From lab to fab : investigating facile and scalable methods of perovskite solar cell fabrication

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2021

Lew, J. H. (2021). From lab to fab : investigating facile and scalable methods of perovskite solar cell fabrication. Master's thesis, Nanyang Technological University, Singapore.
<https://hdl.handle.net/10356/153119>

<https://hdl.handle.net/10356/153119>

<https://doi.org/10.32657/10356/153119>

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**FROM LAB TO FAB: INVESTIGATING FACILE AND
SCALABLE METHODS OF PEROVSKITE SOLAR CELL
FABRICATION**

Lew Jia Haur

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2021

FROM LAB TO FAB: INVESTIGATING FACILE AND SCALABLE METHODS OF PEROVSKITE SOLAR CELL FABRICATION

Lew Jia Haur

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Master of Engineering

2021

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Assoc Prof Nripan Mathews

Authorship Attribution Statement

This thesis contains material from 2 papers published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapter 5 is published as Bashir, A., Lew, J. H., Shukla, S., Gupta, D., Baikie, T., Chakraborty, S., . . . Akhter, Z. (2019). Cu-doped nickel oxide interface layer with nanoscale thickness for efficient and highly stable printable carbon-based perovskite solar cell. *Solar Energy*, 182, 225-236.

DOI:10.1016/j.solener.2019.02.056

The contributions of the co-authors are as follows:

- Dr Amna and I designed the experiment which includes the fabrication of nanoparticles, as well as what characterization tools to use to characterize the interlayer as well as the resultant device.
- Dr Amna and I synthesized the nanoparticle and paste. We then optimized the printing parameters of the device.
- Dr Sudhanshu helped with EIS analysis.
- Dr Disha and Dr Tom Baikie helped with synchrotron measurements and data analysis.
- Dr Sudip helped with Rietveld refinement analysis and DFT calculations.
- Dr Annalisa and Rahul helped with TRPL measurements.

Chapter 6 is published as Li, J., Dewi, H. A., Wang, H., Lew, J. H., Mathews, N., Mhaisalkar, S., & Bruno, A. (2020). Design of perovskite thermally co-evaporated highly efficient mini-modules with high geometrical fill factors. *Solar RRL*, 4(12), 2000473-. DOI:10.1002/solr.202000473

The contributions of the co-authors are as follows:

- I optimized the laser parameters and settings for P1P2P3 processing for both thin film and fully printable processes.
- Dr Li Jia prepared the sample and evaporated of the perovskite layer.
- Dr Herlina and Dr Wang Hao sputtered the contacts.

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Lew Jia Haur

Abstract

Perovskite solar cells have seen dramatic improvements in terms of device efficiency. In a short span of a decade, the device efficiency improved from 3.8% to beyond 24%. Low cost of precursor materials coupled with highly facile spin coating techniques used to fabricate perovskite solar cells have contributed to the impressive improvement of efficiencies in the short time frame.

However, most of perovskite solar cells that reported efficiencies beyond 23% employs a spin-coating technique for cell fabrication, followed by an evaporation step to deposit the contacts. Also, these high efficiency numbers are only recorded on small areas smaller than 1cm^2 , which has little real-world applications. Furthermore, this spin coating method has high material wastage, and usage of the thermal evaporator limits the throughput required by industrial needs. These scaling issues, coupled with the low stability of the perovskite material in the presence of moisture, remain as one of the main stumbling blocks that hinders the commercialization of this promising technology.

An alternative architecture that could pave the pathway towards the commercialization of perovskite solar cells would be the fully printable mesoscopic design employing carbon material as a counter electrode. The mesoscopic layers are printed and sintered, and the device is completed by infiltrating the pores with perovskite precursor solution. This highly scalable and facile method of perovskite solar cell fabrication, coupled with high throughput and little material wastage, seem to offer the best compromise of what it takes to commercialize this promising technology. This architecture offers reasonable efficiencies of up to 15%, offers high scalability to 70cm^2 in size. Furthermore, the carbon electrode serves a dual-purpose role of charge collector and extractor, as well as a protective layer against moisture ingress.

Like the earlier section, the high efficiencies of fully printable mesoscopic solar cells are reported based on small surface area with large amount of masking. This could lead to erroneous and exaggerated PCE values. In this thesis, systematic experiments have been

outlined with the aims to properly evaluate and further improve the performance of the fully printable mesoscopic perovskite solar cell.

Firstly, the active area effect on the efficiency, as well as the effect of masking on the device efficiency is being investigated. Secondly, systematic scale up of the printable solar cell is being discussed. A 70cm² module with 10% PCE values is fabricated.

Next, experiments are planned to enhance the device performance. Optimization of additive concentration improved pore filling and device performance. A thinly printed Cu:NiO_x is introduced as an p-type oxide interlayer between carbon and ZrO₂. A well aligned energy level of the p-type oxide with the valence band of the perovskite material should enhance charge extraction, improving device performance.

The last part of the chapter also includes preliminary investigation of encapsulation. Various means of encapsulation are discussed. The second part of this chapter discusses about the optimization the patterning process using laser ablation. A combination of encapsulation and laser processes are essential to ensure the translation of perovskite technology from the lab to commercial scale.

Finally, the final chapter draws a conclusion and summarizes the thesis. Further works are also being discussed, which will help to facilitate the push towards commercialization of printable perovskite solar cells.

Lay Summary

Perovskite solar cells are a type of new solar cells. The light absorber layer is made up of an inorganic-organic hybrid material with a perovskite crystal structure. The perovskite material can be made simply by mixing the precursors in a suitable solvent and is deposited on the substrate using a simple spin coating approach. In the lab setting, high efficiency numbers have been achieved. In a short span of 10 years, efficiencies have improved from 3.8% to more than 24%, rivaling that of silicon solar cells. The light absorber material absorbs more light as compared to silicon, and hence perovskite solar cells use less material and are potentially much cheaper to produce at scale.

Despite these positive points, perovskite solar cells suffer from stability issues as well as scalability issues. These issues need to be addressed before these solar cells could be commercialized. Moisture in the surrounding air degrades the perovskite absorber layer. The spin coating process deposits less than 10% of the solution on the substrate, rendering the rest as waste. Also, the spin coating process is only suitable for substrate sizes up to 10cm x 10cm. Beyond that size, there will be an issue of film uniformity.

To address this issue, a fully printable mesoscopic device stack was invented by a research group from China led by Prof Han. A screen printer is used to print a titania/zirconia/carbon scaffold. A subsequent infiltration of perovskite solution into the scaffold completes the device. This enables the development of a low cost and facile production of perovskite solar cell. This type of architecture can produce a reasonable efficiency of 12.8%. The carbon serves as both the hole conductor and electrode, further reducing the cost of the solar cell. The carbon electrode can also serve as a barrier to act against moisture ingress, helping to improve the stability aspect of the solar cell.

This architecture offers a well-balanced design that has reasonable efficiencies, high scalability, and low cost of manufacturing. Hence, this investigation of this architecture is the main highlight of this thesis. One major concern is the lack of consistency in reporting

of device efficiencies, as well as missing data of upscaled devices in published works. This might cast some doubts in the scalability of the printable perovskite solar cells.

The first chapter aims to understand the effect of mask shading on the reported efficiencies of the solar cell. After comparing the results obtained by various degree of shading, the next step is to optimize the width of the solar cell. This is critical, as the size of the solar cell can have great impact on the device efficiency. After optimizing the width, the optimized design is implemented in mini modules connected in a series fashion. This helps to mitigate losses due to recombination and resistive losses, and the resulting mini module obtained an efficiency exceeding 10%.

Next, the efficiency of the printed perovskite device needs to be improved. The effect of a p-type metal oxide is examined. The p-type oxide could help to extract more charge from the absorber layer by having a better energy level alignment, enhancing the performance of the device. The chosen p-type oxide for investigation is copper doped nickel oxide (Cu:NiO_x). When the metal oxide interlayer is added, the efficiency of the printed device is improved.

Finally, in the last chapter, ways to further improve the device efficiency and stability are being discussed. In a bid to further enhance the stability and efficiency aspect of the device, attempts were made to remove the short chain molecule as well as methyl ammonium cation in the perovskite. Primary investigations show that lamination with EVA proves to be a robust mean of encapsulation; a device with proper encapsulation lasted more than year on a rooftop exposed to weather elements. During the encapsulation process, process refinements are made to accommodate the shortcomings. One method is to replace manual soldering with screen printed contacts, and to replace the back glass with tempered glass.

Acknowledgements

This dissertation would not have been possible without funding from the Nanyang Technological University (NTU), Energy Research Institute @ NTU (ERI@N) and Singapore-Berkeley Research Initiative for Sustainable Energy (SinBeRISE).

I would like to thank my supervisor, Assoc Prof Nripan Mathews for his constant support and encouragement. He is always encouraging me to expand my horizons and always supportive of my ideas. I remember the first time I met him I was an undergrad with horrible GPA, and he was giving me an interview for my undergrad thesis on perovskite solar cells. In a blink of an eye 4 years have passed. From an undergrad to a Project Officer, now I'm finishing my Master's thesis and doing a perovskite startup under his valuable guidance. Without him, all these would not have been possible. I am extremely grateful and appreciate of his belief in me.

Next, I would also like to thank Prof Subodh for the trust and patience he had with me. I can still remember the various projects he tasked me to; going overseas in less than 3 months into the job, to going to factories to handle the FATs and various research institutes to arrange for collaborations. It was an eye-opening experience, and it really helped me in my career growth and development.

I am very grateful to my fellow colleagues whom made this journey easier. Dr. Frederick Carl Jr (Fritz) is one of my craziest colleagues I ever had in my research career. We were always trying out new experiments, tearing things apart, repairing broken things, with our dear lab manger Ms Heryani screaming us not to destroy the lab (ok it was a joke we aren't that horrible). We also spent so much time scratching our heads over the various deadlines and student reports. It was a pleasant working experience with you, and it's something I'll cherish for a long time. Let us catch up soon yea!

Now, I would like to express my gratitude for Ms Heryani for keeping everyone safe and sane in the lab. Being the lab manager, especially for me and Fritz, is not an easy job, and

I am glad to have worked with you! From setting up the lab together and helping to clean up with the mess, to solving equipment issues to talk about everyday life, I am glad and honored to have known this awesome lady.

I would also want to thank the other members in the CREATE lab for making my time at CREATE much more enjoyable.

Daymond for the badminton games and good deals, as well as constructive meetings and discussions to help push the project forward. For Prem, please take good care of your current wife (slot die coater), don't abuse her, and get 20% PCE! Please suggest to Prof to get you a wife upgrade soon! Li Jia, thank you for helping with all the evaporation work and stuff. It's been a pleasure to help you optimize the laser etching process to put in the Joule paper and let's see if we can get to setup a new laser in CREATE soon!

Also, thank you Dr Amna, Rahul, Mathilde and all the other interns that made life in lab interesting! Congratulations for Amna for getting ur PhD, and all the best for you Rahul and Mathilde! With your crazy ideas and hardworking approach, I'm sure it's not going to be an issue for the two of you!

Finally, I would like to thank my family and my wife for standing by my side during this crazy period of time. This thesis wouldn't have been possible without the support from you all. No words can express my appreciation and gratitude towards the tolerance you all had for me during the times I was missing out in family gatherings and stuff due to work commitments.

GRAD LO!

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Chapter 1 Introduction

Chapter 1 gives an overview of the thesis. A simple introduction to perovskite solar cells is given. Perovskite solar cells have attained high efficiencies in the lab settings and have great commercialization potential. For successful commercialization, perovskite solar cells must be made more stable and scalable. A suitable fabricating method of screen-printing is investigated. Following which, the research gap of improper measurement is identified, giving rise to the motivation to design of experiments and writing of this thesis. The research findings are reported in various journals and are explained logically in the next few chapters of the thesis. Finally, the last chapter gives a summary and overview of the possible directions which future research further explore.

1.1 Introduction

Perovskite solar cells are a new generation of solar cells that can be fabricated using simple and facile methods. The reason behind the rapid advancement in photo-conversion efficiencies (PCE) is due to its excellent opto-electronic properties such long and balanced charge carrier lifetimes, high absorption coefficients, direct band gap, and solution processability.

However, these highly efficient perovskite cells are reported with measurements on a small active area (usually $\sim 0.09\text{cm}^2$), as the fabrication process is not mature and suitable enough to replicate the defect-free and uniform layers at larger areas. This small area is not practical for real world applications. Another issue at hand is the unstable nature of perovskite solar cells. Moisture in the air degrades the organic charge transport layer as well as the perovskite layer. Hence, there is a dire need to develop processes and understanding on how to improve the enhance the stability of perovskite solar cells, as well as development of processes to enable the scale up of perovskite solar cells to a useful scale.

To overcome these shortcomings of perovskite solar cells, an alternative approach is to use the facile and highly scalable method of screen printing to fabricate the solar cell. In this approach, the mesoporous functional layers are printed using a screen printer. This approach offers a highly repeatable and uniform device stack over a large area, which serves as the foundation to up-scaling of perovskite solar cells. In this approach, a conductive carbon layer is used to replace the hole transport layer as well as the conductive metal electrode.

Highly efficient carbon-based perovskite solar cells have been widely reported, but only with a small active area with respect to the size of the printed electrode. This equalizing method of solar cell measurement inevitably leads to exaggerated PCE values being reported, which might result in dismal scale up results.

This thesis aims to describe and examine the crucial processes to fabricate fully printable perovskite solar cells and effect of active area and shading on PCE values. Following which, the processes and parameters will be optimized for scale up. Experiments and novel processes are trialed to enhance device efficiency and reduce cost. Findings from investigation of encapsulating methods will be expected to have an impact in process flow of device fabrication, and hence modifications are required and explained. The expectations from encapsulation should make the perovskite market-ready and stable enough for more than 10 years of operation. This could be the final push this revolutionary technology needs to emerge into the market.

1.2 Objectives and Scope

The thesis provides a logical process flow to evaluate the processes required to push printable perovskite technology towards commercialization. More than often, reports of highly efficient cells are based on active areas of 0.09cm^2 , which is not practical nor useful for real-world applications. The reason why 0.09cm^2 is chosen is that this is the size of the evaporated electrodes on the spin coated devices. Printed solar cells have much larger electrode sizes, and the masking process which aims to normalize the playing field, ironically leads to exaggerated PCE values. This could manifest itself during scaling up, when the PCE values could not be replicated.

As such, the objectives and scope of this thesis are as follow:

1. Establishing an understanding of how the effect of shading affects the reported efficiencies.
2. Establishing an understanding of the optimal width and scaling up the device to mini module level.
3. Offer insights on possible ways to enhance the device efficiencies
4. Offer insights on what could be done to further improve the performance and stability of the devices to push them closer towards commercialization status.
5. Continual improvements and optimizations to the various processes.

1.3 Dissertation Overview

This thesis aims to address the gaps between lab and commercial fabrication of perovskite solar cells. From proper reporting of PCE values of the fully printable architecture to assessment of scalability, the thesis also includes process enhancements to improve device efficiencies as well as stability.

Chapter 1 provides an overview of the gap between lab scale fabrication and real-world applications. The objectives and scopes of this project is directed towards these shortcomings by addressing them in a systematic manner.

Chapter 2 reviews the literature concerning the development of perovskite solar cells. The excellent opto-electronic properties of perovskite are discussed, followed by working principles of perovskite solar cells. An overview of the device architecture is examined, followed by reported works on such devices.

Chapter 3 discusses the principles underlying the synthesis and characterization techniques employed and the methods of data analysis, including discussion of possible errors leading to inaccurate results.

Chapter 4 touches on the effect of shading on the reported device efficiency. From which, analysis is done to understand the optimal width of the devices. The optimal width is found to be between 5mm to 8mm. Using the optimized width, mini modules with minimal losses were fabricated, showing outstanding stability and scalability.

Chapter 5 elaborates on the effect of having a p-type metal oxide interlayer on the device efficiency. A p-type metal oxide with a well aligned energy level should help with charge extraction and enhances the device performance. The p-type nanomaterial is characterized with various characterization tools. Printing a thin interlayer of p-type metal oxide improves the device performance.

Chapter 6 discusses about encapsulation and the optimization of laser patterning process. An initial encapsulation using dissolved polymers is being investigated. Following which, laminating parameters for a polymer interlayer used in glass-glass lamination are optimized. Lastly, a section describing the optimal setting for laser ablation process is being described.

Chapter 7 is a summary and conclusion for the thesis. It summarizes the findings from the previous chapters and gives insights on what needs to be improved on for the printable solar cell to succeed in the market. Further experiments were performed to establish primary research directions to push this exciting technology even closer towards commercial status.

