New light harvesting architecture towards high performance solid-state mesoscopic perovskite solar cells

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy in the Faculty of Science and Engineering

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\( \text{e}^- \) Electron .................................................. 31
\( \text{h}^+ \) Positive charge ions (Hole) ............................ 31

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\( A_{\text{Reverse}} \) Area under reverse bias of J-V curve ............... 98
\( E_g \) Band-gap energy ............................................. 31
\( \phi_{\text{DMSO}} \) DMSO volume fraction in DMF solvent ............. 113
\( J_{\text{MPP}} \) Maximum power point at short circuit current ......... 59
\( R_S \) Series resistance ............................................. 59
\( R_{\text{SH}} \) Shunt resistance ......................................... 59
\( V_{\text{MPP}} \) Maximum power point at short circuit voltage ............ 59
\( V_{\text{OC}} \) Open-circuit voltage ..................................... 50

Acronyms

ASTM The American Society for Testing and Materials .................. 56
BHJ Bulk heterojunction .............................................. 35
CB Conduction band ................................................. 31
CBZ Chlorobenzene .................................................. 44
CdTe Cadmium Telluride ............................................. 23
CIGS Copper indium gallium selenide ................................. 23
DMF N,N-Dimethylformamide ........................................ 40
DMSO Dimethyl sulfoxide ........................................... 40
DSSC Dye-sensitised solar cell ...................................... 23
EDX Energy-dispersive x-ray spectroscopy ............................ 72
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<td>EQE</td>
<td>External quantum efficiency</td>
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<td>ETM</td>
<td>Electron transport material</td>
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<td>FDC</td>
<td>Fast deposition conversion method</td>
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<td>FF</td>
<td>Fill factor</td>
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<td>FTO</td>
<td>Flourine-doped tin oxide</td>
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<td>FWHM</td>
<td>Full-width at half-maximum heights</td>
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<td>GBL</td>
<td>γ-butyrolactone</td>
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<td>HTM</td>
<td>Hole transporting material</td>
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<td>ITO</td>
<td>Indium tin oxide</td>
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<td>LiTFSI</td>
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<td>Methylammonium lead iodide</td>
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<td>6,6-phenyl C61-butyric acid methyl ester</td>
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<td>TCO</td>
<td>Transparent conductive oxide</td>
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<td>TDB</td>
<td>Titanium diisopropoxide bis(acetylacetonate)</td>
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<td>Tetraphenylphosphonium chloride salt</td>
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<td>Tetraphenylphosphonium iodide salt</td>
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<td>UV</td>
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<td>1-s</td>
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<td>AM0</td>
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<td>N-I-P</td>
<td>Negative-Intrinsic-Positive junction</td>
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<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylenedioxythiophene)poly(styrene-sulfonate)</td>
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<td>P-I-N</td>
<td>Positive-Intrinsic-Negative junction</td>
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### Other Symbols
Solar energy has been considered as very promising in term of a potential cost effective and environmentally friendly technology for energy production. Perovskite solar cells (PSCs) are an exciting new type of solar cell technology that has attracted enormous attention recently. Hence, this study aimed to examine the usage of a new film formation method to control morphology of the perovskite photoactive layer in order to improve the understanding of PSC. Here, the concern is on determining how structured perovskite film with high performance and stability can be achieved by tuning the morphology. In this study, experiments that entail the role of perovskites morphology on the performance and stability of PSCs were conducted. In preparing the novel perovskite solar cell used, this study emphasised a combination of the one-step (1-s) and two-step (2-s) deposition methods in order to obtain the new and versatile 1 & 2-s method. It was found that the 1 & 2-s deposition method was able to produce CH$_3$NH$_3$PbI$_3$ (MAPI) films that have tuneable morphologies, crystal sizes and optoelectronic properties in relation with the conventional 1-s and 2-s film methods. By our method, the final morphology could be systematically changed between the extremes of the 1-s and 2-s morphologies. For example, the key SEM experiments revealed that controlling the PbI$_2$ to MAI composition could lead to tuneable morphology. Higher composition of PbI$_2$ lead to more nucleation site to be formed in which determine the final grain size and morphology. Furthermore, the study showed that the morphology could significantly affect the device properties. The use of the new combined method produces MAPI films that have improved light scattering, stronger absorption and enhanced device performance compared to films prepared using the conventional 1-s or 2-s methods. This study also extended the new combination method by introducing the co-solvent blends and examined how the co-solvent composition affects...
the properties of the final films. A comparison of the optoelectronic properties, stability and device characteristics of the perovskite absorbing layer between the well-established conventional depositions methods (1-s and 2-s) and the new combined method 1 & 2-s was also conducted. In this regard, an unexpected improvement in thermal and device stability of the MAPI films prepared using the 1 & 2-s method is found to be related with the amount of Br\(^{-}\) adding to the system. Furthermore, an improved PCE and enhanced stability was achieved by adequately adding Br\(^{-}\) through this new 1 & 2-s method. The study also investigated how the presence of anion (halide) affects the optoelectronic and device properties of CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Br\(_x\), films and device’s properties. The study identifies the mechanisms that explain the decoupling of exchange and growth in perovskite-forming stage for these films. This mixed-halide study gave devices with the highest power conversion efficiency of about 13%. From the study, we can conclude that the new 1 & 2-s method is transferable and can be used and improved in other perovskite for future applications in order to obtain a high performance PSCs.

**Keywords:** Perovskite, perovskite solar cells, 1 & 2-s deposition method, mixed halide perovskite, morphology, crystal growth.

**Final word counts:** 38,797 words
Declaration

I declare that, no portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Date: October 5, 2018

Muhamad Zulhasif bin Mokhtar
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I would like to express my sincere gratitude to my most dedicated supervisor, Prof Brian Saunders for his endless support throughout my journey in PhD study. He is the one who has provided me with an exceptional guidance and an excellent atmosphere for me doing this research. I cannot thankful enough for his patience, continuous encouragement and immense knowledge. He is truly one of the best references for my research and writing. Without his dedicated involvement in every single step of my research, I believe that this thesis would have never been accomplished.

Also, I take this opportunity to express my sincere thanks to all the Experimental Officers especially to Mr Eric Whittaker and Ms Polly Greensmith and also to my group members and friends; Frank, Rosie, Qing, Wayne, Dong, Shah, Wani, Melody, James, Hannah, Shanglin, Amir Milani, Nam Nguyen, Qian Chen and Jack Chun-Ren Ke. Their insightful comments, invaluable criticism and stimulating discussions are the most memorable to me and have greatly improved my works. Indeed, this has given me the positive momentum and extraordinary experience.

Finally, I would like to express my heartiest gratitude to my mum and dad, siblings and other family member for their continuous encouragement throughout my PhD study. This accomplishment would not have been possible without them. Special thanks and appreciation to my beloved wife, Dr Norashidah Rahmat for the time listening, caring, patience and supporting me spiritually for all the ups and down.

Thank you.

Muhamad Zulhasif bin Mokhtar
School of Materials
October 5, 2018
...Dedicated to my lovely wife (Dr. Norashidah Rahmat) and beautiful son (Eusoff Zayyan) for caring and supports...
Introduction

1.1 Background

Energy has become a basic human need in our modern society. Over the years, fossil fuel has been used as the main source of energy and the burning of that non-renewable resource has caused the excessive greenhouse gases to be emitted. This has lead to serious environmental problems which could threaten the livelihood of human beings. Consequently, this undermines the balance of the world’s biological system and leads to serious environmental concerns like global warming. The increasing human population has created the demand for more energy and higher use of fossil fuels which caused unacceptable global risks [2]. For example, the energy demand on 1973 was about 55,000 TWh, and it keep to grow to until about 110,000 TWh in 2014 which means the world has to increase more coal production by 40% to cater the demand [3]. In the meantime, despite the ability to replace carbon-based fuel, the use of alternatives like coal and nuclear power also bring environmental problems; for instance, nuclear power plants create harmful by-products that need to be disposed of carefully to prevent a higher risk of radiation. In response, there is a burgeoning demand for sustainable, inexpensive and renewable energy. This has inspired researchers from all around the world to come up with new technologies to generate power. These include using primary alternative energy resources such as solar irradiation, wind, hydro-electric and biomass.
One of the most accessible energy sources is solar power where energy is derived from the most important resource for every existing creature in this world, the sun. As sunlight provides an endless source of energy and it can be harvested almost everywhere on earth, it is deemed as the best solution to overcome the impending global energy crisis. Furthermore, solar is a clean and environmentally friendly source of energy. The advantages of using solar irradiation to generate power has garnered the interest of energy researchers, chemists and material engineers. In this process, solar cells are used to converts incident lights directly into electricity and is better than other technologies which are complex and expensive still.

The most widely available solar cell is the silicon-based solar cell. The solar cell efficiency tables [4] and the latest NREL efficiencies chart [1] reported that the silicon-based solar cell has the highest power conversion efficiency (PCE) reached to approximately 25.6% has shown in fig. 1.1. The PCE of the silicon-based solar cell then levelled off to be 25% for a long period due to some limitations. The use of silicon-based solar cells incurs a higher cost per watt as these cells are costly to fabricate. Moreover, silicon, in bulk is generally fragile which can constrain application on flexible substrates. Thus, researchers are actively developing other photovoltaic devices that could either substitute or complement silicon-based solar cells.

On-going works are currently being done to investigate different type of solar cells such as thin film photovoltaics for example, the second generation thin film solar cell such as CdTe and CIGS. These thin-film SCs which are made by depositing one or more few nanometer thin layers have a champion PCE of 22.3%. Beside that, dye sensitised solar cell (DSSC) is also given attention. However, there are reports that works on these cells have slowed down [1] as researchers face several limitations. Another form of solar cell is the perovskite solar cell (PSC) which was introduced in 2009. The first version of the PSC was presented by Kojima et al [5]. However, this version has a very low PCE of 3.8%. Over the years, researchers have established more PSCs and in 2016, it was reported that the PCE has surpassed the 20% mark, with the certified PCE of 22.1% [10]. Undoubtedly, the current
1.1 Background

Figure 1.1: Comparison of key progressions recorded for Si crystalline solar cells (black curve) and perovskite solar cell (red curve) extracted from NREL efficiency chart [1] (Appendix A.1). The refs = a [5], b [6], c [7], d [8], e [9] and f [10]. It took nearly 3 decades for Si crystalline solar cells to establish 25% power conversion efficiency (PCE) while only less than a decade (7 years) for perovskite solar cells to reach their established PCE of 22%.

PSC has demonstrated a PCE that is comparable to CIGS and almost similar to the PCEs recorded by the commercialised silicon solar cells. As a result, PSC has generated the interest of numerous researchers from across the globe. Some researchers specialising in organic photovoltaics (OPV), solution processing and DSSC are also conducting various further studies on PSC. In this regard, it is evident that there is a rather short learning curve for developing PSCs and progress in this field has been fairly fast and robust.

Due to the rapid development and improvement on PSCs, it is possible that their PCEs will beat silicon-based solar cells in the near future. The use of PSCs is highly sought after as it uses inexpensive raw materials, which entails a lower manufacturing cost compared to other types of solar cells, including the established Si solar cells. This could lead to lower cost of energy generation per watt. However, the potential to commercialise PSCs is still limited as PSCs are very unstable. Studies have reported that PSCs are fragile and highly sensitive to moisture, heat, oxygen and even ultraviolet (UV) light [11]. This presents a case for researchers to examine the chemical stability of perovskite materials to deliver useful information that can be used in the next step of PSC fabrication.
More details about PSCs, including the current progression, architecture, stability and environmental issues are presented in Chapter 2, along with an introduction on how solar cell works based on silicon solar cell are also discussed.

1.2 Motivation

In 1954, Bell Laboratories introduced the first crystalline silicon-based practical photovoltaic device [12]. Over the last 60 years, this technology has gained popularity. The Solar Technologies Market Report, published by the National Renewable Energy Laboratory (NREL) [13] reported that the crystalline silicon technology dominates the world PV market. In this regard, 55% market share for polycrystalline and 36% market share for monocryrstalline-silicon modules are held by crystalline silicon technology. On the other hand, the other 9% comprise of both established and emerging PV technologies, such as polycrystalline thin films, amorphous semiconductors, dye-sensitized solar cells (DSSCs), organics, and quantum dot solar cells. In this light, to reduce the market domination of crystal silicon solar cells, there is a need to introduce alternative technologies that offer high power conversion efficiency (PCE), low manufacturing costs, and excellent stability [14]. In recent years, studies have come out with the prototype example of hybrid organic-inorganic perovskites (HOIP) with methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) that could potentially meet these conditions and someday, cut down the domination of silicon solar cells in the market. Furthermore, over the last three years [10], there are intensive studies on the perovskite-based solar cell have been reported to demonstrate a similar, or more superior quality compared to other PV technologies. It is believed that these PCEs could potentially compete with the existing silicon technology near future [15] as they have lower manufacturing costs and require simple device processing. In line with such efforts, our team proposes several new strategies that could be employed in order to achieve PSCs that demonstrate excellent device performance and stability with a simple processing method.
1.3 Objectives

This thesis presents a project that is based on the premise that we can use a simple, yet powerful technique during the key film formation to control morphology of the perovskite photoactive layer in PSCs. To this end, investigations were carried out to:

i. Characterise the main component of the PSCs; the perovskite itself and determine appropriate stoichiometric control of lead and halide precursors.

ii. Establish the fabrication method for preparing perovskite solar cell in laboratory scale. This objective is very significant as the materials and solar cell fabrication are new to our group and we are the pioneering group within the University of Manchester to fabricate perovskite solar cells.

iii. Establish novel and facile method to cast the active layer solution that provide good control of desired final architecture.

iv. Study new perovskite morphologies.

v. Explore the potential of using architectural control of perovskite particles and morphologies to achieve structured films that maximise the performance, including the PCE and stability.

vi. Extend the use of this new method and explore the new co-solvent blend that will strengthen the PSCs performance in term of PCE and stability.

vii. Apply new Br\(^-\) anion diffusion/exchange and incorporate it into the established perovskite architecture and study its effect on the film properties and device performance.

viii. Study and propose the mechanism of the newly discovered mixed structure of final perovskite system.
1.4 Thesis organisation

This thesis contains several chapters. Chapter 1 presents an overview of the thesis, while the literature review of relevant theories and past studies related to this project is presented in Chapter 2. The next three chapters will demonstrate the research processes conducted in this project.

In Chapter 3, new MAPI film preparation method (1 & 2-s) is introduced. The properties of the new MAPI films are analysed and three novel mixed morphology perovskite photoactive films (x = 0.33, 0.50 and 0.66) were investigated. In this regard, the new 1 & 2-s deposition method has created MAPI films that demonstrated optoelectronic properties and tuneable morphologies linked to the ordinary 1-s and 2-s films (see fig. 1.2). On the other hand, the film created using the 1 & 2-s film method has shown unique properties indicating that they are not simply a combination of those 1-s and 2-s films.

**Figure 1.2:** Depicts the growth of CH$_3$NH$_3$PbI$_3$ (MAPI) films is transformed using a new combined 1 & 2-s deposition method which results in fundamental differences in morphology, optoelectronic properties and device performance (such as PCE and $J_{SC}$) which are tuneable.
1.4 Thesis organisation

In Chapter 4, the new 1 & 2-s method presented in Chapter 3 is extended by introducing the co-solvent blends that will improve the final film properties (see fig. 1.3). This chapter focuses on the effect of the co-solvent blend on the film coverage, optoelectronic properties and device performance. This chapter also includes a comparison of the perovskite absorbing layer with well-known deposition methods, such as the one-step (1-s) deposition and the sequential deposition or two-step (2-s) method. Here, the perovskite films’ basic optoelectronic properties, stability and device characteristics are compared and discussed.

![Figure 1.3: Depicts the overall capping layer morphology of CH$_3$NH$_3$PbI$_3$ (MAPI) final films are improved after introducing DMSO:DMF co-solvent approach into the precursor solution formulation.](image)

Chapter 5 further extends the newly designed MAPI by adding Br$^-$. This chapter will demonstrate how adding Br$^-$ could lead to higher PCE and stability. We will also discuss the mechanism of this new architecture as well discussing how the presence of Br anion (halide) affects the MAPI film’s optoelectronic and device properties (see fig. 1.4). Later in the chapter, a novel mechanism that explains the decoupling of exchange and growth in perovskite-forming stage is introduced.

All in all, this thesis provides insights on the key factors that govern the device performance, including device architecture, preparation methods, morphological control and advanced device engineering. Additionally, future direction (recommendations) for perovskite PV devices are also discussed in Chapter 6.
1.4 Thesis organisation

Figure 1.4: Mechanism for mixed anion preparation via the 1 & 2-s method for the (a) MAPI(B)-MAPI and (b) MAPI-MAPI(B) films. The former film composition is limited by the stoichiometry used in the first (precursor forming) step; whereas, the latter film composition is limited by diffusion that occurs in the second (final film forming) step.
2.1 Abstract

The perovskite solar cell (PSC) has gained a huge amount of interest due to its extraordinary efficiency progression. There are reports that the power conversion efficiency (PCE) has surpassed 22% in the photovoltaics (PV) area. As a result, many studies have committed to find ways to commercialise this new technology. This calls for a thorough understanding of the perovskite material, the construction of perovskite devices and the ways to achieve high PCEs. Therefore, in this chapter, the key factors determining the device performance, such as the deposition methods, crystal growth, surface morphology of the state-of-the-art perovskite material, Methyl Ammonium Lead Iodide, CH$_3$NH$_3$PbI$_3$ (denoted as MAPI) and the latest advanced device engineering will be discussed. This chapter will also look into the stability issues and future directions of perovskite solar cells and explain the basic solar cell operation. It is believed that understanding the perovskite crystallites’ growth process will contribute in improving the performance of PSCs and help find ways to use this new technology to produce large-scale, low-cost and high-performance perovskite solar cells.
2.2 Basic photovoltaics

Solar cells are comprised of semiconductor materials. There are a ‘forbidden energy gap’ between the valence band (VB) and the conduction band (CB) of a semiconductor. A semiconductor is conducting when the electrons (e\(^{-}\)) in the VB are excited to the CB through the absorption of photons or by applying an external electric field. In this light, \(E_g\) (as shown in fig. 2.1) refers to the band-gap energy or the energy required to excite electrons from the VB to the CB. Meanwhile, the positive charge that remains in the VB is known as a ‘hole’ (h\(^{+}\)), and treated as a quasi-particle.

![Figure 2.1: Light absorption process in a semiconductor. A photon with energy larger than the bandgap (Eg) excites an electron (e\(^{-}\)) from the valence band (VB) into the conduction band (CB) (i). A positively charged hole (h\(^{+}\)) remains in the valence band (ii). Electrons and holes can recombine via an external circuit (iii).](image)

The electrons can be diffused freely through the material’s CB while the holes diffused through the VB. The material’s light absorption properties are highly influenced by the size of the band-gap energy. This is because only photons with energy larger than \(E_g\) can be absorbed. This ascertains the highest amount of current can be generated by a device that uses a certain semiconductor. This is because for every wavelength, the solar spectrum comprises of a specific number of photons, hence, the potential current will be higher when more light is absorbed [16].
2.2 Basic photovoltaics

Meanwhile, in a fully assembled solar cell, the photo-excited electrons are extracted out of the device by using carefully engineered material interfaces and doping. As the charge carriers are created (fig. 2.2a), they move into each of their higher conductive material, charge separation will occur at a junction between a high electron conductivity (n-doped) material, and a high hole conductivity (p-doped) material. After the p-n junction has been formed, electrons from the n-doped side will diffuse towards the positively charged p-doped side and vice-versa (fig. 2.2b). These electrons and holes will create a ‘depletion region’ as they recombine in the centre of the solar cell which has no mobile charges (fig. 2.2c).

