TAILORING THE GRAIN SIZE OF METHYLAMMONIUM LEAD IODIDE PEROVSKITE FILM WITH FUNCTIONALIZED RGO FOR ENHANCED MORPHOLOGICAL AND OPTICAL PROPERTIES

Utilizing functionalized rGO to tailor the grain size of $MAPbI_3$ perovskite for properties enhancement.

Submitted in accordance with the requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Hons.)

by

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FACULTY OF MANUFACTURING ENGINEERING

2021

UNIVERSITI TEKNIKAL MALAYSIA

BORANG PENGESAHAN STATUS LAPORAN PROJEK

Tajuk: **TAILORING THE GRAIN SIZE OF METHYLAMMONIUM LEAD IODIDE PEROVSKITE FILM WITH FUNCTIONALIZED RGO FOR ENHANCED MORPHOLOGICAL AND OPTICAL PROPERTIES**

Sesi Pengajian: **2020/2021 Semester 2**

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Signature : ………………………………………….
Author's Name : NUR SABRINA SAHIRA BINTI SYED OMAR
Date : 29th AUGUST 2021

APPROVAL

This report is submitted as partial fulfilment of the subject BMFU4912 Bachelor Degree Project 2 to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka to meet the criteria completion of Degree of Manufacturing Engineering (Hons) Supervisor as follows:

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(PROFESOR IR. DR. MOHD ASYADI 'AZAM BIN MOHD ABID)

ABSTRAK

Sel Suria Perovskite (PSC) adalah salah satu jenis sel suria yang paling terkenal. Bahan perovskite banyak digunakan kerana sifat elektrik dan optiknya yang unggul. Bahan perovskite berfungsi sebagai lapisan penyerap dalam sel suria perovskite, menyerap tenaga foton dan menghasilkan pasangan lubang elektron. Dengan kecekapan penukaran tenaga yang tinggi, ciri fotolistrik yang luar biasa, dan spektrum penyerapan kecekapan yang kuat, metilamonium plumbum iodida adalah salah satu jenis bintang yang menjadikan PSC bersinar. Kerana kualiti yang luar biasa ini, ia adalah bentuk sel suria yang paling stabil. Walau bagaimanapun, PSC terus mengalami beberapa kekurangan yang menggangu reputasinya. Pertama, terdapat kekurangan dalam aplikasi kestabilan jangka panjang kerana terdedah kepada persekitaran terbuka dengan perubahan cuaca yang mengakibatkan reaksi antara kationnya dengan air dan oksigen. Akibatnya, ciri optik dan morfologi gagal. Kedua, morfologi perovskite yang buruk menyebabkan perangkap yang merosot dalam ciri-ciri pentingnya, seperti pergerakan dan penyerapan cas. Kemerosotan ini menyebabkan morfologi rosak, yang akhirnya mempengaruhi kecekapan penukaran kuasa peranti berdasarkan bahan perovskite. Kajian ini bertujuan untuk meningkatkan sifat morfologi dan optik bahan perovskite dengan memasukkan *sulfonated graphene oxide (s-rGO)* sebagai dopan. Oksida graphene yang dikurangkan adalah sintesis melalui kaedah Hummer yang diubah suai, difasilitasi oleh agen pengurangan persekitaran, dan selanjutnya di sulfonasi sebelum dimasukkan ke dalam larutan perovskite dalam keadaan sekitar. S-rGO mengandungi kumpulan fungsi asid sulfanilik yang mencukupi, penting untuk membentuk ikatan dengan kation perovskite untuk menyelaraskan filem nipis perovskite dan mengelakkan pengagregatan. Oleh itu, ia meningkatkan ukuran butiran filem nipis perovskite dan mengurangkan ketumpatan perangkap cas di batas butiran. Dalam kajian ini, pembentukan s-rGO dopan kedalam perovskite disahkan melalui Spektroskopi Raman secara ulasan kajian. Selain itu, Spektrofotometer Ultraviolet-Visible (UV-Vis) digunakan untuk mengkaji analisis sifat optic juga melalui kaedah secara ulasan kajian. Sementara itu, peningkatan morfologi perovskite dianalisis dengan menggunakan Mikroskopi Elektron Imbasan (SEM). Menggabungkan s-rGO sebagai dopan diharapkan dapat meningkatkan morfologi perovskite tanpa mempengaruhi sifat optiknya sebagai bahan aktif dalam sel suria perovskite.