1.4 Findings and Outcomes/Originality

This research led to several outcomes:

- 1) On the effect of masking on PCE performance at cell level, it is found that there is an optimal width of fully printable devices. It is found to be around 5 to 7 mm. When the widths are smaller or larger than the optimal range, it resulted in poorer efficiencies. PCE values of 14% has been reported with no masking involved.

When the devices are masked, there is an increase in Fill Factor, which outweighs the decrease in V_{oc} , resulting in an exaggerated PCE. The resulted in increased PCE from 12% to beyond 14% PCE.

Using the optimized width, the geometry of the device is optimized for further scaling. Modules with 70cm² active area has been fabricated with efficiencies exceeding 10% PCE when measured on the active area.

- 2) For this technology to be viable, the PCE needs to be improved. Introduction of a p-

- type oxide interlayer led to improvements of the device performance, increasing the efficiency from 10% to more than 12% on a 70cm² module.
- 3) The fully printable perovskite solar cells need to be stable for at least a decade for possible commercialization. To improve the extrinsic stability, various means of encapsulation methods are tested. A spray-on encapsulation consisting of a polymer-solvent blend is deployed on the printed solar cells, providing protection to the ambient moisture. After which, the glass-glass lamination is examined, with the laminating parameters optimized to minimize damage to the perovskite absorber layer.
 - 4) To ensure further scalability and improvements to perovskite solar cells, a scalable laser ablation process is investigated. A thin film etching process of P1P2P3 is investigated and optimized for thin-film perovskite systems. The resulting module has a reduced dead area and reduced interconnect lengths, along with improved IV parameters. The mini module recorded an efficiency beyond 18% on 21cm² active area. The laser process is further optimized to be adapted for the fully printable process using carbon electrodes, as this material system poses a different set of challenge and requires further optimization.

Chapter 2 Literature Review

This chapter gives an in-depth review of solar cells. From solar irradiance to the different types of solar cells, and the potential advantages of perovskite solar cell. Perovskite solar cells promise to be a disruptive technology in the field of photovoltaics, only if its shortcomings are properly addressed. The last part of this chapter shows the existing research gap, and thus the motivation for this thesis paper.

2.1 Solar Irradiance

The Earth receives energy from the sun via the form of electro-magnetic (EM) waves. As its name suggests, EM waves have synchronized oscillations of electric and magnetic waves that prorogate at $3.0 \times 10^8 \text{m/s}$ in vacuum. The magnetic field and electric fields are perpendicular to each other and perpendicular to the direction of energy and wave propagation, forming a transverse wave.

Figure 1 Schematic of a EM wave showing perpendicular fields[1]

EM waves have variable wavelengths ranging from less than 0.01nm to more than 10km. EM waves are governed by the equation $E = hf = \frac{hc}{\lambda}$, where E corresponds to the energy of the particular photon, c is the speed of light in vacuum, h is the Planck constant and λ being the wavelength. This suggests that EM waves with shorter wavelengths have higher energies. The diagram below shows a schematic of the EM wave frequency range. From the diagram, visible light forms only a small portion of the EM radiation received from the Sun.

Figure 2 EM Wave spectrum[2]

The figure below shows the distribution of solar energy, or the spectral irradiance of the EM spectrum according to the contribution of the various wavelengths, received by Earth. The yellow region represents the spectral intensity of EM waves received at the top of the atmosphere, while the red region corresponds to the intensity at sea level. The peak irradiance of red region is lower due to reflection back to space and diffusion by the atmosphere. There are dips in several regions of wavelengths in the red region as well, due to absorption from the oxygen and water molecules in the atmosphere. The yellow region is commonly known as Air-Mass 0 or AM0 standard, while the red region is commonly referred as AM1.5G standard. The AM1.5G standard is commonly used in solar simulators to provide illumination approximating natural sunlight, so that researchers can have access to a common standard to evaluate the performances of the non-concentrated solar cell.

Figure 3 Figure depicting AM 0 (yellow) and AM1.5G (red)

Despite the visible light having a narrow range from 400nm to 700nm, it offers approximately 43% of the total energy from the EM waves received on the Earth surface. The rest of the 57% is spread between the sub UV range and beyond infrared range. As such, electromagnetic radiation ranging from 350 to 800nm has the highest

energy intensity as shown by the peak in diagram above [3]. A well designed single junction solar cell should absorb light effectively from this frequency range. A perfectly ideal single junction solar cell will have a PCE of 33.7%, based on the assumption of using an ideal absorber layer bandgap of 1.34eV. This limit is known as the Shockley-Queisser (SQ) limit[4]. Due to various material and technological limitations, the highest reported PCE values of currently available solar cells are more than 20% PCE, but well below the SQ limit. For example, silicon-based solutions have reached 26.7%, while Gallium Arsenide (GaAs) has reached 29.1%. Finally, Copper Indium Gallium Selenide (CIGS) cells have approached 23.4% PCE[5]. The contributing reasons for the deficit is due to the fundamental losses present in all solar cells, namely Carnot losses, emission losses, Boltzmann losses and thermalization losses[6].

2.2 Solar cells

Solar cells can be broadly categorized into 3 generations. The first-generation cells are made of bulk crystalline silicon. Most of the commercially available photovoltaic devices are made up of polysilicon and monocrystalline silicon. Due to the low absorption coefficient of the silicon material, there is a large amount of material used as the optimal thickness of silicon solar cells is around 200 μ m. Also, extremely pure silicon is required for the device fabrication. During the smelting process, huge amounts of energy are consumed to obtain such pure monocrystalline silicon by the Czochralski Growth method. Fabrication of this kind of solar cells also require high vacuum processes, which also adds on to the energy footprint and overhead costs during manufacturing. The figure below shows the differences in the physical crystal structure between mono and polycrystalline silicon, and the differences in the texture of the finished product. Both products are widely available in the market, with the monocrystalline giving higher efficiencies.

Figure 4 Figure showing differences between monocrystalline solar cell and polycrystalline silicon solar cell[7]

Second-generation solar cells are called thin-film solar cells. As compared to silicon-based cells, they are made from micron-thick layers of semiconductor materials. By using less raw material coupled with less costly manufacturing processes, solar cell manufactured from such technology can be produced and sold at a much lower cost, potentially giving them an advantage over their silicon counterparts.

Solar cells that are considered under this category include amorphous silicon, Cadmium Telluride (CdTe), Gallium Arsenide (GaAs) and Copper Indium Gallium Selenide (CIGS). The main challenge is to get high film uniformity across large areas, as well as potential pollution to the environment due to the toxicity of the materials used[8, 9]. The figure below shows the simplified cross-sectional schematics of CdTe and CIGS cells.

Figure 5 Figure showing the two different types of thin film solar cells [10]

Third generation cells are still under research and development. They have the potential to overcome the Shockley–Queisser limit of 33.7% PCE for single bandgap solar cells, as well as having an even lower cost of production. Perovskite solar cells fall under this category of solar cells.

2.3 Perovskite Solar cells

Originally applied to inorganic compounds, perovskite refers to a class of compounds which have the same type of crystal structure as CaTiO_3 . Many different elements can be embedded in this structure, allowing the development of diverse engineered materials.

Figure 6 Figure denoting the perovskite crystal structure

Perovskites have a cubic structure with general formula of ABX_3 . In this structure, an A-site ion sits on the corners of the lattice. It is usually an alkaline earth or rare-earth element and is represented by the blue spheres in the diagram above. B-site ions, in the center of the lattice, could be 3d, 4d, and 5d transition metal elements. They are represented by the yellow spheres in the middle of the crystal structure. X-site ions sit on the face of the 6 sides of the cubic structure, represented by red spheres[11].

Many elements are stable in the perovskite structure if the Goldschmidt tolerance factor is in the range of 0.75–1.0. The Goldschmidt tolerance factor can be described by the following equation:

Equation 1 Equation showing Goldschmidt Tolerance Factor

$$t = \frac{r_A + r_0}{\sqrt{2}(r_B + r_0)}$$

Where r_A is the radius of the A-cation, r_B is the radius of the B-cation and r_0 is the radius of the anion. The basic perovskite material used in solar cells is of the organic-inorganic hybrid type, with the chemical formula Methyl-Ammonium Lead Iodide (MAPbI_3), where A-site cations are represented by methyl-ammonia (CH_3NH_3), B-site cation represented by lead (Pb), and finally iodine (I) represents the X-site ions.

MAPbI_3 offers high absorption coefficient[12], low binding energies [13], bandgap tune-ability[14]. MAPbI_3 has an absorption coefficient up to 10^5cm^{-1} , which puts it in line with other class leading photovoltaic materials such as GaAs. When the iodine halide is substituted with smaller halides such as bromine or chlorine, the resulting perovskite thin film will have a difference in colour as well as a wider bandgap. This allows perovskite films to be altered accordingly to absorb light more efficiently.

Figure 7 Figure comparing absorption coefficients of perovskite against other semiconductors

Figure 8 a) Picture showing color tuning by halide substitution, b) Effect of halide substitution on absorption spectra, c) Effect of halide substitution on band gap

In 2009, Miyasaka [15] developed a 3.8% perovskite sensitized solar cell. In a short span of less than a decade, efficiencies exceeding 22% has been reported [5]. By substituting the various ions in the perovskite structure, researchers are able to achieve better stability and efficiencies. For example, researchers have incorporated chlorine [16] into MAPbI₃ perovskite, allowing the formation of a film with better morphology resulting in better conductivity and higher efficiencies. Substitution of halides also enabled the tuning of the material's band gap [17], allowing for the development of tandem solar cells which requires a large band gap absorber material for the top cell. Another report suggested that having a mix of A-site ions bring about improved improvements. Results have shown that alkali metals at low concentrations help homogenize the halide distribution, allowing a more uniform and improved film quality. However, at higher concentrations, they form recombination-active second-phase clusters, which is detrimental to the device performance.

2.4 Working principles

The basic principle of a solar cell is to convert photons into electrons[18]. In a perovskite solar cell, the process in which photons are converted to electrons can be broadly described in 3 steps, namely:

- A) Light absorption and electron-hole pair generation
- B) Charge separation
- C) Charge extraction.

A pictorial explanation is shown in the figure below.

Figure 9 Figure showing the energy level alignment of the various interfaces of a perovskite solar cell[19]

Light (photons) is absorbed in the perovskite absorber material. Light is made up of photons and they contain energy. The energy contained by a particular photon is governed by the given equation, $E = hc = \frac{hf}{\lambda}$ where E is the energy, h is Planck's constant, c is the speed of light in vacuum, and λ is the wavelength of the incoming light.

For effective photon absorption, the wavelength of the light must correspond to or exceed the difference in energy level between the HOMO (valence band) and LUMO (conduction band) of the semiconductor material, in which in this case is perovskite. Electrons from the HOMO are excited to LUMO level, and an electron-hole pair is created in the perovskite photoactive layer. This electron-hole pair is called an exciton, and they are bounded together by electrostatic coulomb forces.

After the exciton is created, the electrons and holes separate, and are transported to the anode and cathode respectively, as depicted as process 1 in the diagram above. The charge movements are facilitated by the electron and hole transport materials. This is only made possible due to differences in band energy alignment between the perovskite layer and the respective interfaces. The hole transport is facilitated by the hole transport material, whose energy levels does not allow the electrons to pass through. Electrons are collected at the electron transport material, in which the energy level “blocks” the holes from entering. This is shown as process 2 in the diagram.

At the gold anode, holes are being collected and extracted, while electrons are collected and extracted at the FTO cathode as shown in process 3. However, some of the electrons and hole will recombine before they reach the respective electrodes. Recombination is mainly caused by interfacial defects, and these defects will cause a decrease in charge collection [20-22]. The effectiveness of the charge collection will affect current density (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) which in turn affects the efficiency of the solar cell, which will be described in the next page.

2.5 Interpretation of IV data

There are 4 main areas of interest during the interpretation of the IV curve as show in the figure below. They are namely,

- 1) Short circuit current (I_{sc}),
- 2) Open circuit voltage (V_{oc}),
- 3) Fill factor (FF) and
- 4) Maximum power point (MPP).

Figure 10 Typical IV curve of a solar cell [23]

Short circuit current (I_{sc}) refers to the maximum amount of current being extracted from the solar cell. This happens during a short circuit condition where the voltage across the solar cell is zero. Current density (J_{sc}) is the value of I_{sc} divided by the measured area of the solar cell. Open circuit voltage (V_{oc}) condition is when the maximum voltage is being extracted from the solar cell. This happens when the current is zero.

In both scenarios above, the power delivered by the solar cell is zero, as power is a function of voltage multiplied by current ($P = V \times I$). The maximum power point (MPP) occurs at a certain value along the curve in which the respective current (maximum current point or I_{mp}) multiplied by the voltage (maximum voltage point or V_{mp}) will give

the maximum area under the curve. This can be represented by the green area under the curve. The maximum area under the curve would be that when the IV curve is a perfect rectangle; the resulting power output of the solar cell is its V_{oc} multiplied by I_{sc} .

The ratio obtained when dividing the green area by maximum area will be the fill factor, which expresses the “squareness” of the curve. The FF can be a good indicator of how well designed the solar cell is. Increased recombination and leaky pathways have a detrimental effect on the FF.

There are two types of resistances that researchers are keen to address, namely shunt resistance and series resistance. Shunt resistance refers to the presence of alternative leaky pathways that causes power losses. Such a diversion reduces the amount of current flowing through the solar cell and reduces the voltage produced by the solar cell. A high shunt resistance value is highly preferred. On the other hand, series resistance refers to the resistive losses from a variety of sources including charge separation, interfacial defects, resistance from cathodes and external circuits. A low series resistance value is preferred.

2.6 Device architecture

Perovskite solar cells can be broadly categorized into the following architectures and designs, namely 1) Mesoporous structure, and 2) Planar structure. Figure below depicts the differences between the architectures and electrical designs.

Figure 11 Figure showing the different configurations of perovskite solar cells [24]

In a typical perovskite device, the layers are spin coated one after another, after which the top contact is evaporated onto the device. In a mesoporous structure, a mesoporous TiO₂ scaffold is used to increase the surface area for effective charge collection from the perovskite layer. On the other hand, a planar structure does without the mesoporous structure. In the planar structure, the electrical design of the solar cell can be inverted as well, resulting in either a n-i-p (negative-intrinsic-positive) or a p-i-n (positive-intrinsic-positive) design.

Perovskite solar cells made in the early days were mostly of the mesoporous structure, as the solar cell design was derived from dye sensitized solar cells (DSSC). Perovskite solar cells are essentially solid state DSSCs without the liquid electrolyte, with a direct contact between the HTL and the perovskite sensitizer. Over time, the thickness of the mesoporous TiO₂ layer has been optimized, reducing the thickness from tens of microns to less than 300nm. On the other hand, increased loading of the perovskite sensitizer led to a solid capping layer being developed.

TiO₂ works well as an electron transport layer, due to its well aligned energy levels with perovskite's LUMO level. However, a device made with a wide bandgap Al₂O₃ scaffold, which theoretically should not work, posted an efficiency exceeding 10% PCE [25]. To understand the charge separation mechanism, a transient absorption spectroscopic study was performed with devices made with TiO₂ and Al₂O₃ scaffolds. No significant spectral differences between TiO₂ and Al₂O₃ were observed, affirming that perovskite solar cells will work even without an electron injecting mesoporous TiO₂ layer. This showcases the ambipolar nature of perovskite; it can produce charge, as well as transport charges. With improved control over the spin coating and fabrication processes, the need for an electron transporting scaffold was negated, leading to the development of planar devices.

2.7 Advantages and disadvantages of each design

Mesoporous TiO₂ layers often require high annealing temperatures above 400°C to achieve high crystallinity. This restricts the application of mesoporous perovskite devices to rigid substrates, as flexible substrates usually cannot tolerate high temperatures beyond 200°C. Due to its high surface area, the TiO₂ scaffold enables highly efficient charge collection and reduces charge recombination, allowing the device to achieve high PCE values.

Planar structure does not contain the mesoporous TiO₂ layer. This necessitates a high-quality interface between the perovskite film and the various transporting layers to enable effective charge transport, and more than often, the PCE values of such devices are comparatively lower than that of their mesoporous counterparts. Also, the less than ideal interfaces are also a source of imbalanced charge collection, resulting in hysteresis[26].