This part of the solar cell will be positively charged as the electrons are diffused out of the n-doped side, while due to the loss of the holes, the p-doped side will be negatively charged. This difference in charge will form an in-built electric field that pushes electrons towards the n-doped side. At this point, no mobile charges are left in the junction region [17] and the photons will absorbed by this p-n-junction upon illumination, the electrons are excited to the CB which leaves the free holes in the VB. These electrons will be diffused towards the solar cells’ n-doped side and can be extracted by using an external circuit. It can drive an external load which is connected to the circuit before it re-enters the solar cell on the p-doped side and recombining with the existing hole there.

**Figure 2.2:** Shows depletion region details mechanism where (a) charge carriers imbalance caused the electrons to drift, (b) electrons from n-region reached conduction band free to diffuse across the junction and combine with holes, and (c) space charge builds up creating ‘depletion region’ which prevent further electron transfer.
2.3 Silicon solar cell working principle

The mono-crystalline solar cell typically consists of a wafer of p-type and n-type silicon (Si). P-type wafer (light harvesting part) forms base of cell and is thick to absorb as much light and lightly doped to give maximum diffusion lengths. On the other hand, n-type (emitter part) is heavily doped and is thin to reduce the series resistance as much as possible. Referring to fig. 2.3, when light shines on the solar cell, current and a voltage will be produced and electric power will be generated. This process requires a material that could elevate an electron to a higher energy state through light absorption and the higher energy electron needs to flow from the solar cell into an external circuit. Subsequently, the electron is dissipated in the external circuit and returns to the solar cell. In this regard, despite the numerous materials and processes could fulfil the condition for photovoltaic energy conversion, in practice, almost all photovoltaic energy conversion utilise semiconductor materials, specifically the p-n junction discussed above.

Figure 2.3: A cross section of a solar cell shows the basic operation of solar cell. (i) Electron-hole pair generation, (ii) current generation and (iii) charge carrier recombination.

From the discussion above, the operation of a solar cell is basically comprised of several processes;
2.4 Third-generation solar cells

i. Generation of charge carriers, which involve creating electron-hole pairs through the absorption of incident photons.

ii. Generation of current by collecting the light-generated charge carriers. In this process, the incident photon energy is higher than the band gap, the electron-hole pairs will be generated in the solar cell and the electron ($e^-$) will be collected in n-junction, leaving the hole ($h^+$) behind and moving to the external circuit.

iii. Power dissipation in the load. The circuit is completed when the electron meets up with a hole. This cycle will be repeated throughout the operation.

2.3.1 Brief survey of solar cells

More than 60 years ago, Bell Laboratories (U.S.) fabricated the first reliable solar cell in 1953 based on a diffused junction. The cell had the efficiency rate of 4.5% and subsequently, a cell with the 6% efficiency was fabricated in 1954 [18]. 18 months later, their researchers had fabricated a cell with 10% efficiency [19] while a commercial terrestrial cell with the efficiency of 14.5% were recorded in 1961 [20]. In the early 1970s, Comsat Laboratories (U.S.) developed the ‘violet’ cell which became the first cell to convincingly exceed the efficiency rate of 14.5% figure. This development has opened the doors for the second phase of cell development [21]. It was not until 1983 that another cell with convincingly higher efficiency was successfully developed. The cell was fabricated by the UNSW MINP (Australia) and was the first cell to record the efficiency of 18% [22]. This marks the beginning for the modern period of cell development, but, over the years, the efficiency of the new cells has been within the 25% mark [23]. In this regard, researchers have focused on producing the third-generation solar cells [24] that could overcome the limitations of previous cells such as high production cost.

2.4 Third-generation solar cells

Third-generation solar cells (SCs) are solution processable SCs that have high prospect in the cost effective [25], large scale generation of solar electricity [24]. These cells can be
used to replace silicon solar cells. Third-generation SCs technologies can be put into three categories, polymer: fullerene composite, hybrid polymer and perovskite-sensitized SCs.

2.4.1 Polymer:fullerene and hybrid polymer solar cells

Organic photovoltaic (OPV) represents an attractive, thin-film solar cell technology. Its development has garnered much attention for its ability to provide low-cost conversion of solar energy [24]. Polymer-fullerene solar cell could be categorised under the bulk heterojunction (BHJ) solar cell which has an excellent performance in the field of OPV. Past studies have reported that polymer-fullerene solar cells had reported the efficiency exceeding 11% [26]. In this light, polymer-fullerene solar cell has higher device efficiency as the short circuit current \( J_{SC} \) is increased by controlling aggregation and crystallisation within the BHJ. The most widely used BHJ solar device is shown in fig. 2.4a, where the blend of donor and acceptor component helps the build-up of the active layer [27, 28]. Hybrid solar cells are comprised of solar cells with photoactive layers. Each cell has at least two components with different chemical composition (e.g. nano-colloids and polymer as shown in fig. 2.4b). The hybrid solar cells comprised of a structure with superimposed layers [29]. Each of these layers has a unique purpose to create charge carriers, separate and transfer those charges [30]. In the design, it is aimed to get higher \( J_{SC} \) when there are acceptors can be provided by the strong light absorption properties of semiconducting nanoparticles. The anode is made from the transparent and conductive indium tin oxide (ITO). The hybrid solar cells are mainly composed of hole transporting material (HTM) and photoactive layer where the cells’ operations such as light absorption, conversion and charge separation take place. The electrons are collected by the cathode layer on top of the device, which is mainly made from metal such as, Al, Ag or Au, while the holes are collected by the aforementioned HTM and ITO.
2.4 Third-generation solar cells

Figure 2.4: Device architectures of (a) Polymer-fullerene composite solar cell showing the bulk-hetero junction (BHJ) donor and acceptor materials [31]. (b) Hybrid nanocolloids (NCs)/polymer solar cell. Active layer shows an illustration of the bulk heterojunction composite structure, where the photoactive layer is made up of a blend solution consisting of two components, electron donor (polymer) and electron acceptor (NCs) [32].

2.4.2 Perovskite predecessor: the dye-sensitized solar cell

Perovskite solar cells (PSCs) were first established in 2009 based on the design of liquid electrolyte dye-sensitized solar cell (DSSC) configuration (fig. 2.5a). This device structure had an issue which was inherited from the conventional DSSC: the dissolution of perovskite in the liquid electrolyte which compromise the device stability. Due to this, solid-state HTM was introduced as a replacement of the unstable liquid electrolyte which lead to the use of mesoscopic structure (fig. 2.5b). The ‘meso-superstructure’ (fig. 2.5c) then was used in 2012. Based on these two preliminary structures, in around 2013-2014, researchers constructed the ‘regular’ structure (fig. 2.5d) with the HOIP materials grows within the mesoporous metal oxide (TiO$_2$) and forming a ‘capping layer’ on top. Since then, the regular structures (normal or inverted (fig. 2.5f), based on mesoporous or planar (fig. 2.5e and f) structure have been used widely to fabricate high efficiency PSCs. The recent categorizations of device architectures are elaborated in section 2.7.1.
Figure 2.5: Schematics depiction of perovskite solar cells (PSCs) architectures evolution: (a) liquid electrolyte DSSC structure, (b) solid-state mesoscopic structure, (c) meso-superstructured structure, (d) the regular structure, (e) planar heterojunction structure, and (F) inverted planar heterojunction structure. Adapted and modified with permission from ref [33]. Not that schematics are drawn not to scale.
2.5 What is a perovskite?

A Perovskite is a class of materials with identical crystal structure as the calcium titanate (CaTiO$_3$) as their parent compound. Perovskite was first studied in 1839 by Gustav Rose, a German mineralogist. It was named in honour of Lev Perovski [34], a Russian mineralogist which pioneered studies of these materials. In the field of optoelectronics, starting from the early 1990s, the hybrid organic-inorganic perovskites (HOIP) have been extensively studied because of their excellent optoelectronic properties and prospect for solution-processed fabrication [35].

![Figure 2.6: Perspective view of the 3D ABX$_3$ perovskite crystal structure [36]. A refers to organic cation (CH$_3$NH$_3^-$ or NH$_2$CH$_3$NH$_3^-$), B a divalent metal cation (Pb$^{2+}$ or Sn$^{2+}$), and X represents the monovalent halide anion (I$^-$, Br$^-$, or Cl$^-$).](image)

The HOIP comprise of materials categorised under ABX$_3$ formula; A refers to organic cation (CH$_3$NH$_3^-$ or NH$_2$CH$_3$NH$_3^-$), B a divalent metal cation (Pb$^{2+}$ or Sn$^{2+}$), and X represents the monovalent halide anion (I$^-$, Br$^-$, or Cl$^-$). In this light, a unit cell of HOIP structure consist of eight A$^+$ cations at the vertices of the cubic edges, one B$^{2+}$ cation at the cube centre, while the next species is octahedrally coordinated to six X$^-$ species sitting at the cube’s planes.
2.5 What is a perovskite?

2.5.1 Survey of perovskite progress

HOIP was first used prominently as a dye in dye-sensitised solar cell (DSSC). Kojima et al. reported in 2009 the first use of HOIP as a PSC which generated a PCE of 3.8% [5]. Later, Im et al. optimised the composition of the redox electrolyte and improved the PCE to 6.5% [37]. Both studies reported that the rapid dissolution of the perovskite in the liquid electrolyte had caused the photovoltaic devices to have poor stability. From this point, it was suggested that the use of solid-state configuration as a hole-transporter could solve this problem. Consequently, in 2012, Kim et al. [38] reported that using a device with spiro-OMETAD led to >9% efficiency. The ‘perovskite fever’ [39] did not completely grow until a solid-state cell and stable device was established. Kim et al. replaced mesoporous TiO$_2$ with Al$_2$O$_3$ to obtain the PCE of 10.3% [38] and later, 12.3% [40]. These studies have paved a way for the significant enhancement in the performance of HOIP-based PV devices. In late 2016, a study recorded the best certified PCE of 22.1% [10]. This marks the most exceptional rate of PCE increase in the history of PV. Such achievement could lead to several benefits, such as lower fabrication costs [41], more efficient processing [42], and improved optoelectronic properties of the materials [43].

2.5.2 Why Perovskite as solar cell material?

There are various processes that could be used to produce high quality perovskite thin films. These include solution [44, 45] and vapour-based [46, 47] deposition approaches. These approaches fit the methods used for the industrial production. Consequently, this increases the potential for perovskite solar cells to be commercialised as it potentially enables the PSCs to be mass produced at a lower cost. Furthermore, besides the flexibility in processing them, HOIP materials have outstanding optoelectronic properties that make them a great alternative for PV applications. They have an ideal $E_g$ of $\sim$1.55 eV (MAPI) for single-junction solar cells. One can switch between the organic and halide ion and tune it to be in the range of 1.5 to 2.3 eV [48, 49]. Furthermore, MAPI has a higher optical absorption coefficient compared to other PV materials such as Si, CdTe, CIGS, and amorphous Si:H, as a result, the absorber thickness can be decreased to $\sim$300 nm
2.6 How to control perovskite morphology?

(even less) and this could subsequently reduce material cost. Moreover, perovskites have low exciton binding energy which allows the spontaneous exciton dissociation into free charges after the absorption of light [50]. Lastly, the charge carriers could be freely carried across the 300-nm thick perovskite absorber before they recombined [51] due to the high electron and hole mobility (within the range of 10 to 60 cm$^2$ V$^{-1}$ s$^{-1}$) where the long carrier lifetime (>100 ns) leads to a long diffusion length (∼1 µm) [52].

2.5.3 Weaknesses and challenges

Even though perovskite solar cells have much potential, before they can be used commercially, researchers and engineers need to overcome the current challenges [50]. One specific challenge is that HOIPs with the toxic Pb element could potentially threaten our environment. Moreover, compared to other commercially available solar panels such as Si and CdTe which have the lifespan of 30 years, PSCs do not have long-term stability due to its vulnerability towards moisture [53]. There are also concerns over the challenge posed by the current-voltage (J-V) hysteresis [54] during voltage scanning. The challenges described here could interfere with extensive deployment of PSCs.

2.6 How to control perovskite morphology?

One of the most crucial factors affecting the PSCs performance is the morphology of the perovskite layer. There are many approaches developed to improve morphologies and this section provides a summary of the approaches. The approaches include selecting the lead precursor, compositional/stoichiometric control, solvent-based crystallisation, heat-induced crystallisation and the additive-controlled crystallisation.

2.6.1 Selection of lead precursor

One of the common ways to prepare conventional MAPI perovskite is by spin-coating a 1:1 molar mixture of PbI$_2$ and MAI in suitable solvents, such as dimethylformamide (DMF), dimethylsulfoxide (DMSO) or γ-butyrolactone (GBL) on a substrate using a one-step (1-s) deposition method [38]. Then, the film will be heat treated to remove the solvent and induce the formation of the perovskite. It is known that when GBL is used as the
2.6 How to control perovskite morphology?

solvent, crystallisation of the perovskite phase will start rapidly without undergoing an intermediate phase first. On the other hand, an intermediate phase is formed when using DMF or DMSO. In these cases a PbI$_2$-(solvent)-MAI species formed as an adduct [9, 55]. The presence of the remaining solvent makes the precursor phase have high ion mobility. Then, another heat treatment will be conducted and afterward, the remaining solvent is removed and the perovskite is crystallised. The final film produced can vary, from full surface coverage to sponge-like disrupted film as the morphology of the perovskite film produced is influenced by aspects such as the viscosity of the solvent, the temperature and heating time [56]. Furthermore, the morphology of the perovskite formed can be improved by using halide mixtures, such as adding chloride to the iodide-based precursor solution by using PbCl$_2$. A 3:1 molar ratio of MAI to PbCl$_2$ is often used to ensure that the appropriate final stoichiometry of CH$_3$NH$_3$PbI$_x$Cl$_{3-x}$ is achieved [38]. A thorough analysis of the crystallisation process indicates that the perovskite forms an intermediate organolead mixed halide phase. Later, chlorine evaporation through heat treatment transforms this phase into a pure perovskite phase [57, 58]. There are almost no chloride left in the samples obtained from PbCl$_2$ and MAI [58, 59]. Because of the presence of the chloride ions and the excessive organic MAI compared to lead cations in the solution, it delays the rate of crystallisation. This causes large, continuous crystal domains to grow within the film, resulting in a high degree of surface coverage (fig. 2.7a).

It also worth noting that the use of lead acetate (Pb(Ac)$_2$) as the precursor salt (fig. 2.7e) produces more homogeneous and smoother MAPI layers. Moreover, films prepared from PbI$_2$ and PbCl$_2$ are non-continuous and have large gaps in between perovskite clusters as well as inconsistent thickness (fig. 2.7a, b, c, d) [60]. On the other hand, the films prepared from Pb(Ac)$_2$ are very smooth and show an almost complete surface coverage as well as high consistent thickness of film over the substrate (fig. 2.7e, f). The films were smooth due to the perovskite crystals’ rapid crystallisation with a high rate of nucleation. In this light, the evaporation of the MA(Ac) occurred at a lower temperature and needs only a temperature of 97 °C to sublime [60], whereas, MACl and MAI sublime at higher temperature and evaporate at 226 °C and 245 °C, respectively [60]. Thus, the type of
2.6 How to control perovskite morphology?

lead precursor has a significant influence in the evaporation behaviour as well as the crystallisation dynamics. This causes significant differences in the morphology. For each lead precursor, the efficiencies recorded for the optimised solar cells have the same trend as the surface coverage and the morphology of the thin films. As shown in table 2.1, the film with the higher coverage film recorded the highest efficiency.

![Figure 2.7: Comparisons of SEM morphology with difference selection of lead precursors (a) PbCl₂, (b) PbI₂ and (c) PbAc₂ together with their respective SEM cross-section using different lead source. Figure a-f is reproduced from Ref [60] with permission from the Nature Publishing Group.](image)

<table>
<thead>
<tr>
<th>Lead precursor</th>
<th>Grain size (approx.)</th>
<th>Surface coverage (approx. %)</th>
<th>PCEmax (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbI₂</td>
<td>100 - 500 nm</td>
<td>70</td>
<td>9.3</td>
</tr>
<tr>
<td>PbCl₂</td>
<td>10 - 50 µm</td>
<td>80</td>
<td>12.0</td>
</tr>
<tr>
<td>Pb(Ac)₂</td>
<td>0.5 - 1 µm</td>
<td>100</td>
<td>14.0</td>
</tr>
</tbody>
</table>

*a The SEM images were investigated through imageJ software analysis to estimate for surface coverage from Ref [60]. The surface coverage analysis was done according to the procedure described in section 3.3.4.*
2.6 How to control perovskite morphology?

2.6.2 Stoichiometric-dependent crystallisation

The different molar concentrations of the perovskite precursor mixture ratio that are used in producing the perovskite films generally influence their crystallisation behaviour. Usually, the molar ratio of either 1:1 or 1:0 (PbI\(_2\) : MAI) is used to prepare the MAPI [61]. Here, the 1:1 ratio [37] represents the one-step deposition, while the 1:0 ratio represents the well-known two-step (2-s) deposition method. This 2-s method requires MAI immersion as an additional step to form the final MAPI film [8]. Until now, there are still limited studies on how different PbI\(_2\) : MAI molar ratios affect the final morphologies of the films formed. On the other hand, it has been acknowledged that this variation in this precursor mixture ratio will cause differences in volume expansion of MAPI during formation stage that give rise to different final MAPI morphologies [62].

A study by Zhang et al. used a novel composition precursor PbI\(_2\) + \(x\)MAI which comprised of mixed PbI\(_2\) and partial MAI [62]. In their study, \(x\) was varied from 0.1-0.3M to replace the pure PbI\(_2\) used in the two-step solution deposition. Compared to the conventional two-step approach that uses 100\% PbI\(_2\), when MAI was introduced in the first step, MAPI formation was 10 times faster and no PbI\(_2\) residues were observed during the second step (MAI dipping). The study claimed that the MAPI film morphology was influenced by the amount of MAI utilised in the PbI\(_2\) + \(x\)MAI precursor films during the first step deposition with relatively smoother films were obtained when 0.1-0.2 MAI was used. Figure 2.8a-d show the SEM images of the top views of the PbI\(_2\) + \(x\)MAI (\(x = 0.1, 0.15, 0.2,\) and 0.3) precursor films. In comparison to the pure PbI\(_2\) film, these films have very different morphologies which might vary according to the amount of MAI used in the precursor. Here, putting MAI into PbI\(_2\), \(x \leq 0.2\) creates PbI\(_2\) + \(x\)MAI film that was smoother and had lesser pinholes compared to the pure PbI\(_2\) film. This morphology was almost similar to vapour-phased deposited films. The work reviewed above used lower \(x\) values compared to what were used in this study (later).
2.6 How to control perovskite morphology?