ABSTRACT

Perovskite Solar Cells (PSC) are one of the most well-known types of solar cells. Perovskite materials are widely used due to their superior electrical and optical properties. Perovskite material functions as an absorber layer in perovskite solar cells, absorbing photon energy and generating electron-hole pairs. With high energy conversion efficiency, outstanding photoelectric feature, and intense efficiency absorption spectrum, methylammonium lead iodide is one of the star-growing types that make the PSC shine. Because of these exceptional qualities, it is the most stable form of the solar cell. However, PSC continue to suffer from several flaws that jeopardize its excellent reputation. First, there are flaws in the long-term stability application since it is exposed to an open environment with weather fluctuations resulting in the reaction between its cation to water and oxygen. As a result, the optical and morphological characteristics are flawed. Second, poor perovskite morphology causes traps that degrade in their essential features, such as charge mobility and absorption. This degradation has led to its poor morphology, which eventually affects the device's power conversion efficiency based on this perovskite material. This study aims to enhance the morphological and optical properties of the perovskite material by incorporating sulfonated reduced graphene oxide (s-rGO) as a dopant. The reduced graphene oxide is synthesis through modified Hummer's method, facilitated by an environmentally reducing agent, and further sulfonated before incorporated into the perovskite solution in ambient condition. S-rGO contains sufficient sulfonic acid functional groups, essential to forming a bonding with perovskite cation to align the perovskite thin film and avoid agglomeration. Thus, it increases the perovskite thin-film grain size and reduces the charge trap density in the grain boundaries. In this study, the perovskite doped s-rGO formation confirmed via Raman spectroscopy via critical review. Besides, the Ultraviolet-Visible Spectrophotometer used to study the optical properties analysis also by critical review. Meanwhile, the improvement of the perovskite morphology analyzed using Scanning Electron Microscopy. Incorporating s-rGO as a dopant improve the perovskite morphology without affecting its optical properties as active material in perovskite solar cells. Furthermore, reduced graphene oxide hydrophobic properties help enhance the perovskite stability in the ambient atmosphere.

DEDICATION

To my supportive supervisor and co-supervisor thank you so much for the endless support and guidance,

To my beloved father, Syed Omar Bin Syed Mansoor thank you for the moral support,

To my appreciated mother, Rosenani Binti Hussain thank you for keep giving me moral support, funding, collaboration, encouragement and understanding.

To my dearest friends that you for being there for one another,

Thank you very much for everything.

I love you all.

ACKNOWLEDGEMENT

In the name of Allah SWT, The most humble, gracious, with the highest praise of Allah that I succeed without difficulty in completing this final year of project 2.

First and foremost, I would like to thank my supervisor, Profesor Ir. Dr. Mohd Asyadi ‘Azam Bin Mohd Abid, for his assistance, support, and availability throughout my final year project journey. My dearest superior, Miss Nur Ezyanie Binti Safie, whose assistance and support was also critical to this work's development. I want to thank you for all of your expertise and kindness.

There are not enough words for my mother and father to thank you for everything you do for me each day and the support you offer me in every choice I make. Without you, it would not have been possible, and I hope you are proud of me. Thank you for all the assistance and support in every stage of my life for my family.

Thank you to my precious Mok for always being here after all these years and for keep growing with me. Thank you for making it so wonderful and part of my journey. In my heart, you always have a place.

Thank you for all the beautiful memories, support, assistance, and love from my dearest housemates and best buddy. You know who you are. Who were constantly with me and made these four years the finest of my life thus far. It would have been impossible to get here without all of you, and I couldn't have asked for a more gracious group of people.

My gratitude to Encik Azhar for assisting me with sample characterization and make it possible. To all lab assistants who provide me with complete instruction throughout the process of finishing my lab work. Even though you were just a portion of this journey, you added to its beauty. I shall never forget your contribution, advice, and teaching to all outstanding FKP, UTeM lectures.