However, improvements to the fabrication techniques have reduced this effect of imbalanced charge collection, resulting in a high PCE value when performing IV scans from both directions [27]. Moreover, planar structures allow the fabrication of tandem solar cells, which could allow the realization of solar cells with higher efficiencies that surpasses the SQ limit [28].

2.8 Research Gap to be addressed

In 2014, Han et al from Wuhan has developed a novel method of overcoming the typical problems associated with perovskite solar cells. Highly efficient perovskite solar cells are usually fabricated using spin coated method. However, the process itself is highly time consuming and highly inefficient in terms of material usage. The spin coating process utilizes less than 10% of the material with the rest being wasted. There is only a certain size limit to which spin coating can be applied to that can achieve a highly uniform film, which is imperative for the fabrication of highly efficient devices. Furthermore, spin coated perovskite solar cells utilize expensive hole transport materials, as well as using expensive gold for the evaporation of device contact. The above necessitates the use of an inert glovebox, limiting the scalability and throughput of perovskite solar cells.

In their report, Han et al used a novel screen-printing method to overcome these processing shortcomings [29]. Compact TiO_2 was deposited on the FTO substrate to serve as the blocking layer. A mesoscopic TiO_2 layer is subsequently printed on top. A ZrO_2 scaffold layer is printed on top of the TiO_2 layer, followed by a screen-printed carbon layer. After which, the perovskite solution is infiltrated from the top of the carbon stack. The ZrO_2 layer prevents direct contact of the carbon with the TiO_2 , preventing a short circuit. This device architecture is like that of the mesoporous architecture mentioned in the section above. The mesoporous ZrO_2 scaffold allows perovskite crystals to form within the pores, forming a “pseudo” capping layer similar to that obtained by spin coating. The carbon has a suitable energy level of -5.0 eV, which allows it to be suitable hole transport material. Furthermore, its relative thickness and conductivity makes it a suitable barrier against barrier ingress, as well as an electrical contact, doing away with the need of a thermally evaporated metal contact. This process is highly scalable and economical, while producing a highly reasonably high efficiency of 12.8%.

Figure 12 A) Cross section schematic of the printed triple mesoscopic device B) Energy Band alignment C) Perovskite crystal structure [29]

Shortly after, another group of researchers from China improved the PCE of this fully printable solar cell. The group reported a PCE of 14.9% in a publication in 2015[30]. By introducing a p-type metal oxide (NiO_x) between the ZrO₂ and carbon layer, the hole collection properties are greatly enhanced, leading to reduced recombination enhanced PCE.

Figure 13: SEM imagery showing the cross section of the fully printed device with NiO_x

While the results are encouraging, the fact remains that these results are based on a smaller masked area as compared to the actual active area. For example, the printed active area of the carbon electrode has a size of approximately 1cm², while the reported PCEs are measured on a 0.07cm² active area. This is an erroneous way of measuring solar

cells. The measured active area should be just slightly smaller than that of the electrode area. As reported by various researchers, masking a solar cell incorrectly will register a better FF and reduced V_{oc} , leading to inaccuracy in reported PCE values [31, 32]. The reported PCE values will be exaggerated if the increase in FF due to decreased series resistance outweighs the effect of decrease in V_{oc} . Unfortunately, this appears to be a common trend for fully printable perovskite solar cells as reported PCE values are reported on a very small active area.

To ensure that the results obtained for small devices are reproducible for up-scaled devices, it is imperative to investigate the effect of masking on these printable solar cells, and to come out with an accurate representation of the efficiency at larger area where masking is not feasible. It would also give a clear indication of what PCE values to be expected from the scaled-up module.

To facilitate the module and device design, experiment ideas and procedures were inspired from the literature [33-36], where researchers highlighted the issues and problems that can occur when up scaling the devices. As such, this thesis reports on the following design of experiments. The first step is to investigate the effect of masking, and the effect of active areas sizes and shape on perovskite solar cells. Fully printable devices of varying active area sizes were designed and fabricated using the same facile screen-printing technique.

To prove the scalability of this printing technology, it would be imperative to showcase an up-scaled device. In 2016, Anish et al published a paper[37] on a 70cm² screen printed mini module that yields an efficiency exceeding 10% PCE with outstanding efficiency. Another encouraging report shows the stability of a similar carbon module of over a year [38]. However, for this promising technology to be successful in the market, a more robust encapsulation, further up scaling of device as well as PCE enhancement is required [34, 39].

To establish the feasibility of producing perovskite based modules for the market, findings from the study on effect encapsulation techniques will need to be established, and tested in the real world situation[40]. Modification and fine tuning of the fabrication process is expected to accommodate the different requirements.

Chapter 3 Experimental Methodology

This chapter explains the rationale behind the usage of equipment used in device fabrication, followed by the experimental details in device fabrication. A section discussing the equipment used in characterizing the various properties of the semiconducting material as well as completed device. The in-depth discussion includes the working principles of the equipment, as well as possible sources of errors which can affect the results.

3.1 Rationale for selection of Methods and Materials

For device fabrication, the main process considerations are: 1) repeatability, 2) high scalability and throughput, and 3) cost reduction. Hence, the choice to fabricate perovskite solar cells using a screen printer would be a logical choice. Screen printing is already being widely used in electronic printing industry, as is known to offer these advantages through the inherently simple nature of the machine. When it comes to repeatability and scalability, screen printing can satisfy these two objectives alongside with high material utilization rate especially at high production volumes. This choice is much more suitable than spin coating and evaporation methods, as they have low material utilization rates, high material and machine costs.

For material selection, the cost and ease of getting the chemicals would be one of the main criterions. For this, commercially available pastes and chemicals are used. Low-cost carbon paste is utilized in place of expensive Spiro-OMETAD and evaporated gold contacts. Making screen-printable nanoparticle pastes could be easily scaled up with proper materials and equipment. It is a continual process to procure and test cheaper alternatives on the market. For example, the cost of the printable perovskite device could be potentially lowered by replacing ZrO_2 with lower cost Al_2O_3 paste.

For paste fabrication, a simple ball mill machine is used. This machine helps with homogenizing the components of the paste by mixing them thoroughly. This is a low-cost method that has high scalability potential.

3.2 Device Fabrication and material synthesis

3.2.1 Active area demarcation and substrate cleaning

Fluorine doped tin oxide coated (FTO, <14 ohm per square, 2.2mm thick) glass substrates were first etched with a laser source (1064nm YAG laser, 20kHz pulse) to form the desired pattern, after which the substrates were cleaned with an ultrasonic bath with decon soap

solution, followed by DI water and finally ethanol. Each sonication process is held for 30 minutes. This is done to ensure a clean surface for subsequent deposition of screen-printed layers, as dust and organic contamination could lead to poor printing qualities and subsequently lead to poor device performance.

3.2.2 Compact TiO_2 deposition as blocking layer

Using a screen-printer (MicroTec MT320TV), a layer of compact TiO_2 (Dyesol BL-1) is printed onto the substrate using a suitable screen-printing mesh design. The printed film is allowed to relax for 20 minutes to ensure the bubbles from the lift off process disappear, forming a uniform surface before calcination at 500°C for 30 minutes. These substrates were finally immersed in 100 mM of TiCl_4 solution (Wako Pure Chemical Industries, Ltd, diluted 1:50 volume to volume ratio with DI water) for 30 min at 70°C to fill up the defective “pin-holes”, followed by rinsing with DI water. A final heat treatment of 500°C completes the formation of the blocking layer.

3.2.3 Screen printing of other functional layers

An optimized 450nm thick layer of mesoporous TiO_2 film is printed onto the substrate with a TiO_2 paste (Dyesol NRD-30, diluted with terpineol (Sigma, FG) in weight ratio 1:1.4). Then, the substrates are sintered for 30 minutes at 500°C to improve the crystallinity. Subsequently, a 1.4 μm thick ZrO_2 (Solaronix, Zr-Nanoxide ZT/SP) spacer layer is printed on top of the meso- TiO_2 layer and heated to 500°C for 30 minutes to remove the binders. The ZrO_2 layer serves as a mesoporous scaffold to contain the perovskite crystals, as well as to prevent shorting of the device by acting as an insulating layer between carbon and mesoporous TiO_2 . Finally, carbon paste (Dyesol R&D product) was printed on top of ZrO_2 layer to complete the standard device stack. The substrates were heated at 400°C for 30 minutes to complete the device scaffold.

For each layer, different mesh counts were used due to the varying viscosity and solid content of the pastes used. For example, the carbon paste has big chunks of graphite flakes,

making it essential to use a mesh with a lower mesh count to ensure smooth printing. On the other hand, the blocking layer and mesoporous TiO_2 pastes contain low amounts of solid contents. This enables the usage of very fine mesh counts to ensure tight process controls and high resolution in printing. The mesh counts, screen tension, solid content and viscosity used for each optimized paste is described in the table below. Also, the printing speed is optimized to 50mm/s, and the printing pressure is also optimized to ~ 1.8 Bar with respect to a 2mm screen gap with a 10cm x 10cm printing area. The pressure is chosen to be as low as possible to obtain a consistent print, while reducing wear and tear to the squeegee and mesh. The optimized screen gap is essential for the lift-off process, in which the screen is lifted off the substrate surface, and the paste is transferred onto the substrate. Too small of a gap will provide insufficient tension to lift off from the surface, resulting in a poor print. A higher gap will require higher pressure from the squeegee to transfer the paste onto the substrate, as well as distorted printing due to stretching of the mesh.

Table 1 Properties of pastes and corresponding mesh

	Mesh Count	Tension	Solid content	Viscosity
Blocking Layer	100T	17N/cm	<1%	$\sim 1500\text{mPa.s}$
Meso TiO_2	180T	17N/cm	$\sim 8\%$	$\sim 2500\text{mPa.s}$
Meso ZrO_2	120T	17N/cm	$\sim 20\%$	$35\sim 50,000\text{mPa.s}$
Carbon	48T	17N/cm	$\sim 35\%$	$35\sim 50,000\text{mPa.s}$

3.2.4 Perovskite solution infiltration and ultrasonic soldering

Infiltration of perovskite solution completes the device. For this instance, a 1.2M perovskite solution is made by dissolving 553.2mg of Lead Iodide (PbI_2) and 190.8mg of Methyl Ammonium Iodide (MAI) in 1ml of Gamma Butyrolactone (GBL) and put on stirring on a 50°C hotplate until a clear yellow solution is obtained. 2.5% atomic ratio of 5-Ammonium Valeric Acid Iodide (AVAI) w.r.t to PbI_2 is added to the perovskite precursor solution to promote better crystallinity.

For each device of active area 0.7cm^2 , $3.5\mu\text{l}$ of perovskite solution is dropped from the top of the carbon cathode. Prior to the device infiltration, the device is taped using Kapton tape. The infiltrated device stack is held on a flat surface for 15 minutes, before putting onto a 50°C hot plate for a 90 min heating process to complete the device.

Ultrasonic soldering is performed on the glass to ensure good contact of the crocodile clips when performing IV measurements with the solar simulator.

3.2.4 Synthesis of HTM nanoparticles

Opto-electronic properties of NiO_x and Cu:NiO_x nanoparticles is highly dependent on the processing method employed[41-43] . A simple chemical precipitation method is used to prepare pristine NiO_x and 5% doped Cu:NiO_x nanoparticles by following the procedure described by literature, without any organic surfactants or templating agents to reduce the source of impurities[43]. 6.442 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.25 M) and $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ (0.013 M, 5 atomic % Cu) are dissolved in 50 mL of DI water to obtain a dark green solution. A stoichiometric volume of NaOH (10 M) is added slowly to the solution to adjust the pH to 10 and to allow the precipitation of the product. After 30 min of stirring, the green colloidal precipitation is allowed to settle for 1h. The obtained green precipitate is centrifuged at 12000 rpm for 10 minutes, washed thoroughly with DI water and ethanol multiple times to remove all residual impurities, followed by drying overnight at 80°C in a vacuum oven. Prior to the paste preparation, the nanoparticles are calcined at 400°C for 4h to obtain the black Cu:NiO_x nanoparticle powder.

3.2.5 Synthesis of HTM Paste

The paste for screen-printing was prepared by mixing 1g of above-mentioned nanoparticles in a 100mL mortar pot with 26.00g of ZrO_2 beads (0.33mm diameter), 0.33mL ethanol, 0.16mL acetic acid and 0.16mL DI water. The resultant slush was ball milled at 450 rpm for 6h. After grinding, the resultant slush was mixed with 66mL of ethanol and stirred for 20 min. Then, the stirring was stopped, and the suspension began to separate. After 10 min,

the supernatant colloidal solution was separated and mixed with 10.00 g ethyl cellulose and 8.00 g terpeneol. Finally, the colloidal solution was concentrated by rotary evaporator to remove the remaining ethanol, obtaining NiO_x and Cu:NiO_x paste for screen printing. The pastes contain 10% nanoparticle, 10% ethyl cellulose and 80% terpeneol by weight. The thickness of the original paste was 570 nm, which was further diluted with terpeneol in the different weight ratios (w/w paste: terpeneol, 1:7, 1:5, 1:3) followed by stirring to get different thickness.

3.3 Device Characterization techniques and rationale

3.3.1 *Field Emission Scanning Electron Microscope (FE-SEM) and Energy-dispersive X-ray Spectroscopy (EDS)*

The FE-SEM is used as the resolution of a conventional light microscope is limited by the wavelength of visible light. By using electrons which have a range of much shorter wavelength, the FE-SEM will have more resolving power and greater magnification, allowing resolutions of up to 10nm.

Firstly, the samples are put on the working stage, and the chamber undergoes a high vacuum, down to 10^{-6} torr. This is essential to enable the working of this microscope. Electrons can be easily deflected by air molecules, reducing the coherency of the electron beam which serves to resolve the details of the samples.

Electrons are generated from the filament and are accelerated through the anode. Varying voltages can be used to accelerate the electrons. Usually, atoms of higher atomic mass will require higher voltages to obtain a satisfactory image. The magnetic lenses and scanning coils help to focus the electrons into a nice coherent beam, which is directed to the specimen on the stage. The incident electron beam will have various interactions with the samples, which includes characteristic X-rays, backscattered and secondary electrons. Different detectors are used to extract information out of these different interactions. The working diagram of the SEM is shown below, alongside with the various types of sample interactions. With higher accelerating voltages, the interaction volume of the electrons with the specimen will be larger. For softer samples, this could lead to damaged samples, as the electron beams can result in localized heating.

Figure 14 Working diagram of a SEM, as well as the various interactions of electrons against the sample[44, 45]

The intensity of backscattered electrons generated by electron bombardment can be correlated to the atomic number of the element within the sampling volume. Hence, qualitative elemental information can be revealed. The FE-SEM can be used to observe the cross section of the devices, as well as the shape and morphology of the nanoparticles and films. It is also an essential tool to help understand the size of the synthesized particles. By analyzing the above information, it facilitates the optimization of the layers and particles.

One drawback about using FE-SEM is the size and stability of the sample to be analyzed. As the chamber needs to be under vacuum, the sample needs to be stable under vacuum. Some types of samples might experience outgassing. Also, the size of the sample is limited to the sample holder and is usually smaller than 1cm in length. Another common user error when using data from the FE-SEM is during the analysis of results. The imagery obtained from the FE-SEM is very localized, it might not represent the entire structure; multiple cross-sectional images would be required to verify the accuracy of the data gleaned from

the image.

Energy-dispersive X-ray spectroscopy (EDS) is an analytical technique used for the elemental analysis or chemical characterization of a sample. This is one of the modes commonly used with the FE-SEM. At rest, an atom within the sample contains ground electrons in discrete energy levels bounded to the nucleus. The electron beam may excite an electron from an inner shell, ejecting it from the shell while creating an electron hole where the electron originally was. An electron from an outer, higher energy shell then fills the hole, and the difference in energy between the higher energy shell and the lower energy shell may be released in the form of an X-ray. The amount and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element, EDS allows the elemental composition of the specimen to be measured. This allows the mapping of different elemental components in a compound, or the homogeneity of the sample mixture.

However, there are some overlap in emission peaks, and manual input is required to achieve proper analysis. Also, due to the interaction volume within the sample, the elemental mapping function can only be limited to a low resolution in the micrometer range.

The FE-SEM images and EDS map were acquired using Jeol JSM-7600F Field Emission Scanning Electron Microscope.

3.3.2 *X-Ray Diffraction*

X-ray diffraction (XRD) is a technique used to characterize and identify unknown crystalline compounds. It can also be used to determine the shape and size of the unit cell, the purity, as well as the crystallographic orientation of the sample. The X-rays are targeted towards the sample. The interaction of the incident X-rays with the sample produces constructive interference when conditions satisfy Bragg's Law.