2.6.3 Solvent-induced crystallisation

Solvent-induced crystallisation is when an anti-solvent (non-soluble) is introduced to the initial wet film of the perovskite precursor mixture during spincoating to accelerate crystallisation [63]. An anti-solvent such as toluene or chlorobenzene is spincoated on top of spinning precursor solution to induce the perovskite forming stage. Here, the precursors film become insoluble and wet which contains excess solvent is forced to evaporate and the perovskite layer is rapidly crystallised. In their work on the solvent engineering approach, Jeon et al. used GBL/DMSO mixture to dissolve the perovskite precursors before spin-coating on a 200 nm thick mesoporous TiO$_2$ layer [9]. During the next spin-coating step, the film, which was still wet, was treated with a toluene drop (fig. 2.9a). This is to allow the precursors to be precipitated out of the GBL/DMSO solution, as well as to allow crystallisation of the PbI$_2$/MAI/DMSO adducts. Then, when the film was heated at 100 °C and DMSO was completely removed. Consequently, they obtained an extremely smooth film with crystallites with size more than 500 nm (fig. 2.9b).

Xiao and his team used the same approach to prepare MAPI layers with exceptional smoothness [64]. In their work, chlorobenzene (CBZ) was chosen and dropped on the still
spinning film 4-5 seconds after the precursor was deposited from the DMF to induce rapid crystallisation. The addition of CBZ strongly decreases the solubility of the precursors in the DMF phase. This process is different from the conventional spin-coating procedure; where evaporation of the solvent slowly induces the crystallization and the crystal grow slowly over a longer time period. An extremely smooth film with micrometer-sized grains, as shown in fig. 2.9c was produced due to the presence of a large number of simultaneously created nuclei and the rapid growth of the crystals in the fast deposition conversion (FDC) procedure.

Figure 2.9: (a) Shows solvent engineering procedure for preparing the uniform and dense perovskite film. Comparisons of SEM morphology with difference ‘anti-solvent’ method (b) toluene dripping [9], (c) chlorobenze dripping via fast deposition conversion (FDC) procedure [64], and (d) solvent-solvent extraction (SSE) method [65]. Note that, MAPI perovskite was used for all method described above. Figures are reproduced from stated references with permission from their publishers.

Zhou et al. presented another ‘anti-solvent’ approach [65]. This process is known as solvent-solvent extraction (SSE) which is useful in preparing exceptionally smooth perovskite thin films containing grain sizes of approximately 200 nm (fig. 2.9d). In this process they dissolved the precursors in the high boiling solvent (202 °C) N-methyl-2-pyrrolidone (NMP). The use of this high boiling temperature solvent ensured there was some solvent remaining in the film after the spin-coating process. Then, they immersed the still wet film
2.6 How to control perovskite morphology?

in a bath of diethyl ether at room temperature where the precursors and the perovskite are not soluble. The presence of ether enables the extraction of the NMP from the wet film. This led to the rapid supersaturation of the liquid film and a large number of perovskite nuclei were formed. All of these procedures enable the formation of films with very high surface coverage and comparably large crystal grains (see table 2.2).

Table 2.2: Summary of morphologies of different solvent-induced crystallisation routes and their respective solar cell performance (PCE) from fig. 2.6.

<table>
<thead>
<tr>
<th>Route</th>
<th>Solvent(s) used</th>
<th>Grain size (approx.)</th>
<th>Surface coverage (%)</th>
<th>PCE$_{\text{max}}$ (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anti-solvent</td>
<td>Toluene</td>
<td>500 nm</td>
<td>100</td>
<td>16.7</td>
<td>[9]</td>
</tr>
<tr>
<td>FDC</td>
<td>DMF/CBZ</td>
<td>1 µm</td>
<td>100</td>
<td>13.9</td>
<td>[64]</td>
</tr>
<tr>
<td>SSE</td>
<td>NMP/ether</td>
<td>500 nm</td>
<td>100</td>
<td>15.2</td>
<td>[65]</td>
</tr>
</tbody>
</table>

* The SEM images were investigated through imageJ software analysis to estimate for grain sizes. The estimation was done according to procedure described in section 4.3.7.

* FDC - Fast deposition conversion, SSE - Solvent-solvent extraction.

2.6.4 Heat-dependent crystallisation

One way to ensure the smoothness of the final film is through preheating the solution and the substrate to induce rapid crystallisation of the lead precursor [66]. The lead precursor film (if using the 2-step method) is then immersed in MAX salt solution (e.g. MAI, MABr, etc) in isopropanol (IPA) where the lead precursor is insoluble in IPA. The organic and halide ions from the immersion bath can diffuse through the lead precursor layer to induce the crystallisation of the perovskite phase [67]. In this regard, fine-tuning the temperature and the concentration of the solution is necessary to obtain full surface coverage and complete conversion as these parameters influence the diffusion speed of the ions and the crystallisation rate of the perovskite [68]. Solar cells have a higher PCE when the crystals are larger in size. In this regard, larger grains have lower trap states and recombination as they have fewer grain boundaries [44]. Work by Xiao has provided a thorough discussion of this phenomena [69]. Xiao et al. introduced an additional step of solvent annealing (SA) after the perovskite has been deposited. This created micrometre-sized perovskite
2.6 How to control perovskite morphology?

grains covering the whole thickness of the sample [70]. Thermally annealed (TA) films (fig. 2.10a) showed a significant increase in performance from average efficiencies of 8% to 14.8% after undergoing the SA step (fig. 2.10b). This study was extended by Nie et al. with the aim to produce millimetre-sized grains by spincoating the precursor solution on a hot substrate [44]. Consequently, the process prolonged the growth period of the perovskite crystals due to the presence of excessive solvents with high-boiling point combined with the high temperature above the super-saturation point. Notably, even without any post-annealing process, Fang et al. fabricated device based on hybrid of high-boiling (HB), DMAc/NMP co-solvents and anti-solvent (AS) method that could reach the PCE of 17.09% [71]. Table 2.3 summarise the PCE obtained with different routes of heat treatment procedures.

![Figure 2.10: Show different approach of heat treatment process (a) Thermal annealing (TA), (b) TA and solvent anealing (SA), (c) high-boiling solvent (HB) + anti solvent method (AS) + SA, and (d) Hot-casting (HC) + HB. The Refs A and B [72], C [71] and D [44] are reproduced with permissions.](image-url)
2.6 How to control perovskite morphology?

Table 2.3: Summary of morphologies of different heat-treatment crystallisation approaches and their respective solar cell performance (PCE) from fig. 2.7a.

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Solvent(s) used</th>
<th>Temp. (°C)</th>
<th>Grain sizeb (approx.)</th>
<th>Surface coverage(%)</th>
<th>PCE\textsubscript{max} (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA</td>
<td>DMF/DMSO</td>
<td>100</td>
<td>100 - 500 nm</td>
<td>100</td>
<td>10</td>
<td>[72]</td>
</tr>
<tr>
<td>TA + SA</td>
<td>DMF/DMSO</td>
<td>100</td>
<td>500nm - 1.5 µm</td>
<td>100</td>
<td>15.6</td>
<td>[72]</td>
</tr>
<tr>
<td>HB + AS + SA</td>
<td>DMAc/NMP</td>
<td>0</td>
<td>200 - 500 nm</td>
<td>100</td>
<td>17.09</td>
<td>[71]</td>
</tr>
<tr>
<td>HC + SB</td>
<td>DMF/NMP</td>
<td>180</td>
<td>0.5 mm - 1 mm</td>
<td>100</td>
<td>19.9</td>
<td>[44]</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Thermal annealing, SA = solvent annealing, HB = high-boiling point solvent, AS = Anti-solvent method, and HC = hot-casting method.

\textsuperscript{b} The SEM images were investigated through imageJ software analysis to estimate for grain sizes. The estimation procedure was described in section 4.3.7.

2.6.5 Additive-controlled crystallisation

Using additives in the spin-coating solution is another approach that could ensure homogeneous films are formed. Over the last few years, researchers have devised different perovskites which were formed by adding polymers, fullerene, metal halide salts, organic halide salts, inorganic acids, solvents, and nanoparticles [73]. It is believed that the additives could enhance device performance as the distribution of additives at the grain boundary could passivate the perovskite and decrease non-radiative recombination [73].

The addition of small amounts of methylammonium chloride (MACl), a common organic halide salt, or the phosphonium halides; tetraphenylphosphonium iodide and chloride (TPPI and TPPCl) into the spin-coating solution for the MAPbI\textsubscript{3} perovskite also can significantly improve the homogeneity of the film. The presence of TPPI/TPPCI free ions enhances the growth kinetics, causing more crystal nuclei to grow, creating smoother and more efficient solar cells.

Furthermore, adding dihalide alkanes, like 1,8-diiodooctane (DIO) or the 1,4-diiodobutane (DIB) could significantly increase the solubility of perovskite precursor and reduce the rate of perovskite crystallisation of the during the annealing process. As a result, homogenous films with large crystals are formed as the process is much slower. Similar result can be obtained by enhancing the precursor solubility. This can be done by adding solvents to the
reaction mixture, for example in the formation of FAPbI$_3$ and MAPbBr$_3$. Here, HI was usually added to FAPbI$_3$ while HBr was added to MAPbBr$_3$ [73].

Moreover, adding easily removable species, like ammonium or phosphonium halides could accelerate the crystallisation reaction and induce a high number of crystal nuclei to grow on film. On the other hand, adding less volatile species like the dihalide alkanes or aqueous acids could reduce the speed of the reaction, hence, fewer crystal nuclei grow exceeding 1 $\mu$m [74].

2.7 Perovskite solar cells device engineering

As described in section 2.5.1, HOIP in PV has been used initially to replace the dyes in DSSC. In a typical DSSCs structure, several microns-thick mesoporous TiO$_2$ (mp-TiO$_2$) has been used as a scaffold layer. Here, the dye is used to coat the TiO$_2$ layer and becomes the main light harvester unit. The liquid electrolyte with a redox couple makes contact with the electrodes. The electrolyte acts as a hole collector while the mp-TiO$_2$ transports the electrons. However, perovskite dissolves in liquid electrolyte [5] hence, researchers have moved their focus towards the solid-state hole conductor leading to a new PSCs device engineering described in the next sections.

2.7.1 Device architectures

Numerous researchers, particularly those researching thin film solar PV have paid great attention to this development. Earlier studies developed a planar device structure with the electron transport material (ETM) and hole transporting material (HTM) were sandwiched between the HOIP [75]. These planar structures can be further classified into the conventional n-type, intrinsic, p-type semiconductors (N-I-P) and the inverted p-type, intrinsic, n-type (P-I-N) structure depending on which HTM is encountered first by the light (see fig. 2.11). Researchers have also developed the mesoscopic P-I-N structure. A device’s architecture determines which types of ETM or HTM are being used, as well as the processing method used for depositing the perovskite light absorbing material.
Conventional N-I-P junction

The mesoscopic N-I-P junction as illustrated in fig. 2.11a, is very well-known, widely used structure for producing high-performance perovskite solar cell. Its structure comprises TCO cathode (normally FTO), a 50-100 nm hole-blocking layer (e.g. bl-TiO$_2$), as well as 100-500 nm mesoporous metal oxide (mp-TiO$_2$) that is filled with perovskites and has a capping layer with a thickness of 300-450 nm. It is believed that the mesoscopic layer could improve the charge collection and allow efficient electron injection as it reduces the transport distance. Consequently, a layer of 150-200 nm hole transporting material (HTM) is then topped onto the layer. This is then followed by 70-100 nm metal contact with either Au or Ag.

The earlier mesoscopic perovskite devices have thicker light absorbing layers (>500 nm) which efficiently absorb the incident light [38], but the pores on the layers confined the perovskite to freely grows. This leads to disordered and amorphous phases that caused low open-circuit voltage ($V_{OC}$) and short circuit current density ($J_{SC}$) [76].

Unexpectedly, crystallinity in the perovskite absorber layer could be improved by reducing the mesoporous layer to $\sim$150 to 200 nm [8]. This could improve device performance and efficiency as well as reducing the material cost. Moreover, the pore filling fraction and surface morphology of the perovskite capping layer is significantly influenced by the thickness of the scaffold (mp-TiO$_2$ or mp-Al$_2$O$_3$) [38]. Hence, reducing the scaffold thickness can improve pore filling. It can also optimise the interfacial connection and
charge transport between perovskite absorber and the electron transport layer (ETL) [77]. An adequate coverage of the capping layer also can be achieved. As a result, this could enhance the fill factor (FF) and avoid short-circuiting. Recent literature has recorded the efficiency value of 20.2% (certified) from a perovskite nanocrystal embedded in the porous TiO$_2$ layer [78]. The crystal has a dense and uniform capping layer.

The planar N-I-P structure as shown in (fig. 2.11b) is chosen when researcher opted to go for low cost production. Recently, researchers had considered that charge extraction at HTM is significant for high-efficiency perovskite devices. This is because compared to the electron extraction at the ETM interfaces, the hole extraction at the HTM interfaces is more important [79] to avoid recombination. Now, high efficiencies can be achieved without a mesoporous layer by carefully control the perovskite absorber formation as well as the interfaces between the perovskite, carrier transport layers, and electrodes. To date, the best efficiency for planar N-I-P devices of approximately 19.3% has been recorded [80] after the optimisation of electron selective ITO:TiO$_2$ layer.

In this regard, unlike other device architecture with the same materials and approach, it is known that the planar N-I-P device could boost $J_{SC}$ and $V_{OC}$. However, the planar N-I-P normally exhibit more J-V hysteresis [78], thus, to overcome this issue, researchers have come up with different approaches, including depositing a thin mesoporous buffer layer filled and capped with perovskite.

**Inverted P-I-N Junction**

When the P-I-N structure (fig. 2.11c) is chosen, the deposition order is changed where the HTM is deposited first followed by the perovskites. Here, the perovskites are deposited on a 50 to 80 nm p-type conducting polymer. One example of such polymer is poly(3,4-ethylenedioxythiophene)poly(styrene-sulfonate) (PEDOT:PSS) which is deposited on ITO-coated substrates. To complete the device, 10 to 60 nm organic hole-blocking layer of 6,6-phenyl C61-butyric acid methyl ester (PCBM) and a metal cathode (Al or Au) were used after a 300-nm perovskite thin film is deposited.
Over the last years, the use of more advanced material preparation methods, including the multicycle solution coating process has increased the efficiency of the planar P-I-N device, and so far, the best efficiency recorded is 18.9% [81]. Consequently, the recent development of the P-I-N device structure has allowed the use inorganic materials for electron/hole selective contact. A recent study used NiO and ZnO / TiO\textsubscript{2} layers as the hole and electron selective contacts, respectively. This has differentiated the perovskite device from other devices made from organic materials [82].

The use of inorganic charge extraction layers represents a potentially important development that can increase the possibility of commercialisation. One example is the use of NiMgLiO and TiNbO\textsubscript{2} to produce large (1 cm\textsuperscript{2}), high-efficiency (15%) perovskite cells [83]. Moreover, the use of oxide HTM allows the construction of mesoscopic P-I-N device structure (fig. 2.11d), where NiO/mp-Al\textsubscript{2}O\textsubscript{3} or compact-NiO/mp-NiO are used as the HTM. Here, the highest PCE of 17.3% was recorded by a mesoscopic P-I-N device with a nanostructured NiO film [84].

### 2.7.2 The preparation of perovskite solar cells

The proceeding sections present a detailed discussion on the PSCs component. This discussion will focus on the conventional mesoporous P-I-N structure. Consequently, this widely used architecture has been chosen to construct the device in further chapters.

**The metal oxide blocking layer**

A thin metal oxide blocking layer is required for a PSC to function properly. This is to avoid the anode sides (TCO and TiO\textsubscript{2}) and cathode sides (HTM and metal contact) to make contact with each other. Both the mesoporous film and blocking layer are made from TiO\textsubscript{2} as the metal oxide blocking layer and the mesoporous metal oxide film are usually made from the same material. Theoretically, the best hole-blocking layer is those with maximum thinness and could cover the TCO fully. While in practice, the layer should be as thick as possible so it can cover the whole surface. In this light, the thickness of the layer is strongly dependent on how it is being deposited. There are several techniques
used to deposit compact TiO$_2$, one of the most popular methods is by spray pyrolysis [85] and spincoating [50]. Both of these methods are simple, inexpensive and have relatively good coverage. Researchers could control how thick the blocking layer film is by using different concentration, viscosity and spin speed. There are several studies that discussed how these parameters affect the thickness of the resulting layer [56, 86]. In general, most TiO$_2$ compact layer prepared by spin-coating and spray-pyrolysis will have the thickness of between 20–100 nm. The lower concentration of spray/spin solution will give a thinner film.

The mesoporous metal oxide film

For this study, TiO$_2$ was chosen as the materials for the mesoporous photoanode layer as it is readily available, inexpensive and has no toxic elements. The TiO$_2$ functions as a scaffold for the light absorber material (perovskite) transporting the electron from the perovskite layer to the conductive substrate. It also has a wide band gap of approximately 3.2 eV which makes it fit numerous device architectures [87]. Furthermore, TiO$_2$ is n-doped as there are oxygen vacancies [88]. TiO$_2$ is present in three different phases: anatase, rutile and brookite. The rutile phase is thermodynamically stable at room temperature but this phase only occurs at temperatures exceeding 650 °C. This has limited the use of rutile TiO$_2$ due to large crystal size and need higher temperature which means it will incur more cost to fabricate.

Ideally, the mesoporous TiO$_2$ should have optimum thickness so that the perovskite can absorb the solar spectrums efficiently and not lose its ability to transport electron. Researchers have maximised the contact of the perovskite active area with photoanode by structuring the TiO$_2$ nanoparticles (NP) [89]. Furthermore, space should be given in order for the perovskite to be perfectly crystallised in such confined pores. This is possible by increasing the surface area of the mesoporous metal oxide film by varying the particle size. The smaller the particulate size, the smaller overall pore size, hence the smaller surface area. However, too large surface area could lead to improper perovskite growth. Thus, the balance between two parameters should be achieved so that perovskite could
penetrate efficiently (and sufficiently) into the layer while creating proper capping layer. To date, mesoporous films composed of metal oxide nanoparticles have achieved the highest power conversion with an average particle diameter of around 20 nm. On average, the pore diameter range between (20 - 40 nm) or could be larger [90].

Other studies have also investigated other wide band gap materials such as ZnO [91] and Al₂O₃ [92]. These materials are interesting as they have lower annealing temperature and higher charge carrier mobility [93]. There is also a report showing that, treating the mesoporous electrode in TiCl₄ aqueous solution could improve the performances of perovskite photovoltaic devices [94]. There are several factors that contribute to this improvement. These include the increase in the electron injections, a reduced electron-hole recombination and higher perovskite loading in the mesoporous TiO₂ films.

A study by Marchioro et al. has examined how the TiCl₄ treatment [95] affects the electron transfer dynamics. Here, the treatment of TiO₂ with chlorine enhances the necking between metal oxide nanoparticles and consequently, gain better mechanical strength and electron injection. In addition to the TiCl₄ treatments, there are numerous studies that coated the mesoporous TiO₂ with an insulating oxide, insulating chlorines or polymers to reduce the recombination [96, 97].