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LIST OF ABBREVIATIONS

CdTe	- Cadmium telluride
CIGS	- copper indium gallium diselenide
$CH_3NH_3PbI_3$	- Methylammonium Lead Iodide
$CH_3NH_3PbBr_3$	- Methylammonium Lead Bromide
PSCs	- Perovskite Solar Cells
ITO	- indium tin oxide
$MAPbI_3$	- Methylammonium Lead Iodide
rGO	- Reduced Graphene Oxide
GO	- Graphene Oxide
s-rGO	-Sulfonated reduced graphene oxide
$CaTiO_3$	- Calcium Titanium Oxide
ETM/ ETL	- Electron Transport Material / Layer
HTL	- Hole Transport Layer
TCO	- Transparent Conducting Oxide
FTO	- Fluorine-doped Tin Oxide
LHP	- Lead Halide Perovskites
VB	- Valence Band
SEM	- Scanning Electron Microscopy
UV-Vis	- Ultraviolet Visible Spectrometer
AA	- Ascorbic Acid
LUMO	- Lowest Unoccupied Molecular Orbital
CB	- Conduction Band

CHAPTER 1

INTRODUCTION

1.0 Research Background

In electrical energy, solar energy is generated by the interplay of collected sunlight and heat, which is subsequently transformed back into the light. Solar energy is considered to be one of the most sustainable and environmentally friendly sources of electricity. Malaysia is known for having a pleasant environment, which is why many people visit the nation. Because we have warm, bright days nearly every day of the year, it is beneficial for us to use solar panels. We have an adequate quantity of solar energy on hand. Because of its geographic position in the tropical area, Malaysia reaps the benefits of solar energy generation. Miss Yeo Bee Yin, Minister of Energy, Research, Technology, Environment, and Climate Change, said that if solar panels were installed on all of Peninsular Malaysia's home roofs, the country could generate 1.4 times the amount of energy it does now. Wow, what a fantastic chance we have here. The usage of solar cells helps us save money on energy bills, helps to protect our mother planet, and, last but not least, ensures that we will never run out of available sunshine. Also, Malaysia has a natural tropical environment with typical sunlight received for about 12 hours each day, or around half of our daily routine.

Solar cells in a bundle are becoming more popular. There have been three generations of solar cells developed up to this point as shown in figure 1.1 below. The first generation of solar cells, which is the first kind of solar cell found by an expert, is made of crystalline silicon and is the most advanced type of solar cell. Monocrystalline silicon, polycrystalline silicon, thick-film silicon, and amorphous silicon are all examples of the earliest kinds of solar cells. Polycrystalline silicon is another example. Solar panels constructed of non-silicon materials are the next generation of solar cells, followed by the second generation of solar cells. Two examples of second-generation solar cell technologies are cadmium telluride (CdTe) and copper, indium, gallium diselenide (CIGS). Meanwhile, dye-sensitized solar cells, sustainable solar cells, and perovskite solar cells are the most commonly used or most recent solar cells. The improvements made to solar cells are intended to result in a more cost-effective and stable version of solar cells in the future.