Equation 2 Equation showing Bragg's Law

$$n\lambda = 2d \sin \theta$$

This law relates the wavelength of the X-ray to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected and analyzed.

As each material or compound has its own unique peak intensity and location, the corresponding graph can be cross matched with records to characterize the sample.

The XRD has several benefits. Using X-rays to probe the surface, this method can be considered as non-destructive. It can detect and analyze composition in mixtures and compounds. However, one of the main sources of errors can come from not putting the specimen fully flat, leading to shifting of peaks and inaccurate assessment of the sample. Also, the sample might not be fully prepped and suitable for XRD analysis. For example, if the sample is too thin, the signal might be too weak, and there will be broadening of the peaks.

The working schematics are shown in the figure below. X-rays are generated in the source by bombarding the target (in this case Copper) with electrons. Similar to EDX, electrons from the inner shell are knocked out, and a characteristic x-ray is emitted when electrons from the outer shell fills the vacant hole. The x-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected x-rays is recorded. When the geometry of the incident x-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this x-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

Figure 15 Schematic of a XRD machine[46]

Data is obtained from Bruker D8 Advance diffractometer using $\text{Cu K}\alpha$ radiation in the 2θ range of 10° to 70° .

3.3.3 *X-ray Absorption Spectroscopy*

XAS, or X-ray Absorption Spectroscopy, is a broadly used method to investigate atomic local structure as well as electronic states [47]. An x-ray strikes an atom and excites a core electron usually from the 1s or 2p shell. The electron can either be promoted to an unoccupied level or ejected from the atom. Either of these processes will create a hole. If the electron dissociates, this produces an excited ion as well as photoelectron and is studied by X-ray Photoelectron Spectroscopy (XPS).

As the excited electrons are from the inner shells, energy required to promote them to the valence band and beyond is in the order of thousands of electron volts (EVs), therefore requiring high energy x-ray excitation. Only synchrotron facilities can provide enough acceleration of the particles to provide the x-ray source. X-ray photons corresponds to wavelengths around 1 Angstrom which is on the same order of magnitude as atom-atom separation in molecular structures, so XAS is a useful tool to deduce local structure of atoms. XAS is also utilized in analysing materials based on their characteristic x-ray absorption. It is possible to deduce local atomic environments of each separate type of atom in a compound. Being a non-destructive method, it is a convenient mean to examine samples directly. Structures can be determined from samples that are both heterogeneous and amorphous.

When an x-ray strikes an atom, one of the core electrons is either excited to a higher energy unoccupied state (a transition studied by XAS) or into an unbound state, called the continuum. When electrons are ejected, this is essentially the photoelectric effect and is studied by XPS. Below is a diagram illustrating an atom absorbing an x-ray with the resultant ejection of a core electron into the continuum. Note that the level K refers to the $n=1$ level, L refers to the $n=2$ level, and M refers to the $n=3$ level.

Figure 16 Figure depicting the ejection of a core electron with an incoming x-ray

The wave vector of the electron dictates which subset of XAS will be used (XANES or EXAFS). The kinetic energy E_k and threshold energy E_0 (amount x-ray energy required to promote the electron into the continuum) of the photoelectron can be addressed, after considering the de Broglie equation:

Equation 3: de Broglie equation

$$\lambda = \frac{h}{p}$$

Where p is the momentum of the electron, λ is the wavelength, and h is Planck's constant. The wave vector of the electron is denoted as k , and can be defined as

Equation 4: Wave vector k

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h}$$

As momentum p is defined as $p = mv$, where m is the mass and v is the velocity of the electron. Kinetic energy of the electron is given by $E_k = \frac{1}{2}mv^2$, substitution gives $E_k = \frac{1}{2}\left(\frac{p^2}{m}\right)$

Further rearrangement of E_k allows the determination of the value of k through the equations below.

$$E_k = \left(\frac{h}{2\pi}\right)^2 \left(\frac{k^2}{2m}\right)$$

$$E_k = E - E_0 = h\nu - E_0$$

$$k = \sqrt{\left(\frac{2\pi}{h}\right)^2 2m(h\nu - E_0)}$$

Depending on values of k , different subsets of XAS will be used.

For example, if $0 \leq k < \frac{2}{R}$ (where R is the distance between the x-ray absorbing atom and its nearest neighbour), low-energy X-ray Absorption Near Edge Structure (XANES) will be used, respectively.

If $k > 2/R$, Extended X-ray Absorption Fine Structure (EXAFS) is used. It is apparent from the diagram below that there are three different types of excited photoelectrons upon absorption of an x-ray quantum.

The figure below depicts 3 scenarios that might occur to an inner shell electron when an x-ray is absorbed. The first part shows a photoelectron transiting to an unoccupied valence state, as it does not have enough energy to completely leave the atom. The second type of photoelectron has just enough kinetic energy to be able to escape into the continuum. Multiple scattering processes occur here, between multiple surrounding atoms that neighbour the absorbing atom. The third type and last type of photoelectron has a very high kinetic energy, and weak backscattering occurs in a single scattering process between only one neighbour atom.

Three Parts in a X-ray Absorption Spectrum
depending on the kinetic energy of the photoelectron

Figure 17 Figure showing the different types of photoelectrons and the corresponding characterization techniques

3.3.4 *Electrochemical Impedance Spectroscopy (EIS)*

EIS is a perturbative characterization of the dynamics of an electrochemical process to an applied potential. It is a useful tool for unraveling complex non-linear processes [48]. Operating conditions for relevant devices such as solar cells, batteries and fuel cells are often far from equilibrium and exhibit nonlinear behavior. By applying a small sinusoidal perturbation to a system with a wide range of frequency, one can probe the linear approximation in these kinds of complex systems. The frequency dependence of this impedance can reveal underlying chemical processes.

At this point it is useful to discuss the most common ways to present EIS spectra, and how to glean useful information [49]. First is the Complex-Impedance Plane representation, or Nyquist Plot, in which the data from each frequency point is plotted by the imaginary part on the ordinate and the real part on the abscissa. It is a common convention in the electrochemistry community to plot $-Z$ Imaginary on the y-axis so the data fit into the first quadrant of a graph. Although this type of plot is valuable for identifying how many characteristic features are exhibited by a system, all frequency information is inherently lost. Another common representation is the Bode Plot, in which the impedance magnitude and phase angle are plotted against frequency. Due to the large range of values often encountered in $|Z|$ and f , they are plotted on log scales for easier examination of small values. Again, the high-frequency limit of $|Z|$ yields the values of series resistance, and the low-frequency limit yields the accumulation of series and recombination resistance

The plots are obtained using the Autolab software. Nyquist and bode plots are useful in understanding the interface at which recombination processes are taking place. This helps to pinpoint the specific part of the solar cell that needs to be improved upon. Understanding the frequency to apply to the solar cell requires thorough calculation and analysis; failing which might result in inaccurate representations of data.

3.3.5 *Photo Luminescence*

Photo luminescence is an EM radiation phenomenon due to excessive thermal radiation or incandescence in physical system [50]. In luminescent semiconductors, when the energy of incident photon is equal or beyond the energy bandgap, electrons from the valence band will be promoted into conduction band. Semiconductors generate recombination radiation when relaxing from excited state to ground state.

Absorption happens when an electron is excited to higher energy level from neutral acceptor energy level, and it can also transit to ionization donor energy level from valence band or transit to conduction band from ionization acceptor energy level. Those phenomena can explain the energy band or impurities in the semiconductor [51].

PL instrumentation inspects the optical properties of luminescent semiconductor materials and is a strong and nondestructive characterization method. By analyzing the PL signal, information on the impurities, bandgap as well as band alignment with interfaces can be understood.

3.3.6 *Time-Resolved Photo Luminescence*

Time-Resolved Photo Luminescence is a characterization technique which uses the basis of PL and represents the data as a function of time. By illuminating the semiconducting material with a suitable laser beam, and recombination radiation is emitted. The intensity of the signal is measured over time, typically over the range of nanoseconds. This technique is very useful to help determine the quality of interfaces. A well aligned energy level between two materials will result in fast quenching of the PL signal.

3.3.7 *Surface profiler*

A surface profiler is a metrology instrument for topographical characterization of a product's topmost morphology. It considers a material's primary form and variations of its surface, which are typically characterized as profile height and surface roughness. These features may contribute to a directional lay, or a pattern, which can have a distinct impact on the physical properties of the material under observation.

A surface profile uses high-precision data acquisition components to measure the surface profile of a sample. This is carried out through contact or non-contact methods. Contact surface profilers make physical contact with a material substrate using a sensitive stylus that is drawn across the sample surface. The stylus typically uses a piezoelectric sensor to measure the changes in surface profile, and the differences in signal recorded is translated to a graph on the computer screen using a suitable software.

3.3.8 *Solar Simulator*

A solar simulator is a machine that provides illumination approximating natural sunlight. The simulated sunlight follows the standard of AM1.5G, which gives a good approximation of the sunlight, allowing scientists to characterize and understand the performance of the solar cells. This is so that scientists have a common standard to fall on when discussing device efficiencies. There are two common light sources, either xenon or LED lighting. The specimen is connected to a source-meter, which can apply a range of voltage. Under the light illumination, the solar cell will produce photo-current in response to the voltage sweep. The current is registered by the source-meter and is represented graphically on the computer screen as a Current-Voltage (IV) curve. The IV curve gives important parameters of the solar cell, such as efficiency, voltage, current, as well as fill factor.

Chapter 4 Optimization of active area for upscaling

This chapter aims to understand the effects of shading on the measured PCE value, as well as to find out the optimal size of the printed solar cell for upscaling purposes. Optimization of the printed design is paramount. This chapter also showcases the process development of upscaling a single 0.7cm^2 cell to a 70cm^2 mini module.

4.1 Introduction

Perovskite solar cells have shown unprecedented gains in efficiency, increasing from 3.8% in 2009 to beyond 23%. Beyond its high performance, perovskite solar cells also promise a low-cost manufacturing due to the simple fabrication techniques utilized in its production. However, these kinds of high efficiencies are only recorded using small devices ($>0.1 \text{ cm}^2$) and are fabricated using methods with high material wastage. The active area is usually defined by the area of the evaporated contact, and the size of mask used is slightly smaller than that of the metal contact. In this section, fabrication of perovskite solar cells is carried out using a screen-printing method coupled with perovskite infiltration process. However, for fully printable solar cells with carbon contacts, the active area is usually much bigger at 1 cm^2 . When using a small metal mask to define the active area, this inevitably introduces inaccuracies in measured PCE. Usually, larger solar cells tend to contain more defects, and have lower PCE values. These discrepancies will be further exaggerated when scaling up of the solar cell. Hence, optimization of the printed design is paramount. This chapter aims to understand the effect of shading on printed cells, as well as to optimize the cell design for scale up. In this section, a fully printable monolithic perovskite mini module of 70 cm^2 active area was fabricated with 10.74% efficiency. The highly scalable and efficient nature of the printed large area perovskite solar cells presented here, combined with the low processing costs, could pave the way to perovskite solar cell commercialization.

4.2 Effect of active area and shading

To understand the effect of active area on the PCE values obtained, devices of varying sizes were printed on a substrate. Initial characterization studies include FE-SEM imagery and thickness measurement using a surface profiler. The printed substrate is designed using AutoCAD. The cross-section design is shown in the figure below. The compact TiO_2 layer serving as the blocking layer is defined by the area demarcated by the blue rectangles, while the white rectangles represent the ZrO_2 scaffold layer. The ZrO_2 scaffold layer covers the mesoporous TiO_2 layer (in green) completely to prevent direct contact with the carbon. The overlapping red rectangle represents carbon, which defines the active area as well as serving as a contact across the etch line, defined by the white line break in the FTO (highlighted in yellow).

Figure 18 AutoCad design of the substrate, and cross section schematics of the printed solar cell.

The SEM imagery of the printed device is shown below, showing the cross section of the device.

Figure 19 Cross section imagery of the printed solar cell

The thickness profile of the mesoporous TiO_2 and ZrO_2 layers are measured using the surface profiler and shown in the graph below. The thickness of TiO_2 obtained is around 400nm, while the thickness of ZrO_2 is around 1.5 μm after the initial “hump” from the edge of the print. Figure 20 below shows how the stylus tip moves in relative to the printed layers, and the resulting graph shows the thickness of the respective printed films.

Figure 20 Schematic showing how the surface profiler attains the data

Figure 21 Profile thickness information from the printed layers

The results of the effect of active area size on the PCE obtained are summarized in the graphs below. The cells in this section are of a square design, with the same length and width. The numbers reported are obtained without any optical masking.

Figure 22 Measured V_{oc} of the devices of varying printed active area

Figure 23 Measured J_{sc} of the devices of varying printed active area

Figure 24 Measured FF of the devices of varying printed active area

Figure 25 Measured PCE of the devices of varying printed active area

As it can be seen from the tables above, 0.36cm^2 and 0.25cm^2 offered the best performance as compared to the other sizes. The main contributing factor is the higher FF of the solar cell. When the width of the solar cell decreases from 1cm to 5mm, there is a gradual increment in FF. This could be due to reduced recombination as there is less resistance due to width reduction. This phenomenon is especially prevalent in fully printed devices, as the carbon electrode is much less conductive than the gold electrode used. The increase in width adds significant series resistance to the solar cell, resulting in a decrease in FF. However, when the width goes below 4mm, a drop in V_{oc} and FF is observed. This might

be due to improper charge collection due to edge effect of the printing, leading to improper charge extraction due to non-uniform thickness control. This situation is exacerbated with smaller active areas. This is evidenced by the surface profile-meter, which shows the profile of the printed film. In the figure below showing the profile of the printed film, there is a large hump at the edge of the print which gradually smoothens out to the center of the print.

Figure 26 Surface profiler data showing the non-uniformity in print

This non-uniformity extends up to 500um into each side, affecting a much larger proportion of the active area of the smaller device as compared to larger devices and could be the reason of the relatively poorer efficiencies due to increased recombination due to non-uniformity. This leads to the reduced V_{oc} and FF.

To elucidate the differences in performances obtained by masking, another experiment was done on a 0.7cm^2 (7mm width, 10mm length) device. Optical masks of differing sizes were applied on the device, and the IV measurements were taken on various active areas. The results are tabulated in the table and figures below.

Figure 27 Figure showing the IV characteristic of the samples, as well as summarized PCE

With masking, we can observe two distinct points that is different from the results obtained without masking in the earlier figures above. 1) Reduced V_{oc} . 2) Increased FF.

With increasing masking area (smaller active area), there is a slight decrease in V_{oc} of around 0.03V, from 0.96V to 0.93V. J_{sc} remains similar, while FF shows a big increment. The significant increment in FF outweighs the slight decrease in V_{oc} , leading to an improvement in PCE values. This trend is similar to what Seigo et al reported in their paper[32]. The reduced V_{oc} is due to increased recombination and quenching at the non-illuminated areas. The increased FF is due to the reduced interfacial recombination, which is significant in the mesoporous device structure.

From the results above, it is clear having a combination of significantly larger active area, and using a small optical mask leads to exaggerated and erroneous PCE. This is a worrying sign as there will be discrepancies during the scaling of this technology, as modules are usually measured using the aperture area instead of the active area defined by the mask. There are many journal articles showing high efficiencies with an optically masked area

that is much smaller than the actual active area of the printed perovskite device, leading to exaggerated PCE values being reported[52-55].

As such, it might be more relevant to take the results from devices without masking to set the baseline parameters to achieve when scaling up these kind of perovskite solar cells. The experiment above shows that without masking, a device width of between 5 to 7mm would be optimal. The next step would be to use the finding and scale up the optimized devices to make it suitable for fabrication of perovskite modules. The though process, and the effect of elongating the device length will be investigated in the section below.

4.2 Scaling up: Electrical designs and printing considerations

The aim is to develop a 10cm x 10cm module and show reproducibility and scalability of the underlying screen-printing technology for printing of perovskite solar cells, which will in turn serve as the foundation for future scale up works

A systematic scale up study must be done; in which the following steps are taken:

- 1) Evaluation of long strip design
- 2) Evaluation of 4 strip module
- 3) Establishment of 10cm x 10cm module
- 4) Further upscaling similar methodology, but with bigger screens and equipment

A width of 7mm per strip was chosen to form the basis of the study, in which the cells (strips) are connected in a series circuit design for the module due to the following limitations/considerations established.