**The hole-transporting material**

The hole transporting material (HTM) is deposited on top of perovskite light absorbing layer. Here, the photo-charges generated are carried away from the active layer towards the metal contact of the solar cell by the HTMs. Past studies have explored the use of various materials ranging from polymeric organic semiconductor to inorganic semiconductors in research grade perovskite solar cells. The two commonly used HTMs are, 2,2’,7,7’-tetrakis-N,N di-para-methoxyphenylamine-9,9’-spirobifluorene (spiro-MeOTAD) and polyhexythiopene (P3HT). Figure 2.12 illustrates the molecular structure of the spiro-MeOTAD and P3HT.
The use of spiro-MeOTAD as HTM in perovskite solar cell has been favoured by the PV community, particularly when there is a demand for high PCE since it was first introduced by Bach et al. to their SSDC device [98]. The conductivity of spiro-MeOTAD thin films is strongly influenced by whether there are any additives and/or p-dopants. Spiro-MeOTAD is usually deposited by spin-coating. In this light, the Spiro-MeOTAD is an amorphous organic p-type semiconductor with glass transition temperature of 121 °C and a large band gap. The colourless thin films can be obtained from the solutions by casting. It is highly soluble in organic solvents such as toluene and chlorobenzene. There are several additives such as 4-tert-butylypyridine (TBP) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) that are frequently included in the spin-coating formulation. There are reports that the presence of TBP could change the perovskite’s conduction band and slow down the electron-hole recombination which results in the improvement of the open circuit voltage [99]. Meanwhile, when Lithium ions are added to the HTM, the perovskite’s conduction band is usually moved downwards [100]. This increases the electron injection which leads to enhanced $J_{SC}$. In addition to their influence on the perovskite’s surface properties, the additives can improve the charge transport in the bulk HTM. A study by Snaith et al. has extensively examined how LiTFSI affects the ‘hole’ mobility and conductivity of spiro-MeOTAD by accelerating oxygen oxidation which can be termed as the ‘photo-doping’ [101].
2.7.3 Solar cell characterisation

This section provides the important standard measurement of a perovskite solar cell. The components involve in this measurement are the reference solar irradiance, J-V sweeping using an external bias, as well as the measurement of a quantum efficiency.

Reference solar spectral irradiance

The solar spectrum employed in the measurement is one of the most significant parts of the standard perovskite solar cell characterisation. The American Society for Testing and Materials (ASTM) has standardised the spectral irradiance which has been widely used among PV researchers. The black spectrum in fig. 2.13 illustrates the extra-terrestrial solar spectrum or the Air Mass Zero (AM0) as defined by the ASTM E-490 standard [102]. ‘Air Mass’ is a unit which signifies the spectrum path length where light has to travel horizontally through air comprising of the temperature, humidity and pressure levels. The AM0 has no extra-terrestrial irradiance, where the irradiance integration is equal to 1366.1 W/m². As it passes through the earth’s atmosphere, scattering and absorption decrease the solar irradiance. After going through the scattering and absorption, the attenuated solar spectrum reaches the earth’s surface. This is illustrated through the red spectrum in fig. 2.13 which is denoted as AM1.5G in accordance to the ASTM G-173-03 standard. This standard includes ‘1.5’ with the Air Mass at zenith angle of 48.19 °, with specific atmospheric condition and tilts at 37°, towards the equator. The ASTM G-173-03 standard also depicts the hemispherical global (G) irradiance consisting of both direct and diffused light [102]. The AM1.5G standard integrated spectral radiance is 1000.4 W/m².
Current-voltage characteristic

The current density-voltage (J-V) of the device can be used to evaluate the performance of a solar cell. This process applies the external voltage across the solar cell and measures the current response. The J-V characteristic curve is normally measured in the dark and under illumination. Here, reverse bias is represented by the electrons injected from the counter electrode (metal contact, Au) side while the forward bias depicts the potential bias injected into the device from the photoanode side (FTO/TiO$_2$) [103]. The ideal solar cell during the dark measurement illustrates typical diode behaviour and the corresponding J-V curve measured known as the dark current curve. As an example, a normal P-I-N junction perovskite solar cell, at low applied voltage, no or very little current can flow through the metal oxide (TiO$_2$) semiconductor. As a result, the multimeter or potentiostat detects no or limited current. When the voltage is increased, this will increase the charge density and raise the quasi Fermi level in the TiO$_2$ [104]. Consequently, the dark current dramatically increased in the junction where the electron can flow freely to the HTM as the quasi Fermi level reached the TiO$_2$ conduction band. The electrons then recombine with holes and flow to the metal back contact then to the external circuit. Meanwhile, similar electron-hole recombination process controls the light current. This causes photo-generated charge
carriers to be lost under the illumination. During the standard AM1.5G illumination, the photocurrent flows in an opposite direction of the dark current as the solar cell now acts as the current source (See fig. 2.14).

![Figure 2.14: a) A typical dark J-V curve of a solar cell. b) A typical J-V curve of a solar cell measured under illumination. c) The black dot on the J-V curve marks the point where the electrical power output is maximum and also shows the fractional between those maximum parameters which is also known as FF.](image)

The J-V curve shape is controlled by the generation of photocurrent and the electron-hole recombination [105]. When there is no or limited potential bias, most charge carriers are collected before they recombine. At this point, regardless of the applied potential, the photocurrent charge carriers move almost independently. Here, the short circuit photocurrent, \( J_{SC} \), occurs when there is no potential being applied and the solar cells act as sole current supply. After the voltage is further increased, there is more recombination as the photocurrent carrier charge gradually decreases and lost its kinetic energy [106]. Consequently, the J-V begins declining to the point where there is no photocurrent flows anymore and all of the charge carriers are recombined. This limiting point is referred to as the open-circuit voltage potential, \( V_{OC} \).
There are also other parameters that can be obtained from the J-V characteristic. This includes the power conversion efficiency (PCE). Equation (2.3) is used to define the PCE.

\[
FF = \frac{J_{MPP}V_{MPP}}{J_{SC}V_{OC}}
\]  

(2.1)

\[
Efficiency, \eta = \frac{P_{el}}{P_{in}} = \frac{J_{MPP}V_{MPP}}{P_{in}}
\]  

(2.2)

\[
\eta = \frac{J_{SC}V_{OC}FF}{P_{in}}
\]  

(2.3)

According to the equation, PCE is the fraction of incident power, \(P_{in}\) that is transformed into electrical power, \(P_{el}\), which is obtained from the power curve. Here, the electrical power is defined as the product of \(J\) and \(V\). The maximum power point (MPP) depicts the maximum power curve while \(J_{MPP}\) and \(V_{MPP}\) denote the corresponding voltage and current.

The fill factor (\(FF\)) is another significant parameter of the solar cell. It describes the ‘squareness’ of the J-V curve and represents the ratio between the \(J_{MPP}\) and \(V_{MPP}\) product and \(J_{SC}\) and \(V_{OC}\) product based on eq. (2.1). Figure 2.14c illustrates that \(FF\) is presented as the ratio between the two rectangles spanned by the product of \(V_{MPP}\) and \(V_{MPP}\), and \(J_{SC}\) and \(V_{OC}\). Equation (2.1) can be rewritten as eq. (2.3) by using the \(FF\) definition.

Shunt resistance and series resistance also important parameter used to troubleshoot the solar cell. Series resistance, \(R_S\) and a shunt resistance, \(R_{SH}\) can be presented by the analogous solar cell circuit to explain the resistive losses. Figure 2.12a presents the equivalent circuit with the parasitic resistances (\(R_S\) and \(R_{SH}\)). The \(R_{SH}\) is caused by the loss of currents associated with defects within the solar cell which lead to current leakage. Current leakage in the PSCs is might due to a flawed metal oxide compact layer that failed to fully prevent the photoanode (TCO), causing the photocathode (HTM) to make contact, hence the short circuiting. Figure 2.15b and c schematically depicts how the \(R_S\) and \(R_{SH}\)
2.7 Perovskite solar cells device engineering

affect the J-V characteristics of a solar cell. The figure also shows that the decrease of the FF of the device is caused by either the increase in $R_S$ or a decrease in $R_{SH}$ or combination of both.

![Figure 2.15](image)

**Figure 2.15**: (a) Equivalent circuit of a solar cell. IL represents the solar cell after being illuminated. The influence of (b) an increasing series resistance, $R_S$ and (c) a decreasing shunt resistance, $R_{SH}$ on the J-V curve and FF of a solar cell [106]. See arrows.

**J-V hysteresis**

The J-V hysteresis of PSCs has been an important issue when measuring the PCE. The hysteretic behaviours of a PSC are depending on many factors such as scan direction, scan rate, voltage range, precondition, as well as device architecture [107]. Migration of iodide ions is believed to cause hysteresis [108] and this phenomenon is believed to include accumulation of ions at the perovskite/TiO$_2$ interface [109]. The scan rate is known to plays an important role during the bias sweeping and it determines the shape of the curves, hence the different in efficiencies. In many cases, the reverse scan always gives better curve and efficiency. For example, Christian et al. reported that the efficiency of their cells under reverse scan increases with the increase of scan rate, whereas the efficiency under forward scan decreases [110]. They also stated that hysteresis between reverse scan and forward scan will becomes more noticeable when the scan rate is increased, and the hysteresis might be eliminated by using an adequately slow scan rate. The PV performance might also be different with different starting biases and scan range.

**Quantum efficiency**

The quantum efficiency (QE) represents the fraction of incident photons that are transformed to electrons that reach the external circuit and is a function of wavelength. The
QE can be described in two ways; the external quantum efficiency (EQE) and the internal quantum efficiency (IQE).

The EQE is also known as the incident photon-to-electron conversion efficiency (IPCE). This constitutes the photons emitted from the solar simulator that come in contact with the active areas in the solar cell. This can be obtained by measuring the solar cell photocurrent under the monochromatic irradiation. The QE is a very significant measure for solar cells as it gives information on the current that a given cell will produce when illuminated by a particular wavelength. If the EQE is integrated (summed) over the whole solar electromagnetic spectrum, \( \phi(\lambda) \), one can evaluate the current \( (J_{SC}) \) that a cell will produce when exposed to the known solar spectrum according to eq. (2.4).

\[
J_{SC} = q \int \phi(\lambda).EQE(\lambda)d\lambda
\]  

(2.4)

2.8 Stability issues

Stability is an important issue for perovskite solar cells. Until now, the lack of stability hinders the prospects for their commercialisation. To overcome this, there are many ways that can be adopted to mitigate this stability issue. Characterising the perovskite film in detail can help to realise the best processing method to improve the stability. Most studies have conducted visual observation and measured the device performance over time [111]. For example, there is a study that uses ZnO as ETM and NiOₓ as HTM resulted an increase in the stability of PSCs where the considerable PCE preservation of above 80% was achieved after 60 days [28]. Meanwhile, it was also reported that the combination of TiO₂ and ZrO₂ as ETM can also help to sustain the performance over 1000 hr in ambient air. It was proposed that the inclusion of ZrO₂ can help guard the perovskite layer [112].

Adding to that, one also can easily measure the degradation process by making a visual observation on the changes of the films’ colour. A transformation to transparent, brighter film indicates less light absorption and more degradation due to materials dissociation. This can be confirmed and examined through the UV-VIS test. X-ray diffraction (XRD)
2.9 Instrumentation

This section will provide basic understanding of key instruments in determining optoelectronic properties of perovskite solar cell. Present study uses UV-VIS, photoluminescence, XRD and XPS to investigate carriers’ dynamic in PSCs while SEM to physically examine the topographic features of the fabricated layers.

2.9.1 Ultraviolet-visible spectroscopy

The optical properties of perovskite films can be examined using the ultraviolet-visible (UV-VIS) spectroscopy. This process is done to analyze the light absorption of each layer of the perovskite solar cell (PSC). In this regard, one of the factors which determine the fabrication of good PSC is the light absorbed by the light-absorbing material and the light reflected by the whole system. Thus, the UV-VIS spectrum is significant as it will determine how efficient the solar cell is in capturing the light. In a UV-VIS spectrometer, the detector measures the ratio of light transmitted (I) through the sample where it is compared with the light incident (I₀) on the sample. For a given wavelength, the absorption (A₂λ) can be calculated based on the absorbance in eq. (2.5) [114].

\[ A_{\lambda} = \log_{10} \left( \frac{I_0}{I} \right) \]  

The sample’s absorbance is presented as a graph at different wavelengths. After the acquisition of a UV-VIS spectrum, an optical bandgap (\(E_{g, opt}\)) can be obtained by using a Tauc plot [115]. Normally, the x axis represents photon energy (hv) and y axis present (\(\alpha hv\))1/r, where \(\alpha\) denotes the material’s absorption coefficient and r represents the nature of the electron transition. Here, r could have different values due to the different distributions of energy levels; r equals to 0.5 for the direct allowed transition, while r equals to 2 for the indirect allowed transition [116]. It is preferred to use a material with
a direct transition for photovoltaic applications as compared to materials with indirect transition. It is because absorbance is stronger (higher absorption coefficient which means less materials needed, hence thinner cell). Figure 2.16 presents the MAPI’s common Tauc plot derived from a UV-VIS spectrum. The figure shows that this direct transition material has a band gap of 1.51 eV.

![MAPbI3 absorbance and photoluminescence](image)

**Figure 2.16:** Steady-state absorption and photoluminescence of CH$_3$NH$_3$PbI$_3$. The inset shows corresponding Tauc plot displaying extrapolated optical band gap [85].

### 2.9.2 Photoluminescence and decay time

The photoluminescence (PL) and time-resolved photoluminescence (TRPL) method can be used to probe perovskite’s electronic structure. In this measurement, the electron-hole pairs in perovskite active layer are generated by the photons when a beam is incident to the film. Subsequently, the electrons and holes will recombine through either a radiative or by non-radiative processes. During the rapid non-radiative scattering processes, electrons and holes relax to the perovskite band edges in its quantum structures [117]. It could be observed that, in the direct bandgap materials such as the perovskite, the carrier pairs normally recombine radiatively through near band edge transitions. Thus, we can obtain useful information from the band structure and the carrier states in quantum structures of perovskite by measuring the PL spectrum. Figure 2.17a presents a schematic diagram of a
2.9 Instrumentation

PL spectrometer used in this work as well as absorption and relaxation processes leading to emission (b).

Figure 2.17: (a) Experimental setup used to determine the photoluminescence of a photo converter material. (b) Absorption and relaxation processes leading to photoluminescence [104].

PL enables the study of the mechanism determining the charge carrier dynamics within a system down to the sub-nanosecond time scale. This is because the PL of semiconductors is a direct monitor of the charge carrier dynamics. The method of time-resolved photoluminescence (TRPL) via time-correlated single photon counting (TCSPC) is used to analyse a charge carrier dynamics [118]. Such data provide times characteristic for relaxation (or decay time, $\tau$) process [119].

2.9.3 X-ray diffraction spectroscopy

A useful tool that can be used to examine the perovskite’s crystalline structure and phase is X-ray diffraction (XRD). The XRD is based on the electromagnetic waves scattering in the Angstrom range (X-rays) on structures which have almost the similar physical dimension (see fig. 2.18).
2.9 Instrumentation

Figure 2.18: Schematic representation of the scattering processes in an XRD measurement [120].

Diffraction patterns are formed as constructive interference can only occur on the materials’ periodic lattices. Bragg’s law (eq. (2.6)) is used to quantify the relationship between the angle of constructive interference and the distance between lattice planes \(d\) [120];

\[
nλ = 2dsin(θ)
\]  

(2.6)

where \(n\) denotes order of interference, \(λ\) refers to the wavelength of X-rays (usually Cu Kα: \(λ = 1.540562\) Å), \(d\) denotes the lattice spacing and \(θ\) is the angle of incidence. The structures dimension can be resolved within the range of about 0.1 nm to 20 nm, considering the angles from 0.5° to 100° (2θ).

2.9.4 Scanning electron microscopy

Scanning electron microscopy (SEM) can be used to examine the morphology and aerial topography of perovskite. An electron microscope has a high resolution which enables researchers to view minutes solar cell features that could not be resolved using an optical microscope. SEMs use of an electron beam as the illumination source which allows it to produce high resolution images (i.e. ~ 5 nm). The main components of a SEM in which electron beams are produced using a field emission gun (FEG) are shown by fig. 2.19.
The FEG produces exceptionally intense, fine beam as it has a very sharp tip made of single crystal tungsten [122]. The electrons from the tungsten crystal are pulled by the applied vacuum and the induced electric field between the cathode (tungsten) and anode. After being emitted from the electron gun, the electron beams will radiate in all directions until they pass the condenser lens that make them parallel. Then, the beam angle will change as the parallel electron beams pass through the scanning coils. This allows the location of electron spot on the sample to be changed. The objective lens focuses the electron beam to a spot with an adjustable size. It is important to note that the samples used for SEM should be conductive or they must be coated with conductive elements such as carbon or gold. This allows the scattered electrons to be collected by a detector once the electron beams hit the sample’s surface. The electrons pass through a photomultiplier in the detector and create spots on the screen. The brightness of the spot generated on the screen depends
on how dense the scattered electrons from sample surface are. The final image will be produced in form of a cluster of dark or bright spots as the electron beam is scanned over a sample. In this project, SEM is used to examine the morphology of perovskite films. Here, the presence of pinholes in the films determines the device performance [123].

2.10 Aims for project

From this chapter, it is known that the final morphology is strongly dependent on the deposition of perovskite precursor and the crystallisation behaviours during perovskite film formation. This can be affected by the selection of lead precursors (section 2.6.1) and/or anion, composition of the main reactants (section 2.6.2), selecting solvent and anti-solvent (section 2.6.3), heat treatment (section 2.6.4) as well as using additive (section 2.6.5). Hence, the main aim of this project is to realize those approaches into a simple combination approach that can control the final perovskite morphology to be used in perovskite solar cells (PSCs). In this light, we may establish the novel film fabrication methods (Chapter 3), solvent blend, halide exchange and study the new perovskite morphologies (Chapter 4 and Chapter 5). In doing so, the potential of using the architectural control of perovskite can be explored to achieve better understanding on how to improve film properties, device performance and stability of PSCs.
3

Tuning CH$_3$NH$_3$PbI$_3$ crystal growth and properties by a new combination method

3.1 Abstract

Perovskite solar cells progressively garnered huge attention due to their efficient power conversion, as well as their prospective application. In this regard, the most popular perovskite in research is CH$_3$NH$_3$PbI$_3$ or MAPbI$_3$ (MAPI). Typically, one-step (1-s) and two-step (2-s) deposition methods are used in preparing MAPI films. Often times, the morphology of the MAPI which was prepared by using these methods could vary from relatively large one-dimensional (1D) crystals to smaller three-dimensional (3D) cuboid crystals. The current research combines 1-s and 2-s deposition to produce a new MAPI film (1 & 2-s) on mesoporous TiO$_2$ photoanode structure. This 1 & 2-s involved an initial step, in which a variety of stoichiometry mole ratios (x) for the PbI$_2$ + xMAI solution were used to deposit precursor films (1-s method). Subsequently, the films were dipped in a MAI solution (2-s method) in order to produce the final MAPI films (1 & 2-s). The morphology of the final MAPI films comprised of 1D and/or 3D crystals and each type of crystal’s proportion was tuneable using x. This combined method for the preparation of the film has shown improved light scattering and photoluminescence spectra. These data revealed a systematic red-shift as the x values increased. As shown by the transient absorption spectroscopy data, the lifetime decreased as x was increased while the studies
on solar cell studies shown that there was a systematic variation in the current density, power conversion efficiency (PCE) and hysteresis index with $x$. It was observed that the interfacial area of the MAPI crystals controls the optoelectronic and device performance properties. The most optimal combination of a morphologically enriched photoactive layer, absorption and PCE (9.0%) were observed in film with $x = 0.33$. The 1 & 2-s method should apply to other perovskite formulations and the new insights concerning MAPI crystal growth conditions, morphology and material properties established in this study should also be transferable.