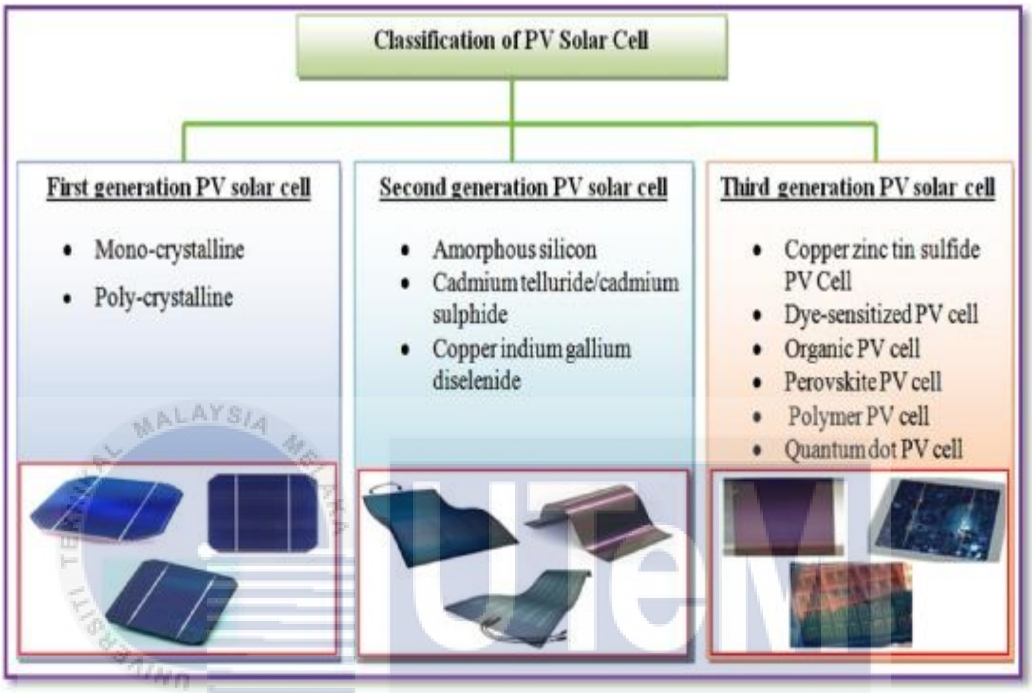

Figure 1.1 Classification of Photovoltaic Solar Cells

In this research, I'm concentrating on the kinds of Perovskite materials that are being used in solar cells. It is a substance with the crystal structure form ABX_3 that is used to make perovskite materials. The crystal structure of this kind of crystal structure is the same as that of calcium titanium oxide. The letters 'A' and 'B' represent cations, and X represents an anion that forms a bond with both. Two components in the Perovskite itself contribute to the enhancement of the characteristics of PSC. The ammonium lead iodide ($CH_3NH_3PbI_3$) and the methylammonium lead bromide ($CH_3NH_3PbBr_3$) are the two components that have been discussed before (Kojima et al. 2009). Out of these two components, methylammonium lead iodide ($MAPbI_3$) is emerging as the brightest star in the solar cell community, thanks to the tremendous improvement in the quality of perovskite solar cells, which has resulted in significant improvements in energy conversion efficiency, with recent devices achieving more than 31 % conversion efficiency (Sha el 2015). The following properties of the $MAPbI_3$

Perovskite result in a well-defined architectural structure. According to Safie and colleagues (2020), the photoelectric characteristics of methylammonium lead iodide are superior, with a smaller binding force of the excitation energy and strong coefficients of absorption spectrum (up to 104 cm^{-1}); this characteristic contributes to improving the stability of solar cells, which was the primary goal of this research. Furthermore, when $MAPbI_3$ is present, the Perovskite's light-absorbing component can gather the sun's rays more efficiently than when it is not there. Another advantage is that due to its high dielectric constant, electrons and holes can be transported and collected efficiently; this feature will improve the absorption ability of solar cells (Zhou et al. 2018).

The benefits of $MAPbI_3$ PSCs are many and continue to grow in popularity; nevertheless, PSCs still face several constraints that reduce the quality and long-term viability of the technology. The major shortcoming of $MAPbI_3$ PCS is their inability to maintain long-term stability of operation. Because of environmental variables such as heavy rainy seasons, intense sunlight radiation, and oxygen, $MAPbI_3$ PSC quickly deteriorate and lose their stability as shown in figure 1.2. In addition, $MAPbI_3$ PSC are also susceptible to degradation and degradation (Agresti et al., 2016). The optical and morphological characteristics of $MAPbI_3$ PSC will be degraded as a result of the constraints that they encounter. In terms of optical characteristics, the deterioration will result in the conversion to a broad bandgap, the formation of a surface trap, current leakage, and a reduction in the capacity to absorb sunlight. From a structural standpoint, deterioration of the $MAPbI_3$ PSC will result in ion movement at grain boundaries, grain size reduction, decreased short-term stability, and a reduction in light-harvesting efficiency.

If we consider the current situation, one of the most effective methods to enhance the stability of the photovoltaic device is to use functionalized graphene oxide as an addition to assisting in the elimination of the restriction. In addition, due to the hydrophobic nature of graphene and its derivatives (Suragtkhuu et al., 2020), graphene may serve as an interfacial layer in the $MAPbI_3$ PSCs structure acting as an additional shield to protect the perovskite thin film from moisture absorption. Eventually, this graphene with hydrophobic characteristics that offer extra protection will assist in overcoming the deterioration possibilities caused by the reasons listed above, such as when it constantly rains for an extended period during the rainy season. In addition, graphene has been extensively utilized as transparent electrodes in photovoltaic systems PSCs because it has greater transparency in the visible area than traditional indium tin oxide (ITO) transparent electrodes in the visible region. Moreover, it has been shown to have very high carrier mobilities (Zhang et al., 2016).

Furthermore, it benefits from being bipolar, meaning that it may be used as both a photoelectrode and a counter electrode (Koefoed L. et al., 2017). Apart from that, according to Kim et al. (2018), graphene exhibits exceptional mechanical flexibility and bending endurance, making it a suitable substitute for flexible transparent electrodes in the fabrication of flexible photovoltaic systems. On the other hand, the literature has only a small number of research that focused on enhancing the shape and optical characteristics of perovskite films by adding functionalized rGO to increase the efficiency and stability of solar cells.