A series connection is preferred due to the need to reduce power loss. The FTO glass substrate has relatively low conductivity. This limits the module design to be of a series design instead of a parallel design. A series module design allows high voltages while keeping the current flow low, which is critical in reducing energy loss as heat when transmitting along the FTO substrate. Also, higher voltages will be more suitable for real-world application usage. Examples will be direct powering of small devices requiring 5 to 12v, in which the mini modules can be customized to provide the necessary voltages. Grid applications can be made towards parallel design, making it easier to mitigate the impact of shading on voltage input into the inverter.

Keeping in mind the above-mentioned design limitation, the next priority is to get an optimized width for each cell. From the results of the previous section, it seems that a cell of 5mm to 7mm seems to be the best option. Furthermore, simulation data literature [33] has also shown that the optimal width is shown to be between 5 to 8mm.

4.2.1 Evaluation of long strip design

As such, 7mm (width) by 90mm (length) design is implemented to investigate the effect of elongation of the device. As compared to 5mm width, a cell with 7mm width will have less dead area (interconnect width is taken to be 2mm regardless of 5mm or 7mm cell width) when connecting cells in series manner in a module. This will allow more efficient use of the glass substrate as less space is wasted. In theory, the device should achieve similar efficiencies obtained to that of the small devices, as the distance travel by the charge is similar. The design of the long strip is as shown in the figure below.

Figure 28 Image of the printed solar cell with long length

This solar cell with long length is also fabricated using the same facile screen-printing method, just with a different screen design. For this design, 25l of perovskite solution is required for proper loading of the perovskite crystals in the mesoporous scaffold. The IV curve of the champion device is shown in the figure below.

Figure 29 IV curve of the 6.3cm² champion device

4.2.2 4 Strip mini module design and results

Following which, a mini module was fabricated using the same width, but with a 100mm length. The mini module consists of 4 long strips connected in a series. The area of the module is 28cm^2 (4 strips x 7mm x 100mm). In a series design, current matching is of outmost importance, as the shown by the equations below, where N is the number of cells in series; M is the number of cells in parallel. The cell with the lowest current will limit the current output of the module.

Equation 5 Equation showing how the module parameters are affected by the module configuration [2]

$$I_{SC}(total) = I_{SC}(cell) \times M$$

$$I_{MP}(total) = I_{MP}(cell) \times M$$

$$V_{OC}(total) = V_{OC}(cell) \times N$$

$$V_{MP}(total) = V_{MP}(cell) \times N$$

In this design, 25ul of perovskite solution for each strip is required to achieve proper infiltration. Figure below shows the designs of the mini module, while the table further below shows the reproducibility of PCE values obtained by the devices. The schematic below shows 4 cells connected in series, with a 4mm intercell spacing between the TiO_2 strips. The carbon counter electrode goes 1 to 2mm beyond the etch line and connects with the FTO anode of the adjacent cell. This safety distance can be minimized to reduce dead area in future designs, as improved understand of the paste rheology is expected from this experiment.

Figure 30 Cross section schematic of the 4 strip mini module

Figure 31 Pictures of fabricated mini modules

Table 2 Statistical analysis of the ten (10) 28cm² mini modules

	Voc (V)	Jsc (mA/cm ²)	Pmax (mW)	Fill Factor (%)	Efficiency (%)
Average	3.49	20.31	288.18	52.57	9.3
Std Dev	0.14	1.56	29.07	3.24	0.94
Maxima	3.75	22.82	345.24	57.27	11.14
Minima	2.94	16.03	219.28	43.64	7.07

The results above show good encouragement for upscaling of perovskite solar cells using a facile screen-printing approach. The results show reasonable reproducibility for 10 modules; an average of more than 9% PCE is measured on the active area. The main drop in performance is due to the decreased FF, which can be attributed to two reasons, which is described in the next page.

Firstly, there is increased recombination due to increased area as well as possible non-uniform printing due to edge-to-edge printing. Edge-to-edge print is described in the figure below.

Figure 32 a) Normal printing b) edge-to-edge printing c) example of edge-to-edge print on module

Figure 28a) describes how a typical small cell is printed with respect to the glass. Figure 28b) shows the improper way of screen-printing, or edge-to-edge printing, in which the printed layer extends all the way to the edge of the glass substrate, which is shown in figure 28c).

Secondly, large interconnecting gaps between each cell leading to high series resistance losses could be another factor causing low FF. In the next section where the focus is the upscaling to 11x10cm, the above-mentioned issues will be addressed; intercell gap will be reduced and the substrate is made slightly bigger to ensure uniform printing. An increase in efficiency from improved FF should be expected from the larger module.

4.3 Scale up to 11cm x 10cm mini module

The next step is to ensure the scalability of the screen-printing method of fabricating solar cells. Using information and experience from the previous experiments in the earlier sections, an up-scaled mini module on a 11cm x 10cm area is fabricated with minimal efficiency losses. A schematic of the printed device is shown with the printed layers, as well as a picture of the printed device is shown in the figure below.

Figure 33 Schematic of the 10-strip module

Figure 34 Picture of 10-strip mini module

With a greatly improved understanding of the rheological behavior of the screen printable pastes during the fabrication of the 4-strip mini module, it is possible to reduce the interconnect gaps in between the serially connected cells in the modules. The closeness in which adjacent cells can be printed are mainly determined by three factors, namely screen mesh count and thickness, paste viscosity and finally substrate wettability. With a larger mesh count, the holes are bigger, allowing more paste to pass through during the printing process. A thicker screen also allows a thicker printed layer to be deposited. When screen-printing with a low viscosity ink on a hydrophilic substrate, this could lead to spreading of the printed ink during the settling period, leading to a loss in accuracy and resolution. This ultimately leads to wider layers being printed to accommodate larger tolerances, leading to less-than-optimal prints. This is clearly illustrated in the figure below, where a thick and wide film is deposited on the substrate. [56].

Figure 35 Figure showing schematic of screen printing and the possible issues

For this application, the pastes are optimized to have a moderately high viscosity and the print is further optimized by varying the mesh count of the screen-printing mesh. This results in overlapping layers being printed to an accuracy of 200um. This results in has two positive effects: higher geometric fill factor (GFF) and improved electrical performances. A higher GFF means a larger active area within the same given substrate size, resulting in larger active areas and subsequently improving electrical output. This is especially critical when translating this technology to the competitive market, where any tiny incremental

addition of power output is valuable. In this case, the advantage of using a 7mm cell width is apparent. A module employing a 5mm cell width will have a more dead area equating to wasted space on the substrate. With a higher GFF, the inter-cell distance will be smaller. As a result, less power is lost through the comparatively resistive FTO conductive layer. This reduces the series resistance, theoretically improving the FF, resulting in better device efficiencies and higher power output per given substrate area.

In the 11cm x 10cm mini module, there are 10 cells connected in a series design. The IV curve of the above-mentioned device is shown in the figure below.

Figure 36 IV curve of the 10-strip module

It was observed that the fill factor for the larger module with an active area of 70 cm^2 (10 strips x 7mm x 100mm) is higher than that of the smaller module. The 70 cm^2 module has a smaller interconnect width of 2mm (1.5mm + 0.5mm) as compared to the 4mm width of the smaller module. As the distance is reduced between interconnects, this reduces the amount of series resistance contributed by FTO, hence improving the FF of the bigger device. The close-up schematic of the design is shown in the figure below.

Figure 37 Close up schematic of the design of spacing between cells for the 10-strip module

According to the equation 5 earlier, as the module is composed of strips connected in a series fashion, the V_{oc} of the module is the sum of the individual strips added up together. The current output of the module is determined by the smallest individual current output out of the 10 strips in the module.

Table 3 Summary of the IV characteristics of the modules

	Scan Direction	V_{oc}	$J_{sc}(\text{mA}/\text{cm}^2)$	Fill Factor (%)	Efficiency (%)
70cm² module	Reverse	9.63	17.72	62.9	10.75
	Forward	9.29	17.97	60.49	10.1
28cm² module	Reverse	3.72	19.60	57.5	10.46
	Forward	3.63	19.58	57.3	10.19

A batch of six modules were made, of which three were 70cm² modules, and three were 28cm² modules. The average of each of the modules were summarized in the table above. Interestingly, the V_{oc} per cell is higher in the larger module than the smaller module, and the smaller module registered higher current densities. This could be attributed by two reasons.

Firstly, larger module has a much smaller overlap of ZrO_2 over the TiO_2 layer. During measurement no masking is used. There could be less recombination due to a smaller mesoscopic volume, resulting in higher voltages. On the other hand, the higher current density registered by the smaller module might be due to the exact same reason; the active area used in calculating the current density might be underestimated due to extra volume

of ZrO_2 , resulting in higher J_{sc} values. Secondly, the larger module has a smaller intercell distance. With a lower series resistance, the corresponding V_{oc} drop will be less. Also, this results in a higher FF in the larger module.

Nevertheless, it is not impossible to rule out the fact that there might be optimization required to properly optimize the print of the 70cm^2 module. The low current might be due to a misprint on a certain portion of the module as tolerances are much smaller, especially for the 0.25mm overlap of ZrO_2 on the right-hand side. All these suggests that there are room for further improvement.

In conclusion, this chapter reports several findings. Firstly, for fully printable solar cells, reported PCE values on journals could be overestimating the actual PCE values attainable by this architecture. The extent of the over-estimation was discussed. Following which, the width of the printable solar cell is optimized to lay the foundation for scale up work. A large single cell was fabricated, followed by systematic scale up of the printed solar cell. From a single cell, a mini module was developed with 28cm^2 active area, which finally led to the fabrication of a 70cm^2 module measuring more than 10% PCE on active area.

Chapter 5 Optimization of active area

The PCE of hole conductor free carbon-based perovskite solar cells could be limited by the non-ideal charge extraction and recombination losses at the various interfaces. This chapter aims to improve the device performance by two methods. Firstly, the concentration of Ammonium Valeric Acid Iodide (AVAI) is being optimized to improve pore filling. 2.5% is the optimized doping concentration. Secondly, the perovskite-cathode interface is being modified. The inclusion of copper doped nickel oxide (Cu:NiO_x) nanoparticle interlayer in carbon-based perovskite solar cells can enhance the device PCE. Cu:NiO_x nanoparticles are synthesized by a simple chemical precipitation method and is made into a screen-printable paste. The Cu:NiO_x is sandwiched between the ZrO₂ and carbon layer. A perovskite mini module with 70 cm² active area employing a 80nm thin Cu:NiO_x layer shows an improved PCE of 12.1%. IV scans show that the introduction of Cu:NiO_x on top of the mesoporous scaffold increases the I_{sc} and FF.

*This section is published substantially as

Cu-doped nickel oxide interface layer with nanoscale thickness for efficient and highly stable printable carbon-based perovskite solar cell. Amna Bashir, Jia Haur Lew, Sudhanshu Shuklaa et al.

Solar Energy Volume 182, April 2019, Pages 225-236

DOI: 10.1016/j.solener.2019.02.056

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5.1 Introduction

Fully printable perovskite solar device with mesoporous carbon counter electrode have shown great potential for high stability and ease of scaling up. A mesoscopic device is printed using a facile screen-printing method, and the perovskite solution is then infiltrated from the top of the device stack. The highly scalable fabrication method makes it highly desirable towards industrial fine-tuning and development. High abundance, low cost, suitable energy level and hydrophobic nature of carbon makes it an excellent candidate for printable counter electrode and hole transport material.

However, poor interfacial charge transfer could be one of the limiting factors of carbon-based devices. The poor interface could be due to lack of control during the nucleation and crystallization process of perovskite crystals, as well as improper energy level alignment. Additives are known to improve material properties. Investigation and optimization of the AVAI additive is important to realize good pore filling and device performance.

In addition, the charge carrier extraction by carbon electrode alone is not as efficient as conventional HTM. Inorganic materials such as NiO; CuI, CuO_x, CuSCN, and CuGaO₂ have been reported to be promising alternatives to their organic counterparts. NiO_x appears to be a promising candidate because of its intrinsic p-type semiconducting nature, high optical transmittance, deep-lying valence band of 5.4 eV and excellent stability to be used as an interlayer between ZrO₂ and carbon.

Despite the advantages offered by NiO_x, the performance of NiO_x-based devices is still unsatisfactory. Poor performance can be attributed to its high series resistance due to the low intrinsic conductivity of the NiO_x films. The partial doping of metals such as Copper can increase p-type conductivity, and possibly mitigate losses in FF and J_{sc}. Cu doping of NiO_x shows greatly improved electrical conductivities, improving the efficiency of planar devices. Hence it is of significance to study the theoretically positive effect of Cu:NiO_x on fully printable perovskite solar cells with carbon electrode.

5.2 Experimental Procedures

AVAI is brought from Greatcell solar materials and is used as it is. Varying concentrations of AVAI is added to the perovskite precursor solution made with GBL, as described in Chapter 3.

NiO_x and Cu:NiO_x nanoparticles and pastes are synthesized as described in Chapter 3.

The solar cell is fabricated using a facile and low-cost screen-printing method as described in Chapter 3.2. The HTM paste is printed between the ZrO₂ and carbon layer. The printed devices are infiltrated in a controlled glovebox environment with the perovskite precursor solution. The completed devices were tested using a solar simulator.

The synthesized Cu:NiO_x nanoparticles are characterized by the X-ray Absorption Spectroscopy structure (XAS) at the XAFCA beamline of Singapore Synchrotron Light Source at an energy of 8979 eV, corresponding to the Cu K-edge. All XAS measurements are collected at a ring energy of 0.7 GeV and a ring current of ca. 200 mA.

5.3 Results and Discussion

5.3.1 XRD analysis of Nanoparticles

The figure below shows the X-ray diffraction (XRD) pattern of NiO_x and Cu:NiO_x nanoparticles after heat treatment at 400 °C. All the diffraction peaks have indexed to the cubic structure of NiO_x . Both NiO and Cu:NiO_x nanoparticles exhibit similar diffraction patterns with characteristic peaks corresponding to NiO at 37.21° , 43.23° , 62.79° , 75.40° . No other diffraction peaks corresponding to any impurities are observed, suggesting successful doping of Cu^{2+} ions at Ni^{2+} lattice sites while maintaining the lattice structure. Having similar ionic radii, Ni^{2+} ions are susceptible Cu^{2+} ions replacement at the lattice sites. Reports have stated that Cu inclusion in a NiO_x structure is related to the Ni vacancy generation in certain compositional range[57, 58]. This is also noticeable increment of the relative intensity of crystalline peaks of Cu:NiO_x nanoparticles and the narrowing of full width at the half maximum (FWHM) of the peaks as compared to that of pristine NiO_x nanoparticles, suggesting improved crystallinity with little distortions to the crystal lattice, as well as larger grains. The crystallite size of NiO_x was calculated to be 12.9 nm, while a slight increase of crystallite size is observed in Cu:NiO_x , at 19.6 nm. A representation of the crystal structure of Cu:NiO_x is shown where the blue spheres, grey spheres and red spheres correspond to the Cu, Ni and O atoms, respectively.

Figure 38 Figure showing (a) the XRD spectra of the nanoparticles, and (b) the representation model of Cu:NiO_x [59]

5.3.2 SEM and EDS Imagery of Nanoparticles

The nanoparticles are analyzed using FESEM and morphological images are shown in the figure below. The SEM imagery shows that the particles are spherical. There is less observed agglomeration in pristine NiO_x nanoparticles as compared to Cu:NiO_x nanoparticles. This could be due to the Cu:NiO_x nanoparticles having higher surface energy and surface tension in comparison to NiO_x , which could increase agglomeration tendencies. Furthermore, the nanoparticles are synthesized without any ligands, which could further promote agglomeration of the nanoparticles. A typical nanoparticle size of less than 100 nm is observed in the SEM imageries.

Figure 39 SEM imagery showing (a) NiO_x nanoparticles and (b) Cu:NiO_x nanoparticles[59]

Energy-Dispersive X-ray Spectroscopy (EDS) is conducted to on the synthesized nanoparticles to confirm the composition. Copper (Cu), Nickel (Ni) and Oxygen (O) are detected, and the relative concentration of Ni, Cu and O are determined to be approximately 47.0%, 3% and 50% respectively, suggesting that the doping of Cu in NiO_x is between 5 to 6% and is in good agreement with the doping ratio of Cu in NiO_x planned in the experimental section (section 3.2.4). Elemental mapping of synthesized Cu:NiO_x is shown in figure below, showing homogenous dispersion of the various elements.