### 3.2 Introduction

There has been a drastic rise in the interest towards perovskite solar cells in recent years. In 2014, there were over 400 publications on perovskite, and there were over 1000 in 2015 alone [124, 125]. This is largely due to reports on the dramatic increases of power conversion efficiencies (PCE) which could exceed 20% [10]. This chapter presents a novel, combined method for preparing MAPI films. MAPI is a highly popular perovskite system [126] in current photovoltaic field. The MAPI photoactive layers can be prepared by using two fundamental deposition methods; the 1-step deposition (here we noted as 1-s) is a method that uses a solution with a stoichiometric ratio of two perovskite precursors (PbI$_2$ and MAI), as well as casting films from the solution [127]. The next method is the popular 2-step deposition (we noted as 2-s) method which comprises of sequentially depositing the PbI$_2$ onto a mesoporous TiO$_2$-coated substrate before it is dipped into a MAI solution [8]. During this process, anti-solvent additives may be used to control crystallisation [64]. The 1-s and 2-s methods result in significantly different MAPI morphologies. The morphology of MAPI produced by the 1-s is often 1D, and branch-like, while the morphology of MAPI from the 2-s method is often 3D and in cuboid shape [6, 128]. In this regard, there is no simple method which allows the preparation of intermediate morphologies with a tuneable transition from 1D to 3D morphologies even though such ability to tune the morphology of perovskites is vital both to increase the basic understanding of the relationship between interfaces and its optoelectronic properties as well as for the practical
solar cell performance optimisation [129]. Thus, this study hypothesises and proves that a combination of 1-s and 2-s method (abbreviated here as 1 & 2-s) along with reaction stoichiometry control can produce perovskite films with tuneable morphologies, as well as optoelectronic properties similar to those of 1-s and 2-s derived films.

Many studies have used 1-s method to prepare perovskite films [130–132] as it is easy and straightforward to obtain the desired stoichiometric MAPI composition. However, uncontrolled crystallisation often creates films with a high number of pinholes and has low surface coverage and this would decrease the performance of the solar cell. In contrary, the 2-s method normally produces films with less pinholes which create higher efficiencies [133, 134] however, the PbI$_2$ might not be completely converted in this process [135]. On the other hand, the remaining PbI$_2$ will reduce the light absorption and photocurrent. This remnant PbI$_2$ will also decrease recombination [136] and even increase the current density, which may increase the power conversion efficiency [137].

The present study will examine the use of a new method that combined both 1s and 2-s methods to produce perovskite photoactive layers. We termed this combination method to be 1 & 2-s. Note that the ‘&’ will only be use to refer to our new combination method. Figure 3.1 presents the general reaction sequence in the first step which involved PbI$_2$ + $x$MAI solutions and this approach has significant effects for the characteristics of films and devices. Here, $x$ represents the stoichiometric ratio of MAI used. The $x$ value of 1.0 corresponds to MAPI produced by 1-s (fig. 3.1b) while the $x$ value of 0 corresponds to MAPI from 2-s (fig. 3.1d) and as shown, the $x$ values of 0.66, 0.50 and 0.33 correspond to 1 & 2-s (fig. 3.1c). The proportions of MAPI prepared by 1-s and 2-s were tuned with the control of $x$, for instance, the $x = 0.50$ film will correspond to half of the MAPI which has been prepared using the 1-s method while the remaining half correspond to the MAPI prepared using the 2-s method.
3.2 Introduction

![Figure 3.1](image-url)  
**Figure 3.1:** (a) Overall sequence of reactions where \( x \) is the stoichiometric ratio of MAI used for the solutions. The other rows depict (b) 1-step deposition (1-s), (c) combined 1 & 2-step deposition (1 & 2-s) and (d) 2-step deposition (2-s) methods. The middle and right hand columns show photographs of precursor and final films on mesoporous TiO\(_2\), respectively. Note that, compact blocking layer of TiO\(_2\) is not included and ITO was used as substrate. For (b), which had \( x = 1.0 \), there was only a final film (and, no MAI dipping). The dimensions of the films were 20 x 15 mm.

There are only a handful of MAPI studies that explored the reaction stoichiometry of the precursor solutions. A study by Zhang et al. investigated mixed PbI\(_2\) and MAI solutions at specific MAI mole proportions to prepare planar MAPI films. These films were deposited and then dipped into a MAI solution [62]. In contrast to their method, this present study will use higher \( x \) values. Moreover, Zhang et al. did not use a mesoporous TiO\(_2\) coated ITO substrate and a perovskite was not formed before dipping the films in the MAI solution. On the other hand, in the process described in this report, an initial (precursor) perovskite film with excess PbI\(_2\) was formed before the films were dipped into the MAI solution (fig. 3.1c). Meanwhile, a study by Roldán-Carmona et al. [137] aimed to obtain devices with high efficiency by using the 1-s method combined with non-stoichiometric ratios of...
PbI$_2$ to MAI and anti-solvent devices. However, similar to Zhang et al., a relatively low $x$ values also were used and the films were not dipped into a MAI solution during the second step.

Over the years, the perovskite film engineering has faced a significant challenge to obtain perovskite films that have controlled, and highly tuneable morphologies [6, 44]. In this regard, MAPI films’ crystallisation behaviour is highly influenced by aspects including the type of surfaces, solvents/additives used and the deposition methods such as spincoating, thermal evaporation or chemical vapour deposition [129]. Thus, this report presents a novel and straightforward approach which allows MAPI morphologies to be tuned and enabled the investigation of the relationships between the film morphology and optoelectronic properties. The morphology of MAPI films was investigated using optical microscopy and SEM. EDX was used to probe the PbI$_2$ whereabouts within the active layer. UV-visible, photoluminescence and TAS data were obtained for the films and the effects of morphology established. We also prepared solar cell devices to study the relationships between morphology and the device performance. It is demonstrated that the combination of the 1 & 2-s method was able to bring deliberate control on the optoelectronic properties, film morphology, and MAPI solar cells performances. Moreover, this study has identified a morphologically-enhanced system that allows a device to obtain a good PCE. This novel and facile combined approach could also enable the achievement of different variation and tuning of the morphologies for other perovskite films and devices.
3.3 Experimental procedure

The study focuses on fabricating perovskite films by using the new 1 & 2-s combination methods and characterise their optoelectronic properties. The devices are fabricated to investigate their performance and relate those data with the crystal growth and morphologies. The key procedure can be separated into three phases; materials preparations, perovskite films preparations and device fabrications.

3.3.1 Materials

Isopropanol (IPA, anhydrous, 99.5%), methylamine (> 98%), HI (99.95%, 57 wt% solution in water), 4-tert-butylpyridine (96%), lithium bistri fluoromethanesulfonimidate (LiTFSI, 99.95%), PbI$_2$ (99.999%), N,N-dimethylformamide (DMF, anhydrous, 99.8%), and poly(3-hexylthiophene) (P3HT, $M_n = 54,000$-$75,000$), titanium diisoproxide bis(acetylacetonate) (TDB, 75 wt % in IPA) were all purchased from Aldrich and used as received. 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-MeOTAD, Fenglin Chemicals, 99.5%) was also used as received.

3.3.2 Perovskite film preparation

MAI was synthesised according to the method reported elsewhere [138]. This involved the dropwise addition of 30 mL of aqueous HI solution (57 wt %) to 27.9 mL of an aqueous solution of methylamine (40 wt %) in an ice bath with stirring. The cold solution was stirred for 2 h, and the solvent was evaporated using a rotary evaporator. The crystals were washed using diethyl ether three times and dried in vacuum oven. ITO/Glass slides (2 cm × 1.5 cm) were cleaned by sonication in a 1% Hellmanex solution in boiling water for 15 min followed by rinsing with water and IPA and cleaning in ultrasonic for 5 min and dried using a nitrogen stream. Titania paste (Dyesol 18-NRT, 70 µL, 1:5 in ethanol) was spin-coated onto the cleaned glass slides at 5000 rpm for 30 s to form a 250 nm mesoporous scaffold (mp-TiO$_2$). The films were then annealed at 500 °C for 30 min. Next, solutions of PbI$_2$ + $x$MAI in DMF containing PbI$_2$ (1.0 M) and $x = 0, 0.33, 0.50, 0.66, 1.00$ M of MAI were spin-coated onto the mp-TiO$_2$ layer (Figure 1). Note that $x = 0$ and 1.0
correspond to the 2-s and 1-s methods, respectively. The values $x = 0.33$, 0.50 and 0.66 correspond to the 1 & 2-s process. The solutions were kept at 70 °C during spin-coating. The spin-coating conditions employed were 2000 rpm for 40 s for the first step and 6500 rpm for 60 s for the second step. The films were dried at 100 °C for 15 min (or 30 min for 1-s, $x = 1.0$). The dried films ($x = 0$, 0.33, 0.50 and 0.66) were washed with IPA for 3 s and then dipped in 20 mL MAI (10 mg/mL) for 15 min. They were then dried at 100 °C for 15 min. The films were kept in a desiccator over P$_2$O$_5$ in the dark prior to investigation.

### 3.3.3 Device fabrication

The full step of fabrication can be referred to fig. 3.2. Briefly, the laser-patterned, ITO-coated glass substrates (20 Ω/sq) were cleaned by ultrasonication in a 2% Hellmanex solution, rinsed with deionized water and IPA, treated with 10% NaOH and dried. A blocking layer of compact TiO$_2$ (bl-TiO$_2$, 45 nm) was then deposited by spincoating TDB (75 µL, 0.15 M) solution in 1-butanol at 2000 rpm for 60 s. The procedure was repeated using a TDB solution (0.30 M) and the substrate was heated at 125 °C for 5 min. A mp-TiO$_2$ layer was then deposited as described above. Perovskite photoactive layers were then deposited as described above. The P3HT HTM layers (100 nm) were deposited by dynamic spincoating of P3HT in toluene (15 mg/mL) at 4000 rpm for 20 s. Following the approach of Heo et al., Li-TFSI salt and TBP in acetonitrile were added to P3HT solution [138]. The fabrication procedures were performed in ambient air (40% relative humidity). Devices were also prepared using Spiro-MeOTAD as the HTM. In that case HTM deposition followed established literature procedures [38, 139]. All devices were stored as described.
3.3 Experimental procedure

Figure 3.2: Depicts overall sequence of PSC fabrication consist of (a) deposition of photo-anode (bl-TiO$_2$ and mp-TiO$_2$). FTO was chosen as TCO due to excellent high-temperature processing for the TiO$_2$ deposition, (b) perovskite layer formation, (c) deposition of photo-cathode (HTM and Au back contact) and (d) device measurement under standard procedure.
3.3 Experimental procedure

3.3.4 Physical measurements

The surface morphologies were investigated using a Philips XL30 FEI -SEM. The accelerating voltage used was 15kV and the secondary electron (SE) detector was chosen. The EDX was used to probe the element for the materials of interest. The images from the SEM were processed and analysed using the ImageJ software. To calculate the percent coverage, a yellow outline was used to delineate the crystals from the background as depicted by fig. 3.3. The automated threshold was conducted and included only the dark black areas (pinholes). The % coverage was determined by subtracting the total pinhole area from the total area of the image and normalising the difference with the total image area.

![Image of surface morphology](image_url)

**Figure 3.3:** Example of image used for calculation of the coverage. This SEM image was obtained for the final 1 & 2-s film prepared using $x = 0.66$ and is taken from fig. 3.7. The yellow outline was used to delineate the crystals from the bare mp-TiO$_2$.

XRD data were obtained using a Bruker D8 Advance diffractometer (Cu-Kα). The films obtained were scanned between 10 and 50° with a step size of 0.02. For these measurements the films were prepared and measured under a nitrogen atmosphere. Film absorption was recorded using a Perkin Elmer Lambda 25 spectrometer. Optical images were obtained using an Olympus BX41 polarizing microscope with Olympus U-AN360-3 rotatable analyser and polariser filter. PL spectra were obtained using an Edinburgh Instruments FLS980.
3.3 Experimental procedure

Photoluminescence spectrometer. Pump-probe micro to millisecond transient absorption spectroscopy (TAS) measurements were conducted on mp-TiO$_2$/MAPI/Spiro-MeOTAD films excited by a dye laser (Photon Technology International GL-301, sub-nanosecond pulse width) pumped by a pulsed nitrogen laser (Photon Technology International GL-3300). A quartz halogen lamp (Bentham IL1) was passed through a monochromator and used to probe changes in the absorption characteristics of the films as a function of time after the laser excitation. The probe light was detected using home-built silicon ($\leq 1000$ nm) or In$_x$Ga$_{1-x}$As ($\geq 1000$ nm) photodiodes and an oscilloscope. Perovskite films were kept under flowing N$_2$ gas during the measurements. All TAS measurements employed 567 nm laser pulses (25 $\mu$J cm$^{-2}$).

3.3.5 Device characterisation

The current density-voltage (J-V) or current-voltage (I-V) characteristics were measured using the I-V solar simulator unit (fig. 3.4a) that consist of a Keithley 2420 sourcemeter and 100 mW/cm$^2$ illumination (AM 1.5G) with a calibrated NREL certified Oriel Si-reference cell. An Oriel SOL3A solar simulator was used for these experiments. The active area of the devices (representative solar cell is shown on fig. 3.4c) was defined using a square aperture within a metal mask and was fixed at 0.16 cm$^2$ housed by an Ossila PV test board (see fig. 3.4b). Forward and reverse direction sweeps were measured with a sweep rate of 100 mV/s.
3.4 Results and discussions

This section discusses results and key findings of perovskite solar cells produced by novel combination 1 & 2-s method. This new method has shown unique properties and demonstrated that PSC’s morphologies are tuneable.

3.4.1 MAPI morphology tuning using stoichiometric variances

The control of the stoichiometric ratio ($x$) was used for the PbI$_2$ + $x$MAI reaction (fig. 3.1a) and with the 1-s ($x = 1.0$), combined 1 & 2-s ($x = 0.66$, 0.50 and 0.33) or 2-s ($x = 0$) deposition to prepare varying MAPI films (see fig. 3.1b – d). The first step was producing the precursor films by spin coating the PbI$_2$ + $x$MAI solution ($x = 0$ to 1.0) on top of mp-TiO$_2$, then the film was dried at 100 °C. For $x < 1.0$, the second step comprised on converting the excess PbI$_2$ into the final MAPI film by dipping the precursor film in a MAI solution. Meanwhile, the 1-s ($x = 1.0$) film was prepared as a final film in one step (fig. 3.1b). It was observed that all of the precursor films that were prepared from the...
PbI$_2$ + xMAI solutions with $x = 0.66$, 0.50 and 0.33 all turned to dark colour prior to the final MAI dip (as shown in the middle column of fig. 3.1). The precursor films had less transparency and became yellow, which showed the presence of residual PbI$_2$. After being dipped into the MAI solution, the films’ remaining yellow colour turned to black indicating the conversion of the excess PbI$_2$ into MAPI.

A polarised optical microscopy (POM, fig. 3.5.) was used at the beginning of the study to examine the morphologies of the final MAPI films. The figure presents the polarised light optical microscopy images (fig. 3.5a – e) for different final MAPI films which have been prepared using solutions with different $x$ values (shown). In this instance, (a) corresponds to 1-s while (e) corresponds the 2-s method. Meanwhile the 1 & 2 -s combined method was used to prepare (b) to (d) (see fig. 3.1c), (f) illustrates the analyser (A) and polariser (P) directions used. The figure illustrates that the film from the 1-s method has 1D needle-like crystals (fig. 3.5a, $x = 1.0$). The crystals had lengths of more than 60 $\mu$m while their widths ranged from 2 to 5 $\mu$m. The POM images illustrate the 1D morphology for the 1-s film (fig. 3.5a) has orderly transitioned into a 3D nanocrystal morphology for the 2-s film (fig. 3.5e, $x = 0$). Furthermore, the films from the 1 & 2-s method (fig. 3.5b - d) show that when $x$ was 0.33 from 0.66, the 1D crystal shrunk and largely formed shorter, branch-like structures. The mp-TiO$_2$ exposure (pinholes) has also increased as $x$ decreased. This shows that the tuning of the morphology and capping layer coverage using the combination 1 & 2-s method by varying the value of $x$ was possible.
3.4 Results and discussions

**Figure 3.5:** Polarised light optical microscopy images (a – e) for various final MAPI films prepared with different solution \( x \) values (shown). (a) and (e) correspond to 1-s and 2-s methods, respectively. (b) to (d) were prepared using the 1 & 2-s method (See fig. 3.1). (f) Shows the Analyser (A) and polariser (P) directions used.

SEM was later used to examine the precursor films and final films for a more thorough examination of the changes in morphology. The SEM images (fig. 3.6) show the precursor films which were prepared by using the \( \text{PbI}_2 + x\text{MAI} \) solutions. The first column on the left shows the values for \( x \) used. It is worth to note that the film with \( x = 0 \) comprised only \( \text{PbI}_2 \). Meanwhile, all of the 1 & 2-s precursor films (\( x = 0.66, 0.50 \) and 0.33) have MAPI and \( \text{PbI}_2 \) mixtures. The insets show the expanded view and minute 3D nanocrystals that can be observed more closely. As shown by the precursor illustrated in fig. 3.6, one can observe significant changes in the morphology as \( x \) decreased where the length of the 1D crystal decreases and more branched morphology was formed. It could also be observed that there are no 1D crystals for the \( x = 0 \) film. In this regard, the 1D crystals formed by \( x = 0.66, 0.50 \) and 0.33 were similar to those for the 1-s (\( x = 1.0 \)) film (fig. 3.7, top row), this could indicate that these changes were caused by MAPI. The right hand column of fig. 3.6 presents the highest magnification image insets showing the presence of nanocrystals, which cover the surfaces of the large crystals. These nanocrystals show a similar feature as those observed on \( \text{PbI}_2 \) (\( x = 0 \)). Hence, it can be concluded that the
morphologies for the 1 & 2-s precursor films comprised of 1D MAPI crystals which are covered with relatively small 3D PbI$_2$ nanocrystals.

Figure 3.6: SEM images for precursor films prepared from PbI$_2$ + $x$MAI solutions. The values for $x$ are shown. The film with $x = 0$ contained only PbI$_2$. All of the 1 & 2-s precursor films ($x = 0.66, 0.50$ and $0.33$) contained mixtures of MAPI and PbI$_2$. The insets show expanded views and small 3D nanocrystals can be seen. The scale bars are 50 $\mu$m, 10 $\mu$m and 500 nm, from left to right, respectively.