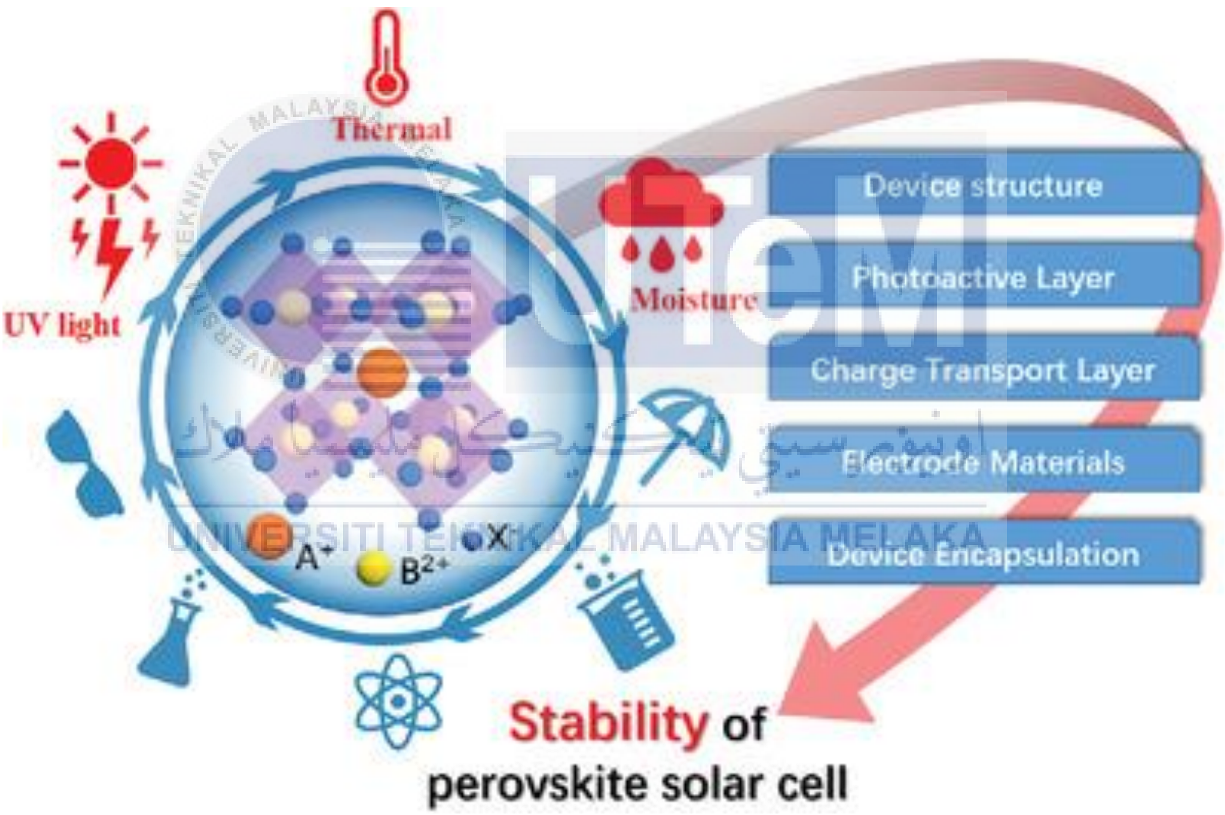

Figure 1.2: Factors of degradation of PSC thin film (Wang et al., 2019)

1.2 Problem Statement

Methylammonium lead iodide PSC are well known for their excellent electrical and optical properties in the applications of solar cells. $MAPbI_3$ Perovskite material acts as an active layer that plays a role as the absorbing film in PSC. Poses characteristics of high coefficient of light absorption help the whole visible solar spectrum by ultra-thin films of solar cells around 500 nm (Yin et al. 2014). These features that belong to the $MAPbI_3$ Perovskite make it possible to manufacture low-cost at high volume, high-efficiency, small, lightweight, and compact solar panels.

However, the aspect of short-term and long-term stability is the main challenge for $MAPbI_3$ PSCs. The main weakness of the PCS is the long-term stability of operations as it is exposed to the high heat and humidity uncovered area for the long term. The factors that lead to the deterioration and stability of the solar cells because of environmental variables such as heavily raining seasons, extreme sunlight radiation, and oxygen. These factors lead to the swift destruction of $MAPbI_3$ PSC, which do not last long (Agresti et al., 2016). The limitations faced by the $MAPbI_3$ PSC will cause a defect in optical and morphological properties.