Figure 40 Figure showing the elemental mapping of Nickel, Oxygen and Copper [59]

5.3.3 XAS of Nanoparticles

The oxidation state of Cu and Ni is determined by comparing the differences in edge position and white line intensity of the X-ray Absorption Near Edge Spectrum (XANES) of the Cu:NiO_x sample and standard reference compounds.

Figure 41 XANES spectra showing 2+ oxidation state of copper in Cu:NiO_x [59]

For the XANES analysis Cu₂O (Cu⁺) and CuO (Cu²⁺) are used as standards to determine the oxidation state of Cu in Cu:NiO_x. The figure above shows the XANES for Cu:NiO_x (blue), with Cu₂O (red), CuO (black). The main peak positions of Cu:NiO_x corresponds most similarly to CuO, indicating that Cu is in the 2+ oxidation state. The ligand field splitting of the Cu 4p orbitals in Cu⁺ gives rise to additional transition around 8982eV,

which is characteristic of Cu^+ compounds. This peak becomes less pronounced as it shifts from Cu^+ to Cu^{2+} , which is additional proof that the Cu in Cu:NiO_x is in 2+ oxidation state as there is no visible second peak around 8982eV.

Figure 42 XANES spectra showing oxidation state of Ni in Cu:NiO_x [59]

Figure 43 above shows the XANES spectra for Cu:NiO_x (red), NiO_x (blue) and NiO (black). NiO (Ni^{2+}) is used as a reference for finding the oxidation states of Ni in NiO_x and Cu:NiO_x . The XANES spectra show that the main peak energy of Cu:NiO_x is mostly similar to NiO , suggesting that Ni in Cu:NiO_x has oxidation state of 2+. While for NiO_x , there is a little shift in the peak position toward higher energy. It is possible that the average oxidation state of Ni in NiO_x is higher than 2+. The edge positions of Cu:NiO_x are closer to NiO , suggesting the majority of Ni in an oxidation state of 2+ with a small percentage of the Ni possibly in the 3+ oxidation state.

Figure 43 Figure showing 1st shell analysis of Cu:NiO_x [59]

A first shell analysis of the Cu:NiO_x is performed to determine the bond length changes in NiO that could result from the insertion of Cu into the NiO_x matrix. The data were processed with a k-weight of 2 and k-range of 3.5–9.1 Å.

The oxidation states of Cu and Ni are determined mostly to be at 2+. Extended X-ray Absorption Fine Structure (EXAFS) fitting is first done with CuO and NiO standards to find the ratio of CuO and NiO_x in the sample. Theoretically during the nanoparticle synthesis process, around 5% of Cu should be doped into NiO_x matrix. EXAFS analysis indicates the presence of around 5.4% Cu in the sample, which is within the experimental uncertainty limit. The Cu-O bond length is typically in the range of 1.88–1.96 Å while the Ni-O bond length is approximately 2.07 Å. Table 3 below shows the bond lengths obtained from the first shell analysis of Cu:NiO_x with respect to the crystallographic file extracted from the DFT calculations.

Table 4 Table showing bond lengths of the various compounds [59]

Bond	Coordination Number	Ref (Å)	R(Å)
Cu-O1	2	2.081	1.825
Cu-O2	4	2.227	1.78
Ni-O1	2	1.991	1.906
Ni-O2	2	2.081	1.996
Ni-O3	2	2.134	2.089

For both Cu and Ni, bond lengths are found to be decreased as compared to the reference values. Ni atom is found to be coordinated to 6 oxygen atoms with bond lengths ranging from 1.91 to 2.09 Å, which is in the range of previously reported Ni-O bond lengths. Cu atom is found to be at a symmetric coordination with 4 planar and 2 axially coordinated oxygen atoms. It is well known that the Jahn–Teller (JT) effect is responsible for the distortion of CuO₆ octahedra, which results in a compressed Cu²⁺ octahedral structure and there is a possibility of the same JT effect resulting in the shortening of the Ni-O bonds as well.

5.4 Characterization of Pastes

The nanoparticle films are characterized to understand the effect of Cu^{2+} doping on the electrical and optical properties, as well as morphological changes of NiO_x nanoparticles after during the paste preparation and thermal annealing processes. The respective nanoparticles are mixed with terpineol and ethyl cellulose to prepare a paste for screen-printing on the glass substrate.

5.4.1 FESEM & Four Point Probe

The top morphology FESEM image of the screen-printed films on a glass substrate are shown in the figure below. The insets are of the respective photos of the printed films. The FESEM imagery showed mesoporous morphology with agglomerated spherical nanoparticles. The porous structure is essential for perovskite solution infiltration. Without the right porosity, there will be poor crystallization within the scaffold. It is evident from figure below that there is an increased agglomeration with the addition of Cu into NiO_x .

Figure 44 FESEM imagery of (a) NiO_x , and (b) Cu:NiO_x morphology [59]

To understand the effect of Cu^{2+} doping on the electrical conductivity of NiO_x , pristine NiO_x and Cu:NiO_x films are printed on glass, and the sheet resistance of the $\sim 400\text{nm}$ films are measured using a four-point probe. The results are shown in table 5 below. For comparison, the sheet resistance and conductivity of carbon is also included in the table.

Table 5 Electrical properties of various films on glass substrate [59]

Sample	Sheet Resistance Ω/cm^2	Conductivity S/cm
NiO _x /glass	1.0×10^6	2.0×10^{-3}
Cu:NiO _x /glass	1.0×10^3	0.2
Carbon/glass	10.15	0.76

The sheet resistance is reduced significantly when 5% of Cu introduced into NiO_x. Reduction in sheet resistance of NiO_x is mainly due to the increase of carrier concentration with Cu doping. The p-type conductivity of NiO_x could be ascribed to the excess oxygen within the lattice site that creates vacancies in the normally occupied Ni sites. To preserve overall electrical neutrality, two Ni²⁺ ions will be converted to Ni³⁺ for every Ni vacancy site. As Ni³⁺ ion is unstable, it will change from one Ni²⁺ site to another. The mechanism makes it like as though positive holes are moving. The Ni³⁺ site acts as impurity level above the filled band and the excitation of electrons to these sites leaves mobile holes in the band. It is reported in literature that the substitutional doping of the material with an appropriate dopant is an effective method to increase the conductivity of p-type metal oxides by introducing more defects, resulting in increased amount of Ni³⁺ [60, 61]. It is highly possible that the dopant Cu on Ni site increases the concentration of hole thus enhancing the film conductivity.

5.4.2 Photoluminescence (PL) and Time-Resolved Photoluminescence (TRPL)

To investigate the charge separation efficiency of NiO_x and Cu:NiO_x films, steady state photoluminescence (PL) and time-resolved PL (TRPL) studies are used to probe the perovskite films and various interfaces. ZrO₂ infiltrated with perovskite is used as reference for the study as its valence band is not suitable for hole injection. The band alignment of the functional layers of the printed solar cell is shown in the figure below.

Figure 45 band alignment of the functional layers of the printed solar cell

PL intensity is the strongest with perovskite and ZrO₂, as there is no quenching of PL signals due to mismatch of energy levels. When carbon is added onto ZrO₂, followed by perovskite infiltration, there is significant quenching of the PL intensity. Maximum PL quenching is observed when Cu:NiO_x interlayer is printed between ZrO₂ and carbon.

Figure 46 Figure showing the PL intensity of perovskite with various interfaces [59]

TRPL measurement was performed with excitation wavelength source of 400 nm and detection on all the emission bands. The decay curve is fitted with bi-exponential decay function. The PL decay of infiltrated ZrO_2 film exhibits a time constant of 8.4 ns whereas, for ZrO_2/C , $\text{ZrO}_2/\text{NiO}_x/\text{C}$ and $\text{ZrO}_2/\text{Cu:NiO}_x/\text{C}$ are 5.4, 4.2 and 2.09 ns, respectively. PL and TRPL results confirm the increased quenching in the film. This suggests that there could be improved charge transfer, and possibly improving device performance from the inclusion of a thin Cu:NiO_x interlayer.

Figure 47 Figure showing the time resolved signal decay of perovskite with various interfaces [59]

5.5 Device optimization and results

5.5.1 Results for optimized AVAI concentration

The effect of AVAI concentration on the infiltration within the mesoscopic scaffold is investigated thoroughly. AVAI is widely known in the community to form 2D perovskites when mixed in small amounts into the perovskite precursor solution [38]. The fully printed devices are infiltrated with perovskite solution from the top. The solar cells are tested using solar simulation and subsequently broken to perform SEM analysis. The figure below shows the FESEM imagery of the device cross sections infiltrated with perovskite solution containing varying concentrations of AVAI.

Figure 48 SEM imagery of device cross section containing varying amounts of AVAI

From the figure, AVAI is shown to be beneficial for the infiltration of the mesoscopic device. When there is no AVAI (shown as 0:40) in the perovskite precursor solution, poor infiltration can be observed as shown in the yellow box. Low infiltration results in poor interfacial contact. It is usually the main attributing factor to comparatively lower PCE values and is a unique problem pertaining this type of perovskite solar cell architecture.

When the concentration of AVAI is increased gradually from 2.5% to 7.5% (shown as 1:40 to 3:40 respectively), much improved pore filling can be observed. Having better infiltration is paramount to improved efficiencies. Along with better contact with the electron transport layer (TiO_2 layer), there should be improved charged transport from the perovskite crystals to the FTO anode. Devices made with varying concentrations of AVAI additive were characterized using the solar simulator. The results are summarized in the figure below.

Figure 49 Results showing effect of AVAI concentration of IV parameters

The results summarized above are of the average of 4 samples for each concentration of AVAI. Without AVAI, the resulting device has poor photovoltaic performances, which is within expectation. The device has poor J_{sc} , which could be linked to the increased defect centers and grain boundaries associated with the poor infiltration of the scaffold.

Even with 1:40 (2.5%) ratio of AVAI added, there is a much-improved pore filling. This is reflected in the PCE of the devices. The main improvement comes from the increased J_{sc} , from less than $5\text{mA}/\text{cm}^2$ to values exceeding $20\text{mA}/\text{cm}^2$, as evidenced by the top right. There is also a marked improvement in FF and V_{oc} of around 30% improvement compared to the one without AVAI. When the ratio of AVAI is increased to 3:40, there is a decrease in PCE values, mainly due to decreased FF. There is also a decrease in V_{oc} and J_{sc} , presumably due to the decrease in conductivity of the film due to increased amount of 2D perovskite, as well as presence of non-conductive alkyl chains of AVAI at the grain boundaries inhibiting charge transfer.

It can be concluded that AVAI improves material pore-filling and subsequently, better device performance. An excess of AVAI (>5% or 2:40 ratio) however is linked to favor the formation of an increasingly 2D variant of the 2D/3D $(\text{AVAI})_x(\text{MA})_{1-x}\text{PbI}_3$ system [38, 62, 63], which exhibits limited charge carrier transport in the mesoscopic device architecture, causing detrimental effect to device performances. Moving forward, the optimized concentration of AVAI to be used for future research is determined to be at 2.5%

5.5.2 Results for optimized Cu:NiO_x interlayer

The device performance is optimized by varying the thickness of Cu:NiO_x and ZrO₂. The thickness of the printed ZrO₂ and Cu:NiO_x layers are varied by diluting the original paste with terpineol. The pastes have a thickness of 1.4μm and 570nm respectively prior dilution. Results of the champion devices with varying thicknesses of Cu:NiO_x and ZrO₂ are shown in the tables below. The initial step is to maintain the same device scaffold thickness. As such, the ZrO₂ thickness is slightly reduced. It is evident that when a moderately thick Cu:NiO_x of 150nm coupled with a thick layer of ZrO₂ (1.3μm) gives dismal results. The device has low fill factor. This might be due to the high series resistance, or that the charged could not be extracted efficiently due to an overly thick scaffold. An possible reasoning is the poor infiltration due to insufficient porosity of the Cu:NiO_x layer.

Table 6 IV parameters of the perovskite devices employing different Cu:NiO_x thickness[59]

Cu:NiO _x (nm)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)	Rsh(ohm)
50	0.9	22.18	0.53	10.59	903.32
80	0.98	22.65	0.57	12.65	1051.28
100	0.95	21.09	0.46	9.14	735.19
150	0.93	16.05	0.44	6.53	587.74

Devices with ~80nm thick Cu:NiO_x and 1.3μm thick ZrO₂ showed improved performance with the high fill FF and V_{oc}. It is clear that a ~80 nm thick layer of Cu:NiO_x gives the best performance, while thinner or thicker Cu:NiO_x films yield inferior device PCE. The variation in FF, J_{sc}, V_{oc} and PCE with different thicknesses of Cu:NiO_x for 8 devices are summarized in the figure below. From the statistics, it is clear that 80nm thick Cu:NiO_x offers the optimal balance in photovoltaic performances.

Figure 50 Figure showing the statistics of the devices with varying Cu:NiO_x thickness [59]

The next step is to understand the effect of changing the thickness of ZrO₂ interlayer. The ZrO₂ thickness is varied while the Cu:NiO_x interlayer thickness is maintained at 80nm. The results are summarized in the table below.

Table 7 IV parameters of the perovskite devices employing different ZrO₂ thickness[59]

ZrO ₂ (nm)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)	Rsh(ohm)
1300	0.98	22.65	0.57	12.65	1043.59
1000	0.88	23.29	0.45	9.33	493.50
800	0.85	17.38	0.47	6.98	235.16
500	0.79	14.84	0.44	6.44	189.22

It is evident that a thicker ZrO_2 is essential for a high performing device. The most logical explanation for enhanced device performance is due to the following explanation. Firstly, the ZrO_2 increases the loading of perovskite crystals. This in turn helps in increasing the absorbing the light more efficiently, generating a higher J_{sc} . Also, the insulating ZrO_2 helps to reduce pathways in which current can leak through.

The figure below shows the cross-sectional FESEM imagery of the perovskite solar cell with Cu:NiO_x film.

Figure 51 (a) FESEM cross sectional imagery of the device, (b) with higher magnification and color coding [59]

The PCE values are higher for samples with Cu:NiO_x interlayer as compared to devices with and without (only with carbon counter electrode) additional NiO_x interlayer. The best device performance with Cu:NiO_x interlayer yields a high V_{oc} of 1.00V, J_{sc} of 22.15 mA/cm^2 and FF of 0.57, giving an improved PCE of 12.79%. The corresponding IV parameters for perovskite solar cells are summarized in the table below. The enhanced performance could be due to the deep lying valence band of Cu:NiO_x (-5.4 eV)[24, 64] forming a better ohmic contact with the perovskite layer, resulting in a large potential difference between the hole and electron transport layers and less potential losses at HTL/perovskite interface. The energy band alignment is shown in the figure in the next page.

Table 8 Summary of effect of interlayer on device performance [59]

	PCE (%)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)
C/(Best)	9.21	0.89	21.13	49.0
Average	9.16±0.49	0.89±0.01	20.92±1.05	49.0±1.9
C/NiO_x(Best)	10.49	0.95	22.09	51.0
Average	10.16±0.18	0.92±0.03	22.20±1.27	49.1±1.2
C/Cu:NiO_x(Best)	12.79	1.00	22.15	57.0
Average	12.04±0.38	0.98±0.01	22.85±0.62	53.2±2.2

Figure 52 Band alignment of the printed solar cell with Cu:NiO_x

IV curves obtained with scan rate of 0.3V/s for devices with the various configurations are shown in figure below. The results showed high reproducibility with an average PCE of 12.04%±0.4 for devices with Cu:NiO_x interlayer. The IV curve below shows the scan direction dependency hysteresis of the devices, and devices with Cu:NiO_x interlayer showing negligible hysteresis with the best PCE values.

Figure 53 IV curves of different configurations, as well as front and back scans [59]

To further investigate the scan-rate dependency effect on the hysteresis, varying scan rates were chosen to apply to the solar cell during characterization. The perovskite solar cell with Cu:NiO_x interlayer exhibits nearly hysteresis-free performance at slow scan rates (0.15 V/s and 0.05 V/s). The data is shown in the figure and table below.

