lowest band gap and 650°C TiO_2/rGO has the highest. The increment in particle size effecting the performances of 650°C TiO_2/rGO and the electron affinity in phase transition favoring the performances of 550°C TiO_2/rGO . In addition, the TiO_2 band gap obtained also recorded lower than previous study due to incorporation of rGO in TiO_2 .
- 4) The chemical bonding analysis of $\text{Ti}2\text{p}$, $\text{C}1\text{s}$ and $\text{O}1\text{s}$ data from XPS data confirming the formation of Ti-O and Ti-O-C bonds in TiO_2/rGO nanoparticles. The peaks in $\text{Ti}2\text{p}$ data and $\text{C}1\text{s}$ data shifted towards lower binding energy as the annealing temperature increased which attributed to the C element in rGO nanoparticles and weakening of carbon networks. Meanwhile for $\text{O}1\text{s}$ data, the presence of TiO_2 , OH and H_2O peaks represent the result from Ti ion implantation process. From point (1) to point (4), the effects of annealing temperature on TiO_2/rGO are studied and objective (i) is achieved.

5) As TiO₂/rGO is fabricated into perovskite solar cell as ETL and spiro-OMeTAD as HTL, the electrical properties of TiO₂/rGO PSC are calculated based on the I-V graph. In conductivity comparison, 550 °C TiO₂/rGO recorded the highest reading in agreement with its performance in previous characterization. It can be conclude that the annealing temperature not just changing the crystallinity phase of TiO₂ but, at the same time controlling the performances of TiO₂/rGO in PSC. Thus, objective (ii) is achieved.

5.3 Recommendation

Further study is necessary in order to improve the findings of present study. The following are the recommendations for future work in this field.

- A study of various dopants for TiO₂ is recommended to be carried out. The purpose is to fully enhance the chemical stability in TiO₂ and improve TiO₂ performance as electron transport material in photovoltaics solar cell.
- Further research on more cheaper and easily available hole transport material in PSC as spiro-OMeTAD expensive.
- Degradation and encapsulation study on PSC as the performances of PSC is limited by degradation problems especially to humidity and surrounding.

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