The top row of fig. 3.6 indicates that the final 1-s ($x = 1.0$) film comprised of 1D crystals that are interconnected and parallel to the POM images (fig. 3.5a). The final films for the other systems ($x < 1.0$) were prepared by dipping the precursor films into a MAI solution before heating as shown in fig. 3.1. This MAI dipping step transformed the excess PbI$_2$ nanocrystals to MAPI based on the right hand side of the equation illustrated in fig. 3.1a.
As observed from fig. 3.7, there are three main structural changes that occurred as the value of $x$ decreased. The first change is the increase in the size of the cuboid-shaped 3D crystals on top of the underlying MAPI 1D crystals. The insets illustrate that as the values of $x$ decreased, the size of 3D crystals (which were MAPI) increased and for $x = 0$, the crystals were 470 nm in size. This illustrates a linear relationship between 3D MAPI nanocrystal size and $x$ as can be seen from fig. 3.8b. The second change is that the 1D crystal became shorter, more interpenetrated and formed flower like structures as $x$ decreased. The third observation is that there is an increase in the total coverage of the mp-TiO$_2$ surface with more small and fewer pinholes. The morphologies for both single methods, 1- $s$ ($x = 0$) and 2-$s$ ($x = 1.0$), are in line with what reported in the literature [127, 139] while the significant and tuneable morphological changes observed when the novel combination 1 & 2-$s$ method with different $x$ variations ($x = 0.66, 0.50$ and $0.33$) were used for this work.
3.4 Results and discussions

Figure 3.7: SEM images for the final MAPI films prepared from dipping precursor films (fig. 3.6) in MAI solutions. The values of $x$ for the precursor PbI$_2$ + $x$MAI solutions are shown. The films with $x = 1.0$ and 0 correspond to 1-s and 2-s, respectively. The $x = 0.66$, 0.50 and 0.33 films were prepared using the combination 1 & 2-s method. The scale bars are 50 µm, 10 µm and 500 nm, from left to right, respectively.
3.4 Results and discussions

Figure 3.8: (a) %Coverage of precursor and final film determined from fig. 3.6 and fig. 3.7, respectively, (b) Effect of $x$ for the PbI$_2$ + xMAI solutions used to prepare the precursor films on average 3D nanocrystal size apparent for the final MAPI films shown in fig. 3.7. The combination 1 & 2-s method used $x = 0.33$, 0.50 and 0.66. Note that $x = 0$ corresponds to the 2-s method. 3D nanocrystals were not evident for the 1-s method ($x = 1.0$).

Summarising all above, the tree-like microcrystals had fewer branches and became longer as $x$ increased. They also became less interpenetrating. This shows a reduction in the nucleation sites’ number-density. This trend is best illustrated by lower magnification images, as shown in fig. 3.6 and fig. 3.7, (first row). During the MAI dipping, the cuboid meso-crystals expanded in size and this was probably triggered by the homogeneous growth and nucleation, as well as a dissolution process [140]. As the proportion of unreacted PbI$_2$ decreased as $x$ increased, it is proposed that the high nucleation density for lower $x$ values was caused by the supersaturation in the PbI$_2$-rich deposition solutions. The microcrystals of the precursor films were covered by PbI$_2$ nanocrystals (discussed above) which were converted to MAPI upon MAI dipping. To assist with the explanations above, the key features are illustrated in the mechanism depicted in fig. 3.9.
3.4 Results and discussions

Figure 3.9: (a) depicts proposed nucleation and growth of MAPI crystals prepared by the 1 & 2-s deposition method (fig. 3.1) and (b) their locations within the solar cell geometry used. The models are drawn not to scale.

The finding recorded above opens the question of why do the changes in $x$ value significantly affect the MAPI films’ morphology? In this regard, the 1D crystal growth at the first step was caused by the balance between homogeneous and heterogeneous nucleation [141–143], consequently, as the proportion of unreacted PbI$_2$ increased, excess PbI$_2$ 3D nanocrystals, as shown in the insets for fig. 3.6, were formed due to the decrease of MAI during the first step. As study by Tidhar et al. [141] had shown that PbCl$_2$ nanocrystals
played the role of heterogeneous nucleation sites for perovskite crystal growth, hence, it is speculated that the heterogeneous nucleation of MAPI flower-like crystals was promoted by the presence of PbI₂ nanocrystals. Thus, the number of PbI₂-triggered heterogeneous nucleation sites increased as \( x \) decreased. As a result, PbI₂ 3D nanocrystals covered the 1D crystal before the film was dipped into the solution and the films were transformed into MAPI after that process. Here, the proportion of 1D MAPI grown using heterogeneous nucleation declined while there was an increase in the proportion of 3D MAPI grown by interfacial conversion of PbI₂ as the value of \( x \) decreased. Therefore, this novel combination of the 1 & 2-s methods allowed systematic variation of the proportion of the MAPI grown by nucleation and interfacial conversion.

As shown in fig. 3.10, this study also measured the films’ XRD along with the diffractogram for PbI₂ for comparison. The architecture of the device used for obtaining the diffractogram is according to fig. 3.10a. It worth to note that \( x = 0 \) corresponds to the 2-s while \( x = 1 \) corresponds to the 1-s (see the scheme on fig. 3.1). Here, for the MAPI films the (002) and (112) at \( 2\theta = 14^\circ \) peaks [127] were prominent. Whilst, PbI₂ was not present in the 1-s film \( (x = 1.0) \) but there were minor PbI₂ peaks observed for the 2-s \( (x = 0) \) and the 1 & 2-s \( (x = 0.33, 0.50 \text{ and } 0.66) \) films at \( 2\theta = 13^\circ \). It is known that fully converting PbI₂ into MAPI by using the 2-s method is very challenging [135, 136, 144] as X-ray diffractograms for perovskites often show the presence of PbI₂ peaks [26, 145]. Here, all of the final films prepared using a MAI dipping step \( (x = 0 \text{ to } 0.66) \) have shown the presence of PbI₂. To prevent the formation of PbI₂ through any degradation involving moisture, the X-ray diffraction for this study was conducted under a nitrogen atmosphere. However, the presence of excess PbI₂ could be caused by the incomplete conversion of 3D PbI₂ nanocrystals at the interface.
3.4 Results and discussions

Figure 3.10: (a) The architecture of the device used for obtaining the X-ray diffractograms. The measurements were run in nitrogen atmosphere to eliminate any possible degradation (b) X-ray diffractograms for final MAPI films prepared using various PbI$_2$ + xMAI solutions (x values shown). The diffractogram for PbI$_2$ is shown for comparison. x = 0 and 1.0 corresponds to the 2-s and 1-s methods, respectively. (c) Variation of the %amplitude for the films from (a) with respect to the x values.

There is also a large probability that the PbI$_2$ nanocystals were buried deep within the mp-TiO$_2$ layer and were not accessible during the MAI dipping in the second step. To elucidate this phenomenon, the effect of the MAI dipping time was investigated for final 2-s (x = 0) films using XRD. It is worth to note that the conversion of perovskite can be probed by the intensity detected at its signature peak (110) using the %Amplitude with respect to PbI$_2$ (001) peak as following equation;

\[
%Amplitude = \frac{100A_{(110)}}{A_{(110)} + A_{(001)}}
\]  

(3.1)
where, $A_{(110)}$ and $A_{(001)}$ are the amplitudes for the MAPI (110) and PbI$_2$ (001) peaks, respectively. From fig. 3.11a, it is clear that the conversion is increased as the dipping time increased (the PbI$_2$ (001) peak became less prominent). The %Amplitude increased rapidly for dipping times less than 2 min and then increased more slowly for dipping times between 2 and 30 min (fig. 3.11b).

![Figure 3.11: (a) X-ray diffractograms for MAPI films prepared using the 2-s method ($x = 0$) with different dipping time. The immersion time was varied as shown. (b) Variation of the % of amplitude of the MAPI (110) peak with $x$ (see text). (c) Images of the films used for (a).]
3.4 Results and discussions

A dipping time of 15 min was chosen in this study because it was in the middle of the region where conversion increased slowly. This value corresponded to %Amplitude = 87%. The diffractograms were recorded under a nitrogen atmosphere which rules out post-preparation degradation involving moisture as the origin of PbI$_2$. Consequently, there is still residual PbI$_2$ left even after dipping time more than 15 minutes. It is attributed to incomplete conversion of PbI$_2$ which was buried deep within the mp-TiO$_2$ layer in which inaccessible by MAI during second step. Other studies have reported that the presence of PbI$_2$ the TiO$_2$ and perovskites could be beneficial as it acts as a blocking layer to prevent recombination [136].

The average grain size for both MAPI and PbI$_2$ crystals (as shown in fig. 3.12) were calculated using the Scherrer equation following Jeong et al. [146]. For these calculations, the full-width at half-maximum heights (FWHM) for the MAPI (110), (202) and (220) peaks were used, and the FWHM for the (001) peak was used in the case of PbI$_2$. The average MAPI crystallite (smallest species) sizes found were between 56 to 73 nm. These species largely originated from MAPI nanocrystals at the mp-TiO$_2$ layer [40, 147].

![Figure 3.12: Crystal size determined from the Scherrer equation as a function of $x$. The detailed calculation of the equation are given in Appendix A.2.](image)

The pore size distribution (average pore diameter of 64 ± 17 nm, see fig. 3.13) of mp-TiO$_2$ measured from the SEM, matched those values for average MAPI nanocrystals (70 ± 14 nm). The average MAPI crystallite size may have increased as $x$ increased.
(fig. 3.12) due to an increase in the proportion of MAPI that was present in the capping layer as relatively large microcrystals and/or meso-crystals. As the microcrystals and meso-crystals’ dimensions far exceed 100 nm (fig. 3.8b and fig. 3.7), the MAPI species found on entire films were mostly the small-sized MAPI nanocrystals within the mp-TiO₂. According to the Scherrer analysis, the residual PbI₂ nanocrystals’ average size was 42 – 47 nm.

**Figure 3.13:** Representative SEM image for mp-TiO₂. The scale bar represents 100 nm. The pore size distribution is shown.

A cross-section of an ITO/bl-TiO₂/mp-TiO₂/MAPI/Spiro-MeOTAD/Au device was prepared to find the residual PbI₂ as discussed above. The ITO/bl-TiO₂/mp-TiO₂/MAPI/Spiro-MeOTAD/Au device contains a final 1 & 2-s (x = 0.5) film. Consequently, the device was examined through EDX and SEM (see fig. 3.14). Here, the atomic% of Pb near the surface was close to what reported in other studies on MAPI [148], and it was also found that the atomic% of Pb increased as the mp-TiO₂ layer increased. Thus, this shows that this finding is consistent with the proposed concept of restricted MAI access as it shown that the PbI₂ was located deep within the mp-TiO₂ layer.
3.4 Results and discussions

3.4.2 Light scattering tuning of MAPI capping layer

A considerable amount of studies have focused on the ability to tune light absorption across a wide range of wavelengths [149], however, there are limited studies which have taken into account the perovskite layers’ capacity to scatter light. In this regard, the increase in the ability to scatter light within the photoactive layers should increase the lengths of the light paths and improve light harvesting capacity [150–152]. Figure 3.15a illustrates the UV-visible spectra for the precursor films while fig. 3.15b presents the final MAPI films. It is worth noting that the spectrum for \( x = 0 \) corresponds to \( \text{PbI}_2 \) and the legends present the values of \( x \) used for the \( \text{PbI}_2 + x\text{MAI} \) solutions. First, the spectra for the precursor films in fig. 3.15a is considered and it can be observed that the films prepared using 1 & 2-s (red, blue and pink curves) show distinct light scattering and the latter have high absorbance values at 900 nm as a result of the Mie scattering [153] from large 1D crystals as shown by the top three rows in fig. 3.6. It can also be suggested that the presence of \( \text{PbI}_2 \) caused the
3.4 Results and discussions

spectra for all of the precursor films to show an absorption peak at 520 nm (see arrows). This is supported by the XRD data for the 2-s \( (x = 0) \) film which shown the presence of PbI\(_2\) (see fig. 3.10 and fig. 3.11a). The spectra for the 1 & 2-s films \( (x = 0.33, 0.50 \text{ and } 0.66) \) also showed a relatively weak band-edge absorption from MAPI at 775 nm.

**Figure 3.15:** (a) UV-Visible spectra of the precursor films. Note that the spectrum for \( x = 0 \) corresponds to PbI\(_2\). (b) UV-visible spectra for the final MAPI films. The values of \( x \) used for the PbI\(_2\) + xMAI solutions are shown in the legends.

Figure 3.15b shows that several features of the spectra have changed considerably after the conversion of the precursor films to the final MAPI films. For instance, in each case, there were changes as the perovskite absorption reached 775 nm and these changes were more prominent for the MAPI films which were prepared using \( x = 0.50 \) and 0.33. Hence, we posit that the levels of energy distribution and perovskite energy gaps \( (E_g) \) for both films were the lowest. As from fig. 3.16, the absorbance value at 900 nm increased when the
value of $x$ decreases, indicating the light scattering was increased for the 1 & 2-s ($x = 0.66$, 0.33 and 0.50) films.

![Absorbance at 900 nm as a function of $x$ for the precursor and final films.](image)

**Figure 3.16:** Absorbance at 900 nm as a function of $x$ for the precursor and final films.

This result could be attributed to the combination between the 1D and 3D crystal scattering. The scattering was probably enhanced as $x$ decreased due to the increase of the 3D crystals, as shown in fig. 3.7. The present study has demonstrated that scattering can be improved by controlling the morphology of MAPI through 1 & 2-s process within the capping layer. This result contrasts to a study by Yin et al [151]. We improved the scattering particles within the photoactive layers of perovskite (on the capping layer) while their team adjust the light scattering within the photo-anode (TiO$_2$ layer) in perovskite solar cell. The 1 & 2-s approach could maintain strong light absorption and offers a promising and useful strategy that can be used to improve light management in perovskite solar cells.

### 3.4.3 Band gap and recombination tuning through morphological control

It is widely known that Photoluminescence (PL) could offer mechanistic information related to the charge transport to TiO$_2$ and perovskite film recombination [154–156]. Figure 3.17a illustrates the PL spectra of the final MAPI films and the legend shows the values for $x$. Figure 3.17b present the expanded view of PL spectra from fig. 3.17a along with interpolated PL curve for virtual $x = 0.75$. Figure 3.17c present the variation of the maximum PL intensity with $x$ while fig. 3.17d presents the relationship of the maximum PL
3.4 Results and discussions

wavelengths with $x$. The data was obtained from the spectra illustrated in fig. 3.17a. Based on the PL, all of the spectra showed strong band-edge emission peak and they were within the range of 777 to 785 nm, this could be due to quenching by mp-TiO$_2$ and incomplete non-radiative recombination. As the value of $x$ increased, the PL intensity for the 1 & 2-s films decreased. The most prominent decrease was observed in film with $x = 0.33$. This trend is parallel to the changes of the absorbance values at 775 nm as shown in fig. 3.15b, suggesting an improved photogeneration for the 1 & 2-s films that have the smallest $x$ values. These results show that tuning of light harvesting was caused by the variations of the systematic morphological variations found within these films.

Figure 3.17: (a) Depicts PL spectra for various MAPI films. The excitation wavelength used was 460 nm. The values for $x$ are shown. (b) expanded view of PL spectra from (a). A calculated spectrum for $x = 0.75$ is shown which was obtained by using $F = 1.5x(0.25F_0 + 0.75F_{1.0})$ where $F_0$ and $F_{1.0}$ are the measured fluorescence intensities for the $x = 0$ and 1.0 films, respectively. (c) variation of the wavelength of maximum PL intensity with $x$. The data were taken from the spectra shown in (a). (d) presents the relationship of the maximum PL wavelengths with $x$.

Figure 3.17d illustrates that the peak PL intensity wavelength for each film is plotted as a function of $x$. There was a red-shift of 8 nm as the value of $x$ increased from 0 (2-s
3.4 Results and discussions

... (1-s film) and the morphological control for these films enabled band gap tuning. Anion [145] or cation [157] substitution in perovskites have been used here to tune the band gap in perovskite, however, the knowledge on the ability to achieve tuning using morphological control during preparation is still in its infancy. The reason for this behaviour is related with the fact that the MAPI film with the highest peak wavelength ($x = 1.0$) had no residual PbI$_2$ as determined from X-ray diffraction data fig. 3.10b. It is known that the PbI$_2$ at grain boundaries could cause passivation resulting in a blue-shift in the MAPI’s PL spectra [155]. Moreover, compared to that from the bulk structure, there was a more prominent blue shift in the PL of the MAPI crystal band edges [158]. Here, as $x$ increased, the surface area-to-volume decreased and 3D nanocrystals replaced those 1D crystals with low surface area-to-volume ratios (fig. 3.7). Hence, the contributions of PbI$_2$ passivation and crystal surface effects to the PL spectra diminished, which caused the red-shift apparent in fig. 3.17.

This study also employed the transient absorption spectroscopy (TAS) to examine how varying the value of $x$ could cause photo-induced separation. Long-lived photo-generated [spiro-MeOTAD]$^+$ cations were examined as a function of time after pulsing the laser irradiation (567 nm) as depicts by fig. 3.18a. This was done by measuring the changes in absorption ($\Delta$OD) at 1600 nm for the architectures of glass/mp-TiO$_2$/Perovskite/Spiro-MeOTAD. Figure 3.18b illustrates the decay kinetics data obtained and the legend presents the values for $x$ which were used to prepare the films. As $x$ increased and shifted from 2-s ($x = 0$) through 1 & 2-s ($x = 0.5$) to 1-s ($x = 1.0$), there was a shorter charge separation lifetime observed. The increased $x$ values led to enhanced recombination kinetics. Here, a prominent fraction of the decay appears to occur on a time scale at a faster rate compared to the instrument response of the transient spectrometer (i.e., $< 1 \mu$s) while in comparison, the charge recombination for $x = 0$, was only within a timescale of 5 – 50 $\mu$s. These findings support the hypothesis there was a decrease in the PbI$_2$ passivation at grain boundaries as $x$ increased and the deposition method shifted from 2-s ($x = 0$) to 1-s ($x = 1.0$). On the other hand, the presence of PbI$_2$ may have delayed the kinetics of interfacial...
charge recombination which consequently leads to longer lived separated states and slowed recombination kinetics.

![Figure 3.18](image)

**Figure 3.18:** (a) The architecture of the device used for TAS experiments. Transient absorption data for mp-TiO$_2$/MAPI/spiro-MeOTAD. The legend shows the values for $x$ used for the preparation of the films.

### 3.4.4 Effect of morphology variation on device performance and hysteresis

Solar devices were produced using P3HT which acts as a hole transporting materia (HTM). The P3HT was chosen as it has suitable material characteristics. For instance, the matrix is less likely to fill the small pinholes as it is larger than spiro-MeOTAD. Moreover, there are many studies on P3HT and it is suitable for roll-to-roll or larger scale fabrication [159, 160]. Meanwhile, the spiro-MeOTAD was also used for devices for the purpose of comparison. Figure 3.19 presents the architectures and energy level for the devices while table 3.1 shows the values of all of the device parameters. The highest PCE was obtained by devices prepared using 1 & 2-s ($x = 0.33$) with an average of 3.04% while the $x = 0.33$ series champion cell showed a PCE of 3.7% (fig. 3.19b). As shown in fig. 3.7, there are pinholes at the capping layers which allowed shunting and hence decreased the values of FF and PCE values. Here, the average PCE for the devices prepared by 2-s devices was 4.23%, which is slightly lower than the 4.5% reported for similar devices by Bi et al [161].

On the other hand, these devices in this study were not optimised since the present study strives to investigate how morphologies could affect the device performance parameters of a series of similarly prepared devices.
3.4 Results and discussions

Figure 3.19: (a) Architectures and energy levels for the ITO/mp-TiO2/MAPI/HTM cells. P3HT or Spiro-MeOTAD were used as the HTMs – see text. (b) J-V curves for the champion 1 & 2-s ($x = 0.33$) cells. (c) to (f) show the variations of $J_{SC}$, $V_{OC}$, $FF$ and $PCE$ with $x$.