Figure 54 Figure showing the effect of scanning speed and direction on device PCE [59]

Table 9 Table summarizing the effect of scanning speed and direction on device PCE [59]

Scan rate (V/s)		0.15		0.05
	Forward	Reverse	Forward	Reverse
Voc (V)	1.01	0.98	1.00	0.99
Jsc (mA/cm ²)	23.44	22.65	22.86	23.73
FF	0.51	0.56	0.49	0.51
PCE (%)	12.07	12.43	11.84	12.10

The incident photon-to-electric current conversion efficiency (IPCE) spectra are shown in figure below. IPCE measurement uses monochromatic light without applying a white-light bias. The integrated J_{sc} from IPCE spectra for devices with NiO_x , $Cu:NiO_x$ and without HTLs was 18.77mA/cm^2 , 19.84mA/cm^2 , and 18.01mA/cm^2 respectively. The integrated J_{sc} from IPCE measurements shows slightly lower value as compared to previously reported IV measurements (table 7 above). The lower J_{sc} from IPCE measurement than from the IV scan was probably due to the dependence of J_{sc} on light intensity, which derived from the trap state in electron transport layer. As IPCE spectra were measured under monochromatic light without bias light, it could result in lower carrier density and a lower trap state filling level when compared to the ones measured in the IV under one sun illumination, leading to more charge recombination and less charge extraction.

Figure 55 Effect of interlayer on IPCE spectra [59]

After achieving an improved PCE with the introduction of Cu:NiO_x on printed perovskite solar cells of 0.7cm² active area, a perovskite mini module with 70cm² active area was fabricated using the same semi-automated screen-printing process. The IV parameters of the perovskite mini module are shown and summarized in the figure and table below. IV measurements are performed under standard reporting conditions (AM 1.5G) without any encapsulation. The champion module recorded an efficiency of 12.10%, with improved V_{oc} , J_{sc} and FF.

Table 10 Effect of Cu:NiO_x on perovskite mini module performance [59]

	Without Cu:NiO _x		With Cu:NiO _x	
	Reverse	Forward	Reverse	Forward
V_{oc} (V)	8.87	8.2	9.57	9.42
I_{sc} (mA)	149.3	136.5	153.2	151
FF (%)	0.51	0.54	0.59	0.58
PCE (%)	9.75	8.75	12.1	11.9

Figure 56 IV curve and picture of perovskite mini module [59]

Finally, the effect of Cu concentration is studied by fabricating the perovskite solar cell devices with various levels of Cu doping in the Cu:NiO_x interlayer. A decreased PCE is observed with 10% Cu:NiO_x. The main decrease in PCE performance is due to reduction in FF and V_{oc}. Further investigation is required to find out the exact reason behind the reduction; whether is it due to electrical properties of the Cu:NiO_x film or is it due to physical surface changes affecting the crystallization of perovskite and subsequently affecting device performance.

Table 11 Table showing tabulated results of varying Cu doping on device performance. [59]

	PCE (%)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF
C/3% Cu:NiO _x (Best)	11.07	0.98	22.28	51.0
Average	10.36±0.54	0.95±0.01	22.41±0.63	48.71±2.2
C/5% Cu:NiO _x (Best)	12.79	1.00	22.15	57.0
Average	12.04±0.38	0.98±0.01	22.85±0.62	53±2.2
C/10% Cu:NiO _x (Best)	10.16	0.95	23.5	47.0
Average	9.74±0.36	0.95±0.02	22.09±0.86	46.53±1.07

Chapter 6 Encapsulation and laser ablation processes

This chapter describes and showcases the various processes developed to enable scaling up of printable perovskite solar cells towards commercial scale. Firstly, improvements made to the stability aspect of the printable solar cells are examined. Extensive shortlisting and optimization of encapsulation techniques are examined and tested. Efforts were made to translate P1P2P3 thin film etching process to enhance the geometric fill factor (the ratio of printed active area vs the substrate area) of modules made with varying processing techniques. Geometric fill factor exceeding 90% has been achieved for thin film designs, while fully printable carbon modules have results of up to 85%. The optimized parameters realized a perovskite mini module recording PCE values exceeding 18% on 6.4cm².

*This section includes data from

Design of Perovskite Thermally Co-Evaporated Highly Efficient Mini-Modules with High Geometrical Fill Factors.

Jia Li, Herlina Arianita Dewi, Hao Wang, Jia Haur Lew et al.

Solar RRL, volume 4, issue 12, October 2020, Pages 2000473

DOI: 10.1002/solr.202000473

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6.1 Introduction

For perovskite solar cell technology to be viable, the scientific community will need to address the stability and scalability concerns of perovskite solar cells. The stability aspect of perovskite solar cells encompasses of two areas: intrinsic and extrinsic stability. The perovskite absorber layer is highly hygroscopic and degrades upon interaction with moisture. Apart from using more intrinsically stable MA-free perovskite, as well as employing the fully printable carbon architecture, physical encapsulation is proving to be critical to ensure the long-term stability of the solar cell in real world operating conditions.

Two levels of encapsulation were investigated and optimized. In the 1st level of encapsulation, a polymer was chosen and dissolved in suitable solvent, and the resulting mixture is sprayed onto the fully printed solar cell to serve as a soft encapsulation. This helps to protect the solar cell from moisture ingress and acts as a buffer layer for the next level of encapsulation. The next layer of encapsulation is a glass-glass lamination technique which is well-established technique in the photovoltaic industry. This allows for a rapid translating of established methods with minimal associated cost and time, which is a critical step in the push of perovskite solar cells towards commercialization.

For the commercialization of perovskite solar cells, ensuring the scalability and efficiency of large area perovskite solar cells is paramount. The geometric design of the module plays a pivotal role in ensuring the minimal losses in active area as well as efficiency. The laser etching process is highly facile and scalable and is commonly used in the thin film industry. The challenges associated with this etching process is the balance between complete removal of the material and damage to the underlying substrate. The laser etching process is described and optimized for thin film-based perovskite system.

Findings from this chapter can prove to be vital in pushing this exciting photovoltaic breakthrough into commercial status.

6.2 Experimental Section

For spray-on encapsulation, various polymers were shortlisted alongside with a suitable solvent. The polymers were dissolved in the solvent in varying concentration, and the mixture were deposited on a perovskite film using a spray-deposition method. The coated films were left in a petri dish filled with water to evaluate their encapsulation.

Following which, parameters for the laminating machine was optimized. The laminated films were further sealed with edge sealing, and then put in water to test the encapsulation.

For the laser etching process, a 50W 1064nm YAG laser is used to perform the P1P2P3 laser etching. The P1 etching was designed to separate the underlying FTO layer into strips that are designated as the cell width, and the complete separation is validated by a simple multi-meter test. The P2 etching is used to separate the perovskite layer into the separate cells, and the process was optimized using a SEM. Finally, P3 etching used to remove the gold contact from shorting the entire cell and was validated using a digital microscope.

6.3 Results and Discussion

6.3.1 Spray Encapsulation Optimization

Figure 57 Schematic of the proposed encapsulation

The figure above shows the schematic depicting the different levels of encapsulation to ensure that the perovskite film does not undergo degradation.

In this experiment, the shortlisted polymers are as following:

- 1) Poly methyl methacrylate (PMMA)
- 2) Polyethylene-covinyl acetate (EVA)
- 3) Poly styrene (PS)
- 4) Poly vinyl butyral (PVB)

The first step of the experiment is to determine the maximum amount of polymer that can be dissolved in the solvent. The highest concentration of solution obtained is 30mg/ml at room temperature, which will be the standard concentration used in this experiment.

The solvent used is toluene. The molecular structures of the above-mentioned molecules and solvent are shown in the figure below.

Figure 58 Molecular structures of shortlisted polymers: a) PMMA, b) EVA, c) PS, d) PVB; and the molecular structure of the solvent e) toluene.

After which, a thin perovskite film is deposited on the glass with a spin coating approach. Following which, a polymer blend with a suitable solvent is sprayed using a pressurized air gun, with the sample on a heated hotplate. The picture below shows the setup in a fume-hood. The air gun setup is connected to a clean dry air source. The air pressure is set to ~85psi for proper atomization of the solution to ensure uniform and smooth coverage of the resulting polymer film, and 30 passes are coated onto the perovskite film. The hotplate temperature is set around 50 degrees to allow fast evaporation of the solvent so that there is minimal interaction and degradation of the perovskite device.

Figure 59 Picture showing the air gun and hotplate setup in a fume-hood

After coating the films with the polymer, a moisture ingress test is done to evaluate the effectiveness of the polymer spray encapsulation. The samples, alongside a pristine perovskite film, was immersed in a petri dish with water. Photographs are taken at set timing to record visual changes to the film.

A drastic change from black color to yellow color is observed for the pristine film without any polymer coating upon immersion. For the rest of the polymer coated films, PMMA seemed to show the least moisture ingress amongst the polymer coated films. PS and PVB coated films showed signs of degradation after 3 minutes of immersion, suggesting that the polymer coating was not robust enough to prevent moisture ingress.

Figure 60 Picture showing the difference in encapsulation strength of various polymers

After this moisture ingress test, new samples were prepared for the heating test. The heat test encompasses of putting the samples in a heated oven at 85°C for 1000h. The objective of this experiment is to evaluate the stability of the polymer layer under elevated temperatures, and establish the minimum encapsulation required for enough protection of the film.

Similar to that of the earlier moisture ingress test, PMMA shows the greatest protection, followed by EVA, PS, then PVB.

6.3.2 Laminating Encapsulation Optimization

The stringent encapsulation requirement for perovskite solar cells to maintain their efficiency mandates the use of a hermetic glass–glass encapsulation to minimize ingress of moisture and oxygen. This type of lamination involves the curing of a polymer laminating material sandwiched in between two pieces of glass. During the curing process, heat, vacuum and pressure is applied to the sample. As the polymer film softens from the elevated temperature, the vacuum pulls out air bubbles, creating a perfect hermetic seal with no air pocket. Further heating initiates the cross linking of the film, and pressure is applied to the sample to ensure a good adhesion after completing the lamination process.

This section describes the process of optimizing of the laminating process parameters to minimize damage to the perovskite device.

The shortlisted film was Ethylene Vinyl Acetate or EVA for short. EVA is widely used in the solar industry, due to its good adhesion and high transparency. It is also able to prevent moisture ingression and is highly durable. This material is also electrically insulative. These ideal physical and optical properties make it an ideal material to be used as an encapsulation material used in photovoltaic applications. The EVA was purchased and stored in a dry box environment to prevent absorption of moisture from the atmosphere.

Table 12 Overall optimized parameters

	Manufacturer recommendation	Optimized process
Temperature	140°C	90°C
Vacuum delay	20 seconds	20 seconds
Vacuum	5 mins	5 mins
Pre lamination	40 seconds	20 seconds
Lamination	7 mins	5 mins
Delayed Opening	1 min 10 seconds	20 seconds

The first step was to optimize the temperature. A lower temperature is more suitable for encapsulation of perovskite, as heat will induce degradation to the perovskite device.

The vacuum time remains unchanged. This is to ensure that air bubbles are fully removed, ensuring a fully hermetic seal. The lack of air space is crucial to minimize the degradation of the sealed perovskite film.

The first experiment was to laminate 100mm x 100mm samples with varying temperatures. 3 samples were tested for each round of temperature change. Laminated films with more than 2 bubbles are considered as failed. When the temperature is 80 degrees or lower, the EVA sheet does not melt fully, resulting in a poor encapsulation. The laminated sample is prone to delamination as well. The results are summarized in the table below.

Table 13 Summary of temperature optimization for lamination

Temperature	Results
140	Pass
120	Pass
100	Pass
90	Pass
80	Failed
70	Failed

After assessing the lowest temperature at which the laminating film can be processed, the next step is to reduce the time at which the films are subjected to elevated temperatures and pressure as to reduce possible degradation.

Two approaches were taken, that is reduction of vacuum time or reduction in lamination time. Attempts to reduce vacuum time were unsuccessful; 5 minutes was the minimum to for the removal of air bubbles. Any reduction in time led to air bubbles forming at the center of the sample. After which, the second approach of reducing the lamination time was taken. The table below summarizes the results with the lamination time as the variable.

Table 14 Summary of the optimized lamination time

Time	Result
7 mins	Pass
6 mins	Pass
5 mins	Pass
4 mins	Fail

In conjunction with the previous heat test, samples were encapsulated using the polymer spray solution, followed by lamination of EVA film between a glass sandwich structure. To address the high water vapor transmission rate (WVTR) of EVA, the four edges of the laminated films are encapsulated with Dow Corning 804 PV sealant for additional protection of the films. From the picture below, additional lamination and edge sealant helps is reduction of degradation of the perovskite film.

Figure 61 Picture showing the different rate of degradation when employing different encapsulation. Top row with Dow Corning edge seal, Bottom row without edge seal.

A batch of 3 mini module has been fabricated and are tested before and after encapsulation. There are no changes to the IV curve, and the module is left out to be stress tested in the exposed environment of a rooftop. After a year of stress testing, the module remained stable and there is little change in the PCE values, despite some changes in the IV characteristics. This is depicted by the figure below:

Figure 62 Figure showing the IV characteristics and picture of the encapsulated mini module before (left) and after a year (right)

During this process, process improvements have been identified due to defects introduced during encapsulation. The large height difference of manual soldering of contacts on the flat surface of the device causes non-uniform stress distribution, causing the cover glass to crack. Improvements can include implementation of silver contact printing, as well as using of tempered back glass instead of a normal float glass. Junction boxes can be included in further scale up processes as to accommodate larger current and voltages, as well as providing a robust connection.

6.3.3 Overcoming geometric fill factor constraints with Laser Etching.

For perovskite solar to be commercialized, the imperative step is to ensure the scalability of the solar cell. Besides the challenge in achieving a large uniform film, the patterning process is crucial towards maintaining the high efficiency of large area perovskite modules. Similar to the approach taken by companies fabricating thin film solar cells, the laser etching process aims to remove materials during different points of the device fabrication process, so that the cells can be electrically isolated. By optimizing the geometric shape of the strips that forms the module, the decrease in module efficiency due to increased resistances associated with larger areas can be minimized.

On the other hand, the laser etching parameters need to be optimized for different layers to minimize damage to the layers, as well as minimizing the dead area. The dead area is as described by the figure below, while the details of the various purposes of the various etchings are described in the following paragraphs.

Figure 63 Schematic depicting the dead area with respect to the active area

As such, it is imperative to understand and optimize the process in a step by step fashion, starting from P1 process. P1 process is described as the removal of the transparent conductive oxide, and in this case, FTO. The process defines the width of the resulting cells. It is important to achieve complete isolation between the adjacent strips as to reduce recombination of charges.

Figure 64 Schematic showing P1 etching to remove FTO layer

P2 occurs after the deposition of the perovskite and HTL layers. In this case, P2 serves to isolate the adjacent cells, as well as to provide electrical contact for the top electrode to connect to the adjacent bottom cell. The substrates are fully coated with perovskite and HTL layers; there is no selective coating. The main challenge for this layer is to completely remove the perovskite and at the same time, minimize the damage done to the underlying FTO layer as well as to the surrounding perovskite. Being a soft material, the perovskite is susceptible towards thermal degradation; the diffused thermal energy could degrade the device stack beyond the scribe lines.

Figure 65 Schematic showing P2 process to demarcate the individual cells

Finally, P3 addresses the issue where all the cells are connected electrically when depositing the top contact via evaporation methods. P3 disconnects the individual cells from adjacent cells, and this final step creates a module that is connected in series.

Figure 66 Schematic showing P3 process to disconnect the cells from shorting

6.3.4 Laser parameter optimization for thin film based etching

Some of the laser parameters can be adjusted to fulfil the various requirements needed for the various processes and are summarized in the table below.

Table 15 Table showing the optimized parameters for P1P2P3 etching using 1064nm laser

	P1	P2	P3
Raster speed	1000mm/s	1250mm/s	1250mm/s
Laser Power	80%	7%	8%
Frequency	20,000Hz	30,000Hz	30,000Hz
Passes	2	1	2

Glass is optically transparent to the 1064nm laser, while FTO absorbs and reacts with it. The process in which the FTO is removed is predominantly pyrolytic; the material removed is due to heating of the substrate material. The laser pulse strikes the substrate material and heats it up beyond its melting point, creating a plume of material vapor in the spot, removing the material. Successive laser pulses next to one another will eventually form the desired etching pattern. The deposited FTO thickness is around 300nm. For complete removal of the FTO material, a minimum of 80% laser power is needed. 2 passes of the laser process required to ensure complete isolation, at a raster speed of 1000mm/s. The resulting etch line is around 150um wide. A simple multimeter probe test is used to test for the continuity of the etched line.

For P2 process, the challenge is to remove the perovskite and HTL material without further damage to underlying FTO layer. The minimum power needed to remove the perovskite and HTL layers is 4%, but the results are not consistent, as shown in the SEM imagery below. The overlapping laser pulses are too staggered; resulting in irregular widths as well as continuity in the film as evidenced by the following SEM imagery.