The degradation will cause the conversion to a wide bandgap, surface trap, and current leakage and drop in the sunlight absorption ability from the optical properties view. This problem will decrease the stability of the $MAPbI_3$ PSC. Meanwhile, from the morphological aspect, the degradation of the $MAPbI_3$ PSC will cause ion migration at grain boundaries, grain size to be minor, short-term stability, and decrease in light-harvesting. These factors lead to the deterioration of the perovskite critical characteristics and strength.

Thus, to tackle the problems mentioned above, this project's main objective is to study the effect of functionalized reduced graphene oxide (rGO) in $MAPbI_3$ Perovskite thin-film. The assumed return is the enlargement of the grain size and tunable bandgap to intensify its morphological and optical properties from incorporating the $MAPbI_3$ Perovskite and functionalized rGO in the thin film. Thus, to see the differences in $MAPbI_3$, the crystal structure grain size and the optical absorbance ability will be examined. Furthermore, the future analysis and effect of functionalized rGO with $MAPbI_3$ Perovskite thin-film on the thin film structure using Raman spectroscopy that show the D and G band properties. Meanwhile, for the thin film's morphological and light absorption spectrum, scanning electron microscopy (SEM) and Ultraviolet-Visible spectroscopy (UV-Vis) was used in study the optical morphological properties.

1.3 Objectives

1. To characterize the Sulfonated reduced graphene oxide (S-rGO) in $MAPbI_3$ Perovskite thin film prepared by the Sulfonation process.
2. To analyze the morphology of S-rGO incorporated with $MAPbI_3$ Perovskite films by using Scanning Electron Microscopy.
3. To investigate the structural and optical properties of S-rGO incorporated with $MAPbI_3$ Perovskite thin film with different surface morphology by using Raman Spectroscopy and Ultraviolet visible Spectrometer based on critical review.

1.4 Scope of the Research

1) To achieve objective 1:

The first process is the preparation of $MAPbI_3$ Perovskite thin film by using two-step spin coating methods. The process begins with the isopropanol combination of methylammonium iodide (MAI) and lead iodide (PbI_2). Second, Synthesis of rGO from graphite via the top-down method. Lastly, surface functionalization through the treatment of sulfanilic acid to the pristine rGO– Sulfonation process.

2) To achieve objective 2:

Preparation of different ratios of S-rGO incorporated with $MAPbI_3$ Perovskite thin-film S-rGO: $MAPbI_3$ Perovskite with 0% S-rGO (100% of $MAbI_3$), 20% S-rGO and 40% S-rGO. Follow by the analyzation of the morphological structure of samples by using Scanning Electron Microscopy. Here, the grain size was the main priority - enlargement of the grain size.

3) To achieve objective 3:

Investigate the optical properties of S-rGO incorporated with $MAPbI_3$ Perovskite thin film by using Ultraviolet-visible Spectroscopy. The focus is on absorbance performance- increase in light absorption ability. Also, to confirm the structural properties of S-rGO incorporated with $MAPbI_3$ Perovskite thin film by using Raman. The main agenda is to check the structure. The quality was than examined from the G band and D band analyses. Both UV-Vis and Raman was performed by Critical Review.

1.5 Rational of the Research

The rationale of research as follows:

1. To analyze the incorporation behavior of graphene-based materials for altering and changing components, including the existence of perovskite composition, morphology and optical properties.
2. Acquiring expertise behind technical analysis by improving the efficiency of perovskite solar cells. Create improved material for use in perovskite solar cells by researching the causes of destruction.

1.6 Thesis Organization

This study is organized as follows: Chapter 1 starts with a research background, problem statement, research objective, and research scope, all of which represent the studies reasoning and research methods and assist in more easily defining the rGO perovskite solar cell's heredity ($MAPbl_3$). In Chapter 2, the overview of the literature on perovskite solar cells ($MAPbl_3$) and functionalized rGO. Chapter 3 Methodology discusses the characteristics and steps involved in manufacturing a $MAPbl_3$ perovskite film utilizing S-rGO. Following Chapter 4, the gathered data will be reviewed and evaluated, and some results from the Critical Review method. Finally, Chapter 5 will end with a conclusion, a proposal, a discussion of sustainable design and development, and the project's long-term learning.