Figure 3.19c –f represent the variation of $J_{SC}$, $V_{OC}$, $FF$ and $PCE$ as a respective function of $x$. It is evident that $J_{SC}$ is the main parameter which affects the PCE, and as $x$ increased, this parameter decreased significantly. In comparison to the SEM data in fig. 3.7, this trend could probably be due to the increased number of pinholes area within the capping layer. These general trends is parallel with what reported in the past studies which highlighted that the PCE of perovskite solar cells prepared using the 2-s method is about double that of the PCE of devices prepared using the 1-s method [61]. However, until now, there is no straightforward way to move from one device to another. The results in fig. 3.19b illustrate the occurrence of a systematic transition from 2-s ($x = 0$) to 1-s ($x = 1.0$) device performance due to the morphological control facilitated by the 1 & 2-s system. The
second last row in fig. 3.7 showed that 1 & 2-s ($x = 0.33$) system was morphologically enriched and could be claimed as the best combined method film. In this regard, the system has potential for future application due to its relatively high PCE value (table 3.1) and high absorbance based on the UV-visible spectra (fig. 3.15).

For comparison, the devices in this study were constructed by using 1 & 2-s ($x = 0.33$) films and spiro-MeOTAD as the HTM. Control devices were also constructed using 2-s ($x = 0$). fig. 3.19c - f, red curves and table 3.1 (SPIRO) present the performance data; the device prepared using $x = 0.33$ shown the average PCE value of $8.64 \pm 0.55\%$ while the $x = 0.33$ series champion cell showed a PCE of $9.35\%$ (fig. 3.19b, red curve). The average PCE value for $x = 0$ was $10.32 \pm 0.86\%$ which is expected. These values were relatively higher than the values obtained by devices prepared using P3HT. This is because the devices containing spiro-MeOTAD [161] have slower recombination. Moreover, these results indicate that the devices with morphologically enriched films ($x = 0.33$) were able to offer the PCE values similar to that provided by the conventional 2-s system although the hybrid 1 & 2-s device efficiencies were a little bit lower than the conventional 2-s method. This is an encouraging result for future research. Pinholes and cavities were still evidenced in SEM survey (fig. 3.7) which still can be improved. The cells were not optimized as the main aim is to see the ability of morphology tuning which is new. Although, this can be improved in the future by carefully optimize the photoanode thickness and switching to better HTM.

PCE hysteresis is one of the important issues pertaining to perovskite solar cell performance [108, 139, 162]. In this, present study the hysteresis index, $H$, was calculated through the following equation [163]:

$$H = 100\left(\frac{A_{\text{Forward}}}{A_{\text{Reverse}}} - 1\right)$$

(3.2)

Where, $A_{\text{Forward}}$ and $A_{\text{Reverse}}$ are the integrated areas under the forward and reverse J-V curves, respectively.
Figure 3.20 shows that the extent of hysteresis was dependent on morphology which and can be tuned using the value for $x$. The origin of the hysteresis for perovskite solar cells has not been completely resolved. In addition, a study highlighted the importance of iodide ions migration [108]. Moreover, accumulation of ions at the perovskite/TiO$_2$ interface is a likely cause for the hysteresis [109]. Kim et al. reported that the extent of hysteresis decreased as the MAPI crystal size increased for devices prepared using the 2-s method [139]. Here, the overall crystal size increased as $x$ decreased. This trend is due to the proportion of 1D crystals – as shown in fig. 3.6 and fig. 3.7. Thus, the present data supports that larger crystals had less ion migration because of their lower surface area-to-volume ratio. Moreover, the $H$ values for the spiro-MeOTAD and P3HT-based devices were similar (fig. 3.20d). This shows that the hysteresis was not affected by the nature of the HTM and supports the view that the morphology of perovskite / TiO$_2$ interface is mostly responsible for the hysteresis [164].
3.4 Results and discussions

Figure 3.20: (a)-(c) Representative J-V curves for various perovskite solar devices based on P3HT as HTM. The x values are shown. The arrows indicated the sweep direction of bias voltage either forward (from $J_{SC}$ to $V_{OC}$, black curve) or reverse direction (from $V_{OC}$ to $J_{SC}$, red curve). The hysteresis indexes (%H) were calculated by normalising the percentage difference of area under curves for both directions. (b) Variation of the hysteresis index with x for P3HT and spiro-MeOTAD perovskite devices. See fig. 3.1 for the meanings of x.

3.4.5 Proposed conceptual model for 1 & 2-s morphologies

This study proposes a schematic model (fig. 3.21) for the 1 & 2-s photoactive layer structures based on the results of the analysis conducted. Here three MAPI crystal environments; microcrystals ($\gg 1 \, \mu m$), meso-crystals ($\sim 0.1 – 1 \, \mu m$) and nanocrystals ($\sim 50 – 80 \, nm$) were found; each crystal environment would control individual optoelectronic properties. Meanwhile, there were traces of excessive PbI$_2$ nanocrystals within the mp-TiO$_2$ layer and more prevalent concentration were found at the deepest regions of the mp-TiO$_2$ layer. It was observed that the average size of the microcrystals will increase, but their number-density will decrease as x increased while on the hand, the meso-crystals’ average size has been reduced. Based on the Scherrer analysis, the largest MAPI species on the film was
Table 3.1: Photovoltaic performance data for perovskite devices measured using the forward scan$^a$.

<table>
<thead>
<tr>
<th>xMAI</th>
<th>HTM</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>$H^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>P3HT</td>
<td>11.98 ± 3.02</td>
<td>0.83 ± 0.09</td>
<td>0.39 ± 0.09</td>
<td>4.23 ± 1.14</td>
<td>15.1 ± 1.9</td>
</tr>
<tr>
<td>0.33</td>
<td>P3HT</td>
<td>9.98 ± 1.14</td>
<td>0.84 ± 0.06</td>
<td>0.37 ± 0.05</td>
<td>3.04 ± 0.44</td>
<td>8.75 ± 0.88</td>
</tr>
<tr>
<td>0.50</td>
<td>P3HT</td>
<td>7.85 ± 0.44</td>
<td>0.83 ± 0.03</td>
<td>0.36 ± 0.04</td>
<td>2.35 ± 0.45</td>
<td>6.60 ± 0.73</td>
</tr>
<tr>
<td>0.66</td>
<td>P3HT</td>
<td>6.73 ± 1.07</td>
<td>0.81 ± 0.07</td>
<td>0.39 ± 0.05</td>
<td>2.17 ± 0.68</td>
<td>4.33 ± 0.52</td>
</tr>
<tr>
<td>1.0</td>
<td>P3HT</td>
<td>6.38 ± 0.8</td>
<td>0.68 ± 0.17</td>
<td>0.41 ± 0.09</td>
<td>1.90 ± 0.95</td>
<td>2.42 ± 0.38</td>
</tr>
<tr>
<td>0.0</td>
<td>SPIRO</td>
<td>24.2 ± 0.21</td>
<td>0.85 ± 0.02</td>
<td>0.51 ± 0.04</td>
<td>10.32 ± 0.86</td>
<td>16.3 ± 1.86</td>
</tr>
<tr>
<td>0.33</td>
<td>SPIRO</td>
<td>21.9 ± 0.50</td>
<td>0.86 ± 0.01</td>
<td>0.46 ± 0.02</td>
<td>8.64 ± 0.55</td>
<td>8.40 ± 0.70</td>
</tr>
<tr>
<td>0.50</td>
<td>SPIRO</td>
<td>18.8 ± 1.5</td>
<td>0.86 ± 0.01</td>
<td>0.44 ± 0.05</td>
<td>7.04 ± 0.63</td>
<td>7.43 ± 0.73</td>
</tr>
<tr>
<td>0.66</td>
<td>SPIRO</td>
<td>16.3 ± 1.4</td>
<td>0.86 ± 0.01</td>
<td>0.44 ± 0.02</td>
<td>6.17 ± 0.97</td>
<td>5.25 ± 0.76</td>
</tr>
<tr>
<td>1.0</td>
<td>SPIRO</td>
<td>13.6 ± 0.5</td>
<td>0.84 ± 0.01</td>
<td>0.46 ± 0.02</td>
<td>5.19 ± 0.34</td>
<td>3.35 ± 1.42</td>
</tr>
</tbody>
</table>

$^a$ The ± values are standard deviations.

$^b$ Hysteresis index.

the MAPI nanocrystals. In the meantime, light scattering is influenced by the presence of microcrystals and meso-crystals. The presence of microcrystals determines coverage, and most importantly, playing that role, it could facilitate the control of the material’s electronic states and properties including PL, $J_{SC}$ and PCE.
3.4 Results and discussions

Figure 3.21: Schematic depicting the proposed structure of the 1 & 2-s ($x = 0.33, 0.50$ and $0.66$) photoactive layers. (a) Precursor film, (b) final film. The three types of MAPI crystals are depicted and are not drawn to scale.
3.5 Conclusion

This study introduced a new combined method (1 & 2-s) for preparing the MAPI film preparation. This study has focussed on three novel mixed morphology perovskite photoactive films ($x = 0.33, 0.50$ and $0.66$). It was found that preparing the films using varying values of $x$ precursor PbI$_2$ + $x$MAI solutions could coherently change the morphology. This study has combined the 1D and 3D crystal morphologies from the 1-s and 2-s methods and the each proportion is considered as tuneable. Here, the PbI$_2$ 3D nanocrystals act as heteronucleation sites to facilitate the 1D crystal growth. The morphology has been shown to significantly affect all of the key properties of MAPI films and devices where the use of the combined method creates MAPI films with enhanced light scattering and have stronger absorption. The perovskite bandgap is significantly affected by the value of $x$ used for synthesis, which in turn, influences the morphology. TAS data show that there was a systematic increment in lifetime as $x$ decreased. The device studies showed that the 1 & 2-s method provided good tuneability of the PCE, $J_{SC}$ and $H$. The 1 & 2-s ($x = 0.33$) system was identified as a novel morphological enriched system that is capable of providing devices with good PCE values. The potential to transform the morphology of perovskite photoactive layers shown in this study should be transferable to other perovskite types and other device architecture including the planar structure. Though, we did a preliminary study to show that our 1 & 2-s method could fit into the planar-type device (not shown) and is worthy to be pursued. The 1 & 2-s method has potential in improving the properties of such perovskite films and device architectures.
Co-solvent blend study: towards optimum morphology

4.1 Abstract

The quality of the perovskite layer is very important in achieving high performing perovskite solar cells. In chapter 3, we have demonstrated the use of combined 1 & 2-s method to gain the understanding of crystal growth within the perovskite active layer, however the question on how to improve overall properties of the films, including their reproducibility, stability, optoelectronic characteristic and coverage, remains unanswered. This study will be the first to introduce the mixed DMF:DMSO co-solvent blend that can be used in the 1 & 2-s method. Furthermore, the preparation of methylammonium lead/Pb iodide perovskite (MAPI) with different DMSO vol % (in DMF) is examined and the data obtained is compared with films created using the conventional 1-s and 2-s methods. This study has determined the best DMSO volume fraction for the film and found that the use of 1 & 2-s method and the DMF:DMSO co-solvent blends has improved the overall crystal coverage and PCE for future works. Here, compared with the films from the 1-s and 2-s methods, the films from the 1 & 2-s method gave superior stability. Therefore, this study advocates that the use of mixed co-solvent blend could offer better versatility which allows aspects such as a perovskite film’s architectural control, device construction and morphology to be adjusted accordingly.
4.2 Introduction

The HOIP solar cell could replace silicon-based solar cells. In recent years, they have generated a fair amount of interest due to its low cost and exceptional photovoltaic performance [165, 166]. There are many studies that have investigated HOIP materials like MAPbI$_3$ (here, we denoted as MAPI) and employed the use of various strategies, such as varying the device’s architectures and using new deposition methods to produce perovskite solar cells which lead to remarkable power conversion efficiency (PCE) of more than 22.1% [50] and improved stability [167]. These mentioned studies prepared the films by using solution-based preparation methods. These conventional methods are well known, where both reactants were in the solution, or, the one-step (1-s) deposition [145] and two-step (2-s) deposition method where one of the reactants was pre-deposited in a solid phase prior to the second deposition step [8]. Here, our study demonstrated the use of a hybrid method where the two methods (1-s and 2-s) were combined to prepare the PSC. The finding of this study showed that PSC’s stability and performance could be improved. This study will be further continued in the following chapter.

As shown in Chapter 3, like other studies [130, 168, 169], DMF was solely used to dissolve the perovskite precursors. Our study found that the fast crystallization rate of DMF-based precursor solution has led to formation of pinholes. A recent report claimed that DMSO is the best solvent to produce high quality and dense perovskite film [9]. In this regard, DMSO has a higher boiling point and has more efficient ability in coordinating the formation of PbI$_2$ [170] and forming adducts [171–173] compared to DMF. Moreover, as the rate of crystallisation is slower in DMSO, it generates larger size of perovskite crystal, hence lower grain boundaries. This makes DMSO a more preferred solvent to prepare PSCs [90] with higher efficiency. In this study, DMSO was used as a co-solvent with DMF. The study aims to scrutinise how co-solvent composition affects the properties of perovskite films prepared using the 1 & 2-s method and to determine the best DMSO volume fraction for the film in improving overall crystal coverage and PCE for future works.
Researchers have developed approaches such as the 1-s deposition [9, 26, 171, 174, 175], and 2-s sequential deposition [26, 64, 70] to produce high-quality perovskite films. The 1-s method usually uses the balanced stoichiometric ratios of the reactants and has produced higher power conversion efficiencies and stability [73, 167, 176]. Moreover, the 1-s solution deposition approach is a simpler method and has potential of lower fabrication cost. This makes it a more preferred approach to produce perovskite films. On the other hand, the 2-s method [177] involved additional step where PbX₂ (X = Cl, I or Br) was spin coated or dipped into MAX solution. It is claimed that the perovskite film coverage on the flat or mesoporous substrates lack homogeneity and consequently, the lack of light absorption. Past studies reported a lower efficiency and performance [9, 175, 178], as the process leads to a higher rate of charge carrier recombination. It is also argued that as there are two phases involved in the reaction, it is harder to have stoichiometric control of the product. In addition, the 2-s method involves incomplete conversion of PbI₂ although there are reports that PbI₂ could increase PCE [173], a device’s stability might be compromised when there is excessive PbI₂ [179]. Therefore, increasing the quality of film quality in the deposition method, as well as a better understanding of kinetics of the film growth is imperative. One way to do this is through ‘solvent engineering’. There is problem when only a single solvent is used; low density films with a narrow processing window [70]. It is claimed that this solvent engineering could produce highly efficient solar cell devices [9, 175] through adjusting the morphology of the perovskite layer in the 1-s deposition. Based on the discussion above, this study will investigate a solvent-assisted film deposition method, using a DMF/ DMSO co-solvent mixture with our new 1 & 2-s deposition method. This is a highly versatile method to produce uniform, large grain-sized crystal coverage with relatively dense film. It is believed that the novel co-solvent blend approach introduced in this chapter will significantly improve the overall qualities, stability and reproducibility of the films.
4.3 Experimental procedures

The study focuses on fabricating perovskite films by using the new 1 & 2-s combination methods with DMF:DMSO co-solvent blend and characterise their optoelectronic properties. The films and devices were fabricated to investigate their properties and relate those data with the effect of using different blends ratio with morphologies. The novel combination step also compared with the conventional methods. The key procedure can be separated into materials preparations, perovskite films preparations (combination and conventional methods) and device fabrications.

4.3.1 Materials

Isopropanol (IPA, anhydrous, 99.5%), chlorobenzene (CBZ, anhydrous, 99.5%) methylamine (> 98%), HI (99.9%, 57% in water), 4-tert-butylpyridine (96%), lithium bis(trifluoromethanesulfonylimide) (LiTFSI, 99.95%), PbI₂ (99.999%), N,N-dimethylformamide (DMF, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, 99.9%), titanium diisopropoxide bis(acetylacetonate) (TDB, 75 wt % in IPA) were all purchased from Aldrich and used as received. TiO₂ paste (Dyesol 18NRT) and 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9’-spirobifluorene (Spiro-MeOTAD, Fenglin Chemicals, 99.5%) were also used as received.

4.3.2 Co-solvent blend precursor solution preparation

MAI were synthesized following established procedure [6] as follow. Briefly, HI acid was added dropwise into methylamine solution with a mole ratio of 1:1 into a 250 mL round-bottom flask in an ice bath for 2 h with stirring [180]. The cold solution was carefully evaporated using a rotary evaporator. The crystals were washed using diethyl ether (20 mL) three times and dried in a vacuum oven at 60 °C. To prepare the blend, 1 M PbI₂ and 0.5 M MAI were added into DMF in 7 mL vial together with 0, 20, 40, 60, 80 and 100 vol% of DMSO co-solvent.
4.3 Experimental procedures

4.3.3 Substrates preparation

ITO/Glass slides (2.0 cm × 1.5 cm, Ossila Ltd.) were cleaned by sonication in a 1% Hellmanex solution in boiling water for 15 min followed by rinsing with water and IPA and cleaning in ultrasonic for 5 min and dried using a nitrogen stream. TiO₂ paste (70 µL, 1:5 in ethanol) was spin-coated onto the cleaned glass slides at 5000 rpm for 30 s to form a mesoporous scaffold (mp-TiO₂) layer. The mp-TiO₂ film was then annealed at 500 °C for 30 min and had an average thickness of 250 nm.

4.3.4 MAPI films prepared using the 1 & 2-s method

This method is depicted in fig. 4.1. The precursor film solutions in DMF:DMSO mixed solvent contained PbI₂ (1.0 M) and MAI (0.50 M) were prepared in a glove box (humidity ~ 2%). Film fabrication was conducted outside of the glove box (humidity ~ 40%). The solutions (70 µL) were spin-coated onto the mp-TiO₂ layer. The solutions were kept at 70 °C during spin-coating. A two-stage spin-coating was employed for precursor film deposition which was 2000 rpm for 10s and 4000 rpm for 20 s. The precursor films were dried at 100 °C for 10 min. The films were washed with IPA for 10 s. Then, the MAI solution in IPA (100 µL, 10 mg mL⁻¹) was dripped and spin coated on the precursor film for 30s. This procedure was repeated twice to give the final films. These films were dried at 100 °C for 10 min and the resulted final films were immediately placed in a desiccator over P₂O₅ and stored in the dark until investigation.

Figure 4.1: Summary of preparation conditions used for the MAPI perovskites during the solvent blend study. The first step involved spincoating a PbI₂ + MAI solution with excess PbI₂ followed by drying at 100 °C to give a precursor film. The second step involved spin coating a MAI solution followed by drying to give a film containing perovskite prepared in both steps, which is termed 1 & 2-s. The volume fractions of DMSO are included.
4.3.5 MAPI films prepared using the 1-s and 2-s methods

Control MAPI films were prepared using the 1-s and 2-s methods and a mixed DMF:DMSO co-solvent blend (60 vol.% DMSO) according to fig. 4.2. For the 1-s method (fig. 4.2a) the solution (70 µL containing 1.0 M of PbI$_2$ and 1.0 M of MAI) was spin coated at 4000 rpm for 20 s on top of mp-TiO$_2$ and was then immediately dried for 10 mins. For the films prepared using the 2-s method (fig. 4.2b), PbI$_2$ (75 µL, 1.0 M) was spin coated onto mp-TiO$_2$ and dried as described above. MAI solution in IPA (100 µL, 10 mg/mL) was dripped onto the PbI$_2$ precursor film and spin coated for 30s to form the MAPI film which was dried as described above.