Figure 67 SEM imagery showing the inconsistent etching width due to poor optimization

To achieve a consistent result, a power output of 7% is required. The raster speed is increased to 1250mm/s from 1000mm/s to reduce the time taken for the process to potentially reduce the thermal damage done to the perovskite layer. The laser frequency is increased from 20,000Hz to 30,000Hz to ensure more overlapping pulses to reduce the jagged effect.

The SEM imagery below shows the removal of perovskite material, and the morphology of the underlying FTO substrate. The perovskite thickness is approximately 900nm, and the width of the line is around 80um. The SEM imagery shows little damage done to the underlying FTO layer with a single pass of laser at 7%. To ensure a good contact between gold and the FTO layer, two adjacent passes were made to widen the gap to approximately 150um.

Figure 68 SEM imagery showing nice and consistent P2 etching with optimized parameters

Finally, for the P3 process, the evaporated gold contacts require more energy to be pyrolytically removed; hence the higher amount of power required. A laser power of 8% is chosen to be the maximum, as any further in power increment in laser power will have negative effects on the FTO conductivity. An experiment was made on 1cm x 1cm sized of FTO glass substrate. The laser makes an etch at the middle of the substrate. A raster test of 40 passes at this energy level shows no detrimental effect to the conductivity of the FTO substrate, while 2 passes of the same process parameters at 9% power shows increased resistance, suggesting damage to the underlying FTO layer. After 40 passes at 8% laser power, the recorded resistance using a multimeter is 32 ohms, while 2 passes at 9% registered a resistance of more than 50 ohms. The results are summarized in the table below. The results suggest that 8% laser output power is the optimal balance between film removal and minimal damage done to the underlying FTO layer.

Table 16 Table showing the effect of laser power and number of passes on FTO conductivity

Passes	0% (pristine FTO)	8%	9%
2	29ohm	32ohm	60ohm
10	29ohm	32ohm	80ohm
40	29ohm	32ohm	1,000ohm

The microscopy imagery shows the distinct differences between P1, P2 and P3 etching on a full device stack. P1 laser etch is on the left and is around 100um, P2 etch is in the middle with a width of 150um, while P3 etch on the right is around 80um wide.

Figure 69 SEM low magnification image showing the differences in P1 (leftmost), P2 (middle) and P3 (rightmost) etch lines on a perovskite device [65]

The above-mentioned etching design and parameters was implemented on a 5cm x 5cm substrate coated with perovskite. There is a slight overlap of P1 and P2 etch, while there is a small safety gap of $\sim 80\mu\text{m}$ for the P3 etch. The resulting mini module yielded an efficiency exceeding 18% on a surface area greater than 6cm^2 with GFF exceeding 90%. The picture of the module is shown in the figure below.

Figure 70 Figure showing PCE of the mini module fabricated using P1P2P3 processes(L), the back view of the fabricated module (R)

6.3.5 Laser parameter optimization for carbon removal

The parameter setting for carbon layer is slightly different as compared to that of the evaporated gold contact. The printed carbon electrode consists of a mixture of graphite chunks mixed with binders. The inconsistent size of the graphite chunks makes the P3 process mentioned in the section earlier highly inconsistent for removal of carbon layer. The power output of the laser is only limited to 8% as explained in the previous section where increased power will damage the FTO layer. For optimization purposes, a 1x1cm printed carbon electrode is printed on normal non-conductive glass. The printed electrode is found to have a resistance of around 40ohms from corner to corner using a simple multimeter. This is shown in the figure below.

For initial understanding, the same parameters gold contact removal is used in an attempt to remove the printed carbon electrode. Despite multiple passes of up to 40 times, the etch line remains conductive, with resistances as low as 100 ohms being recorded across the printed sample. A fully isolated line should have a resistance value exceeding 1M ohm so that the resulting module will have good shunt resistance, indicating little leakage currents and pathways, which are required for efficient modules. Upon inspection with a microscope, there are still bits of carbon that were not completely removed, which could be the source of shorting.

Figure 71 Microscopic image of the etched carbon electrode

For this instance, the P3 process is modified to make a wider etch line. Multiple lines are programmed and etched close to each another, resulting in overlapped areas where the material is removed. This results in a wider etch line which helps to solve the issue. For this, varying parameters were adjusted. The overlapping density, as well as overall width are being optimized. The optimized parameters are tabulated in the table below.

Table 17 Optimized parameters for carbon removal

Etch Width	Overlapping density	No. of passes	Raster speed	Frequency
360um	50um	15	1500mm/s	30,000Hz

The reason for the close overlapping density is to ensure that adjacent lines overlap each other to ensure that there is complete removal of material. Due to the inhomogeneous nature of the carbon paste, a large width of 360um is required to ensure that complete isolation is achieved.

Figure 72 Picture showing successful etching of the carbon film

Chapter 7: Conclusions and recommendations

Implications and Impacts, Future works

This chapter sums up the work done in investigating the suitability of fully printable solar cells. From the basic understanding of how the additives affect the basic crystallization processes, to improving device performances and establishing proper measurements, to scaling up, process weaknesses were identified and improved. Besides a summary of the thorough work done in the thesis chapters, this chapter also includes other research works that could be implemented in future processes to further improve this exciting technology, which could be pushed closer towards commercialization.

7.1 Summary and Conclusion

This thesis covers the basic investigation on the scalability of fully printable perovskite solar cells with carbon counter electrodes. Processes to improve the efficiency and ensuring scalability with stability are the main concerns of this thesis.

Chapter 3 describes the rationale for the development of printable perovskite solar cells, as well as the working principles. Fully printable perovskite solar cell with carbon counter electrode seems to provide the best balance between scalability, cost, and efficiency, as supported by the information gleaned from literature.

Data from literature suggests that a reasonably high efficiency of around 14% could be obtained at a small device scale. However, the approach in which the efficiency numbers are reported leaves much to be desired. A large portion of the printed active area is masked, and the reported efficiencies are typically based on a 0.09cm^2 active area. This method of measuring efficiencies is known to exaggerate the actual efficiency of the device and could potentially cause scaling issues for the printable perovskite solar cell.

In chapter 4, fully printed solar cells are fabricated and measured without masking to find out the optimal size for scale up purposes. Furthermore, the effect of masking is being investigated on a standard 0.7cm^2 device, and suggestions are provided to ensure minimized exaggeration in future reports. For example, a mask slightly smaller than that of the active area should be used, instead of the commonly used 0.09cm^2 masks used for standard spin coated devices. This erroneous method of reporting PCE usually brings about much exaggerated FF values, and this issue is exacerbated when scaling up fully printable solar cells. Chapter 4 shows that the optimal width of the device lies within 5 to 7mm, with device PCE values exceeding 14%. With widths more than 7mm or less than 5mm, the FF drops. This could be due to ineffective charge extraction or increased resistances. Using the optimized width, the printed solar cells are fabricated in an elongated fashion and combined to form a mini module of four cells connected in a series circuit design, with an active area of approximately 30cm^2 . The fabricated mini module posted an efficiency exceeding 10% PCE, which gives good confidence in further scaling. Further upscaling of

the printable solar cell is performed on a 70cm^2 active area with 10 cells connected in a series fashion. The upscaled device incorporated numerous design improvements such as tighter tolerance in printing as well as reduced intercell spacing to reduce resistive losses, hence improving FF values.

Chapter 5 describes the technique used to methodologically enhance the PCE of fully printable perovskite devices. The approach taken is to improve the interfaces between of perovskite crystals. The mesoscopic device uses mesoporous TiO_2 to serve as the electron collection layer, ZrO_2 as the intrinsic scaffold. Carbon serves as the hole conductor as well as the counter electrode.

The first part of this chapter aims to optimize the nucleation and subsequent pore filling of the perovskite crystals using AVAI as an additive. The optimal atomic ratio of AVAI is found out to be 2.5% w.r.t to PbI_2 . The extent of AVAI affecting the pore-filling is examined using cross sectional FESEM imagery. Without AVAI, there is poor pore filling, resulting in poor charge transfer and device efficiencies. Even with minute amounts of AVAI added, there is drastic changes in pore filling, as evidenced by the subsequent FESEM images. Perovskite devices fabricated with this optimal concentration of AVAI additive exhibited the best IV characteristics of high V_{oc} , J_{sc} and FF, suggesting that pore-filling is paramount for good device performance. However, there is a delicate balance in which excess amounts of additives will lead to declined device performances, as shown by decreased efficiencies when 7.5% of AVAI is used. The optimized concentration of 2.5% is used in subsequent experiments below.

In the second part of this chapter, fabrication of Cu:NiO_x nanoparticles and paste is being described. The energy alignment of carbon is at -5.0eV . While the printed carbon layer is suitable to hole extraction, a better aligned energy level with the perovskite valence band would benefit the hole extraction from the perovskite absorber layer. As such, introducing a suitable HTL could bring about enhanced device performances for this kind of fully mesoscopic devices. The Cu:NiO_x nanoparticles are characterized with XRD, EDS and XAS characterization tools. The rationale for doping NiO_x with Cu is to improve the low

intrinsic conductivity of the oxide film. EDS mapping shows uniform dispersion of Cu atoms within the NiO_x matrix. Further examination using XAS suggests that the successful doping of Cu into the matrix, evidenced by the largely similar peak positions. XAS also reveals that during successful doping, Cu remains in 2+ oxidation state, while majority of Ni is in 2+ state while a minority of Ni is oxidized to a 3+ state. The main cause of p-type conductivity of NiO_x could be ascribed to the excess oxygen within the lattice site. The excess oxygen would create vacancies in the normally occupied Ni sites. To preserve overall electrical neutrality, two Ni^{2+} ions will be converted to Ni^{3+} for every Ni vacancy site. As Ni^{3+} ion is unstable, it will change from one Ni^{2+} site to another. The mechanism makes it like as though positive holes are moving. The Ni^{3+} site acts as impurity level above the filled band and the excitation of electrons to these sites leaves mobile holes in the band. It is highly possible that the dopant Cu on Ni site increases the concentration of holes, thus enhancing the film conductivity. XANES analysis shows that the percentage of Cu doping in the matrix is around 5.4%, which is close to the ratio in which the precursors are mixed in the experimental planning section.

The nanoparticles are subsequently made into a screen-printable paste. The thickness of the paste is optimized to be 80nm for implementation into the device structure. The resulting devices have much improved photovoltaic performances as compared to standard devices, such as improved FF and V_{oc} , as well as reduced hysteresis. The devices with Cu: NiO_x also offer a much more robust performance when tested with slow scan rates, suggesting balanced and improved charge extraction from the interfaces. It is shown that 5% doping of Cu into the NiO_x matrix offers the best photovoltaic performances as shown by a 12.79% PCE performance with enhanced V_{oc} and FF, as compared to 3% and 10% doping of Cu. When the amount of Cu doping is increased to 10%, the series resistance seems to increase, leading to a decrease in IV parameters. Finally, the scalability of this approach is verified by fabricating a large 70cm² mini module with a PCE value of 12%.

Chapter 6 contains two sections. For the stability aspect, extrinsic encapsulation is being investigated. A two-layer approach of encapsulation is pursued. In the initial part, a spray

on encapsulation is being optimized. Various polymers are shortlisted, and their concentration in the toluene solvent is being optimized. After simple tests, a 30mg/ml PMMA-based solution seems to provide the optimal protection as compared to other polymers. This spray-on layer provides the initial protection as a buffer layer to protect the film when stronger encapsulation means are explored in the later part. In a follow up experiment, the EVA lamination process is optimized for the perovskite device. The laminating time and temperatures are reduced, which leads to possibly less damage done to the perovskite devices. Finally, the edges of the devices are protected with an industrial-compatible and proven PV sealant from Dow Corning. The devices are left in the heated environment for more than 1000h, and the fully protected device with 3 layers of protection shows no visual sign of degradation, whereas the other devices degraded, turning yellow. The initial batch of encapsulated mini modules saw respectable stability, surviving more than a year when placed in operational conditions.

The benefits of having used a laser scribe to achieve close spacing between the adjacent cells are explained in the next section. Besides the reduction in dead area and increment in active area, the closer spacings can also bring about enhanced device performances as the adjacent cells are closer to each other and thus having less electrical resistance to overcome. The use of the laser etching process is also highly desirable; it is essential to explore scalable methods so that perovskite technology can be deployed at larger scales.

In this section, the laser parameters are optimized for the various patterning processes, resulting in a mini module of efficiencies exceeding 18% PCE at 21cm^2 . Using the same concept, the same technique is extended to etch perovskite mini modules made from the fully printable technique. For the removal of the carbon layer, modifications are done to the P3 process to achieve a wider etching gap as there are unique non-homogenous issues due to the composition of the carbon paste. The optimized parameters for the various processes are summarized.

In all, the 3 chapters show a comprehensive and systematic approach in understanding and producing highly scalable and efficient perovskite solar cells with carbon counter

electrodes, in which some approaches and methods can be extended to perovskite solar cells, such as laser P1P2P3 processing as well as encapsulation methods.

Besides the work shown in the previous chapters, more work can be done to further investigate on the potential of this printable device architecture, as well to improve the stability of the devices. This is further explained in the recommendation section below.

7.2 Future Works and Recommendations

There can be several aspects in which more work can be applied to this interesting and dynamic field of technology. They can be categorized into 3 main groups: 1) cost reduction, 2) efficiency enhancement, and 3) stability enhancement.

In the industrial world, whether a product would be successful depends highly on the value perception, and one key aspect would be cost reduction to keep overhead low and profits high. The intrinsic ZrO_2 layer could be potentially replaced by outer suitable, low-cost wide bandgap insulating materials. The purpose of these material is to serve as the mesoscopic scaffold to hold the perovskite crystals, as well to prevent direct contact of carbon with TiO_2 . The shortlisted materials will need insulating, as well as band alignment that does not allow injection of holes and electrons from perovskite. That will mean a valence band position of -5.5eV and below, and a conduction band above -3.5eV . Furthermore, the particle size and thickness need to be optimized to have an optimal balance of optical transparency, pore size and subsequent loading of perovskite crystals within the pores. Possible candidates include Al_2O_3 or SiO_2 nanoparticles around 50nm in size[66].

Due to the ambipolar nature of perovskite, further cost reductions can be achieved by eliminating the mesoporous TiO_2 layer. This takes away 1 printing and annealing step. Like what has been achieved with planar devices, the interfaces between the perovskite crystals and blocking layer will be of outmost importance. This could be of an interesting topic to pursue further research and be further optimized [67].

In terms of efficiency enhancement, alternate p-type oxides can be explored. The fabrication methods for these oxides need be scalable. Alternative oxides could also show cost reduction in fabrication, as less materials might be used. One good example would be Co_3O_4 , where the nanoparticles are synthesized as it is, compared to additional doping steps required by Cu:NiO_x . Other additives could be used in place of AVAI. As mentioned earlier in the results chapter, introduction of AVAI is known to produce 2D perovskites[38]. These 2D perovskites helps to enhance the physical interfaces between 3D perovskites and the

mesoporous scaffold, as well as resisting moisture ingress. The benefits are two-fold: enhance device efficiencies and enhanced stability. Other additives could be trialed, such as replacing AVAI with molecules containing conjugated chains for enhanced efficiencies [55, 68]. The main challenge for finding a suitable candidate is to ensure the compatibility of the material with perovskite. The carbon chain length, functional groups at the end of the carbon chain, presence of double or conjugated bonds; all these factors affect the nucleation process and have a great impact on the resulting PCE of the device.

The carbon paste could be further optimized. Currently, the carbon paste is made up of a mixture of graphite flakes and carbon black. The graphite flakes serve as the main conducting medium, while the carbon black affects the porosity and interface between the carbon film and perovskite. Optimization of the graphite flake size, as well as the type of carbon black used, can have a drastic effect of the paste properties [69-71]. The ball milling parameters could also affect the homogeneity and dispersion of the mixture. Additives to the carbon paste could be explored to either improve the electrical or physical properties of the carbon film. Addition of silver nano-wires or different types of carbon nanotubes might help to enhance hole-selectivity and film conductivity.

Lastly, improvements to the stability aspect of perovskite technology will greatly enhance the feasibility of commercializing perovskite solar cells. The intrinsic stability of the perovskite can be further enhanced by replacing MA-based perovskites with MA-free alternatives such as Cs-based perovskites. The laminating material can also be changed from EVA to Poly-Alpha-Olefin (PAO) based films, as the WVTR of EVA could be one of the limiting factors that works against making perovskite solar cells more stable. Process enhancements can include screen-printing of silver contacts to replace the uneven manual solder, as well as using of tempered glass for the backing to ensure non-breakage.

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