![Figure 4.2: Summary of preparation conditions used for the MAPI perovskite using conventional methods (a) one step deposition (1-s), and (b) sequential step method (2-s) for the solvent blend study. The 1-s involved spincoating a PbI$_2$ + MAI solution with 1:1 mol ratio to give final film. The conventional 2-s involved spin coating a PbI$_2$ solution followed by a reaction with MAI to give final film after drying.](image)

4.3.6 Device fabrication

The detailed sequence of PSCs fabrication is depicted in fig. 4.3. Briefly, laser-patterned, FTO-coated glass substrates (~8 Ω/sq) were cleaned by ultrasonication in a 2% Hellmanex solution, rinsed with deionized water and IPA, and dried. A blocking layer of compact TiO$_2$ (bl-TiO$_2$) was then deposited by spin coating TDB (75 µL, 0.15 M) solution in
1-butanol at 2000 rpm for 60 s. The procedure was repeated using a TDB solution (0.30 M) and the substrate was heated at 125 °C for 5 min to give an average thickness of 50 nm. A mp-TiO$_2$ layer was then deposited as described above. Perovskite photoactive layers were deposited as described above. The average perovskite capping layer thicknesses for solvent study (DMSO = 0, 20, 40, 60, 80 and 100 vol.%) were $\sim 520 \pm 26$ nm, $260 \pm 23$ nm, $290 \pm 25$ nm, $330 \pm 27$ nm, $350 \pm 28$ nm and $375 \pm 29$ nm, respectively. These values were determined by DEKTAK thickness profilometry. Spiro-MeOTAD was deposited as a hole transport material (HTM). The latter (average thickness of 200 nm) was deposited by spin-coating of Spiro-MeOTAD in CBZ (72.3 mg/mL) at 3000 rpm for 30 s. Li-TFSI salt and TBP in acetonitrile were added to the HTM solution. HTM deposition followed established literature procedures [8, 181]. Finally, a gold layer (80 nm) was deposited on top of the HTM. The active area of the devices was defined using a square aperture within a mask and fixed at 0.025 cm$^2$. The fabrication procedures were performed outside the glovebox in $\sim 50\%$ relative humidity. All devices were stored in a desiccator over P$_2$O$_5$ in the dark until investigation.
Figure 4.3: Depicts overall sequence of PSC fabrication consist of (a) deposition of photo-anode (bl-TiO$_2$ and mp-TiO$_2$), (b) perovskite layer formation, (c) deposition of photo-cathode (HTM and Au back contact) and (d) device measurement.
4.3 Experimental procedures

4.3.7 Physical measurements

The surface morphologies were investigated using a Philips XL30 FEI – SEM. The particle counts and diameter on the capping layer were calculated using image analysis (fig. 4.4) following the method described in our earlier work (Chapter 3, section 3.3.4).

Figure 4.4: Example of image used for estimation of particle counts and diameter. This SEM image was obtained for the final 1 & 2-s film prepared using 60 Vol% DMSO and is taken from fig. 4.7d. (a) The automatic threshold for greyscale was used to differentiate the crystal from its background, and (b) shows the automatic particle numbering executed after declaring the grayscale colour boundary.

XRD data were obtained using a Bruker D8 Advance diffractometer (Cu-Kα). The films obtained were scanned with a step size of 0.02°. For these measurements the films were prepared under a nitrogen atmosphere and were measured using an airtight holder. The diffraction peaks were analysed using Highscore Plus software for manual indexing and were matched with reference from Park et al [182]. UV-visible spectra were recorded using a Perkin Elmer Lambda 25 spectrometer. Photoluminescence (PL) spectra were obtained using an Edinburgh Instruments FLS980 spectrometer.

4.3.8 Device characterisation

The current density-voltage (J–V) characteristics were measured using a Keithley 2420 Sourcemeter and 100 mW/cm² illumination (AM 1.5G) and a calibrated NREL certified Oriel Si-reference cell. An Oriel SOL3A solar simulator was used for these experiments.
(see Chapter 3, section 4.3.3 for detailed setup and instrumentation). Forward and reverse direction sweeps were measured with a sweep rate of 0.2V/s in ∼ 40% relative humidity.

4.4 Results and discussions

This section provides the key findings of perovskite solar cells produced by novel combination 1 & 2-s method, with different co-solvent blend compositions. This improvement has shown unique properties and demonstrated that PSC’s morphologies can be fine-tuned by adjusting their co-solvent blend compositions.

4.4.1 Effect of co-solvent composition on MAPI (1 & 2-s) surface morphology

Our previous study introduced the 1 & 2-s method (Chapter 3) which comprised of a hybrid construction approach combining the conventional 1-s and 2-s film deposition methods where there is a significant stoichiometric imbalance in the first step (see equation in fig. 4.1). Whilst the previous study (Chapter 3) has used DMF as the only solvent, the present study used a DMF:DMSO co-solvent blend to find for the best overall morphology and optoelectronic properties of final film to highlight the advantages of using our novel combination method compared with the films prepared using the conventional 1-s and 2-s method. The effect of DMSO volume fraction ($\phi_{DMSO}$) on the DMF:DMSO co-solvent blend was investigated for MAPI (1 & 2-s) films. Here, the $\phi_{DMSO}$ values ranged from 0 and 100% and it was observed that increasing $\phi_{DMSO}$ lead to more glossy and dense films as depicted by digital photographs (fig. 4.5).
Figure 4.5: Photographs of final film prepared using different co-solvent blend (DMF:DMSO) compositions. The films shown in (a) and (b) are the precursor and 1 & 2-s films, respectively. It is noted that, increasing vol% of DMSO gives more flattened surface, hence more glossy films.

The final films’ morphologies were then examined using SEM. There are two length scales to consider for these films; the micrometer scale (fig. 4.6a-f) and the nanometer scale (fig. 4.6g-l). It was observed that the morphology of the films changed from branched with larger pinholes to a more amorphous, interconnected structure with fewer pinholes as the $\phi_{\text{DMSO}}$ increased. Moreover, the surface coverage calculated from the SEM data (fig. 4.6) showed that the coverage increased with the increase of $\phi_{\text{DMSO}}$ and reached almost 100% (the proportion of pinholes approached zero) as shown in fig. 4.8a. The $\phi_{\text{DMSO}} = 60\%$ film gave largest crystals. There was also an underlying micrometer scale structure that was fan-like and this provided best coverage with fewer micrometer-scale pinholes. The nanometer-scale SEM images (fig. 4.6g-l) were also used to measure the average cubic crystal size that underlying the big 1D MAPI crystal. In this matter, the imageJ software was used and the cubic crystal counts and diameters were established (fig. 4.7). It was observed that increasing $\phi_{\text{DMSO}}$ increased the average crystal size. The size reaches a value of $253 \pm 96$ nm when approaching $\phi_{\text{DMSO}} = 60\%$. Meanwhile, the data shown in fig. 4.7d imply that this $\phi_{\text{DMSO}}$ value has the lowest number of grain boundaries. Similar to what was reported by Cao et al. [170], there was also an increase of crystal size with DMSO content in the mixed DMF-DMSO co-solvent blends for 2-s MAPI films (fig. 4.8b). This could be attributed to the coordination with DMSO. Furthermore, as shown in fig. 4.8c, for
the films prepared using the DMSO, the capping layer thickness increased linearly with $\phi_{DMSO}$. This could be due to the increased viscosity of the co-solvent blends with DMSO where the viscosity of DMSO was 1.96 and the viscosity of DMF was 0.80 cps [183]. The increase in the solution viscosity would minimise the mass loss during spin coating and consequently, increase the thickness of the deposited film.
4.4 Results and discussions

Figure 4.6: Effect of solvent blend composition on morphology of the 1 & 2-s films (MAPI) at the micrometer scale (a) – (f) and nanometer scale (g) – (l). The scale bars are shown below each magnifications.
Figure 4.7: Histogram of crystal diameter for the solvent study of MAPI by combination step. a) 0% DMSO, b) 20% DMSO c) 40% DMSO, d) 60% DMSO, e) 80% DMSO and f) 100% DMSO. The histogram is fitted with the Gaussian plot to calculate for the mean size and standard deviation.
4.4 Results and discussions

Figure 4.8: Effect of DMSO volume fraction ($\phi_{\text{DMSO}}$) for MAPI (1 & 2-s) films prepared using DMF:DMSO co-solvent blends on (a) coverage percentage, (b) crystal size, and (c) capping layer thickness.

4.4.2 Effect of co-solvent composition on optoelectronic properties

As shown by the XRD data for the films (fig. 4.9a), the %amplitude of the MAPI (110) peak for the films containing DMSO increased as the $\phi_{\text{DMSO}}$ increased (see fig. 4.9b). This is normally observed in conventional PSCs [182] as a result of the slower crystallisation which provides more time for the MAI reaction.
4.4 Results and discussions

Figure 4.9: a) X-ray diffractograms for final MAPI film for solvent study using combination 1 & 2-s. The value in round brackets show the vol% DMSO used to prepare the films. b) Depicts variation of %Amplitude for the films from (a) quantified by normalising the difference between peak (110) and PbI$_2$ signature peak (001).

The study also measured the UV-Visible spectra for the films (fig. 4.10a). It was found that the addition of DMSO minimises the light scattering due to the flattened MAPI surface evidenced in fig. 4.6b-f. The study also measured the PL spectra as shown in fig. 4.10c, and found that the PL spectra were significantly influenced by the $\phi_{DMSO}$. In this regard, the PL intensity increased to reach its peak as the $\phi_{DMSO}$ increased in a relatively linear relationship (fig. 4.10d). It follows that as $\phi_{DMSO}$ increased, there was less quenching occurred as the capping layer thickness increased (fig. 4.11). This is because a large proportion of the MAPI could not be quenched efficiently [147] as it was further from the mp-TiO$_2$ interface. The film which was prepared using only the DMF ($\phi_{DMSO} = 0$) had a different nature compared to the other films prepared with DMSO ($\phi_{DMSO} = 20, 40, 60, 80$ and $100$). The DMF films had thicker, poor and inhomogeneous surface coverage. These differences occurred as DMF has weaker ligation strength of Pb compared to DMSO [173] and caused faster perovskite crystallisation.
4.4 Results and discussions

Figure 4.10: (a) UV-visible spectra and (b) The optical density at 900 nm as function of DMSO volume fraction used in the mixed DMF:DMSO solvent blend. (c) PL spectra for the various $\phi_{\text{DMSO}}$ films and (d) The effect of $\phi_{\text{DMSO}}$ on PL intensity counts. All the films from (a) and (c) used glass/bl-TiO$_2$/mp-TiO$_2$/MAPI to mimic device architecture. Peaks at about 825 nm are due to scattering.

Figure 4.11: Maximum PL intensity plotted against the measured capping layer thickness. The data were taken from fig. 4.8c. All the films were deposited on ITO/bl-TiO$_2$/mp-TiO$_2$. 
4.4.3 Effect of co-solvent composition on device performance

In this study we prepared devices for $\phi_{\text{DMSO}} = 0, 60, 100\%$ and measured the J-V data (fig. 4.12). The results (fig. 4.12 and table 4.1) indicate that, compared to the PSCs prepared using $\phi_{\text{DMSO}} = 0$ and 100%, the PSCs prepared using $\phi_{\text{DMSO}} = 60$ vol.% had a higher average PCE ($7.59 \pm 0.84\%$). In addition, the use of DMSO has produced device with negligible hysteresis (see black and red arrows, fig. 4.12). Consequently, $\phi_{\text{DMSO}} = 60\%$ was selected for all subsequent perovskite film preparations.

![Figure 4.12: Representative J-V curves for (a) 0 vol% DMSO, (b) 60 vol% and (c) 100 vol% devices. (d) shows the performance characteristic ($J_{SC}$, $V_{OC}$, FF and PCE) of devices from (a).]
Table 4.1: Photovoltaic performance data for all devices measured in this study. The data shown were obtained using the reverse scan.

<table>
<thead>
<tr>
<th>$\phi_{DMSO}^a$</th>
<th>$J_{SC}$ (mA/cm$^2$)$^b$</th>
<th>$V_{OC}$</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>15.6 ± 1.0</td>
<td>850 ± 20</td>
<td>52.5 ± 1.9</td>
<td>6.92 ± 0.44</td>
</tr>
<tr>
<td>60</td>
<td>15.6 ± 0.8</td>
<td>850 ± 20</td>
<td>57.7 ± 4.4</td>
<td>7.59 ± 0.84</td>
</tr>
<tr>
<td>100</td>
<td>11.8 ± 0.7</td>
<td>870 ± 10</td>
<td>55.8 ± 1.0</td>
<td>5.75 ± 0.48</td>
</tr>
</tbody>
</table>

$^a$ Volume fraction of DMSO used in the DMF:DMSO co-solvent blend.
$^b$ The ± values are standard deviations.

$\phi_{DMSO}$ of 60 vol.% was chosen for further study as it has the best surface coverage combination (fig. 4.6d and fig. 4.8a), near maximum crystal size (fig. 4.6j, fig. 4.7d and fig. 4.8b), higher conversion rate (fig. 4.10) and considerable maximum PL intensity (fig. 4.10c, d) and the best PCE (fig. 4.12d).

4.4.4 Comparison of MAPI films prepared using the 1 & 2-s and conventional methods

The SEM images of the final films obtained using the 1-s are shown in fig. 4.13a, while fig. 4.13b shows the films derived from the 2-s, and fig. 4.13c illustrates the films obtained through the 1 & 2-s method. As shown, films produced using the 1-s method have featureless films with relatively large cracks between large crystals while the films produced using the 2-s methods are composed of cubic crystals ranging from 200 to 400 nm in diameter. Both films have visible porosity as shown by the yellow arrows. Meanwhile, the films produced through the 1 & 2-s film have interwoven, large crystals covered by smaller cubic crystals. This morphology is the combination of both the 1-s and 2-s morphologies.
Figure 4.13: SEM images for MAPI films prepared using 1 & 2-s (a) and (b), 2-s (c) and (d) and 1-s (e) and (f) deposition. Exposed mp-TiO₂ is evident in (e). The arrows highlight gaps between the microcrystals (e) or crystals (d). Scale bars: 10 μm (top row) and 500 nm (middle row). (g) Depiction of the morphologies from 1 & 2-s, 2-s and 1-s deposition.

Figure 4.14 shows the XRD data illustrating that the 1-s films have higher conversion and negligible PbI₂ compared to the 2-s film (which contained some level of PbI₂). The XRD data for the films produced via the 1 & 2-s method are closest to the data for 2-s film (similar peaks location, patterns and widths). These results are parallel with what reported in the earlier study using DMF (Chapter 3, fig. 3.10) where the films produced using the 1 & 2-s method morphologically appeared as a hybrid of the 1-s and 2-s films.
4.4 Results and discussions

The thermal stability of MAPI has generated much interest [78, 143, 184] due to the significance of its potential application. In this regard, when moisture is present, the correspond degradation reaction will generate PbI$_2$ and CH$_3$NH$_3$I [78]. As shown in fig. 4.15a, the films have gone through heat-stress analysis at 150 °C in a humid atmosphere without encapsulation and have visually shown the distinctive stability differences; due to the formation of PbI$_2$. The films from the 1-s and 2-s films methods had changed colour to yellow within seconds and this change became more apparent after 1.0 h. In contrast, the MAPI film produced via the 1 & 2-s method retained most of its color for 2 h of exposure.

This study also examined the solar cells for the above-mentioned films. Figure 4.15d shows the representative J-V curves while table 4.2 shows the key performance parameters. In this regard, the values of the as-made PCE (fig. 4.15c) for 1-s was $4.15 \pm 0.46 \%$, while for 2-s the PCE value was $6.44 \pm 0.54 \%$, and for 1 & 2-s, it was $6.92 \pm 0.44 \%$. The highest values were obtained for the 1 & 2-s method due to the smaller number of pinholes.
4.4 Results and discussions

Figure 4.15: (a) Heat stress images for MAPI films prepared using the three methods (labelled). All films were studied on ITO/mp-TiO$_2$ at 150°C (with humidity of $\sim$60%). (b) Normalised power conversion efficiency (PCE) for 40 days. The PSCs were exposed to $\sim$40% humidity at room temperature. The devices were stored in the dark between measurements and were not encapsulated. Average PCE values (c) and JV-curves (d) for as-made devices are shown.

Table 4.2: Photovoltaic performance data for all devices measured in this study. The data shown were obtained using the reverse scan$^a$.

<table>
<thead>
<tr>
<th>Device</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPI(1-s)</td>
<td>16.0 ± 1.1</td>
<td>700 ± 5.0</td>
<td>36.8 ± 2.4</td>
<td>4.11 ± 0.32</td>
</tr>
<tr>
<td>MAPI(2-s)</td>
<td>17.3 ± 0.8</td>
<td>708 ± 3.6</td>
<td>46.5 ± 2.3</td>
<td>5.68 ± 0.36</td>
</tr>
<tr>
<td>MAPI (1 &amp; 2-s)</td>
<td>15.6 ± 0.8</td>
<td>850 ± 20</td>
<td>57.7 ± 4.4</td>
<td>7.59 ± 0.84</td>
</tr>
</tbody>
</table>

$^a$ The ± values are standard deviations.

This study also examined the stability of the devices at room temperature (fig. 4.15b). Here, it was found that the PCEs for conventional 1-s and 2-s MAPI devices have declined rapidly with time and remained operational for only 7 days. However, the 1 & 2-s device
retained more than 70% of its initial PCE value after 30 days and was more stable than the other devices. Other performance data such as $J_{SC}$, $V_{OC}$ and FF are demonstrated in fig. 4.16. The 1-s film (fig. 4.13e) and 2-s (fig. 4.13d) films either had large cracks or were highly porous, respectively (see arrows). However, the MAPI (1 & 2-s) film had fewer pores (fig. 4.13b). The capping layer thicknesses for the films decreased in the order 1 & 2-s (330 nm) > 2-s (250 nm) > 1-s (230 nm). Consequently, the superior stability of the 1 & 2-s devices was due to the better barrier properties of the capping layer. Hence, the use 1 & 2-s method provided the MAPI devices with higher PCE values and better stability.

Figure 4.16: (a) to (d) Normalised solar cell performance characteristic in 40 days. PSCs were exposed to $\sim$40% humidity at room temperature. The devices were stored in the dark between measurements.
4.5 Conclusions

This study has investigated a solvent-assisted 1 & 2-s deposition method using co-solvent blends. It was observed that the MAPI films prepared using the 1 & 2-s method showed some unexpected thermal and device stability improvement, which could be attributed to an improved capping layer morphology. The inclusion of DMSO as a co-solvent with DMF ($\phi_{\text{DMSO}}$) had a strong effect on the properties and morphology of the films produced through the 1&2-s method. Furthermore, $\phi_{\text{DMSO}} = 60\%$ has shown the best combination of film properties and solar cell performance. The morphology of the perovskite films and crystalline grain size were well controlled by the $\phi_{\text{DMSO}}$ in the solvent preparation method. These results provide useful progress towards understanding the growth kinetics of perovskite films and a better control of the solution-processing for low-cost and highly efficient perovskite solar cells.
A study of CH$_3$NH$_3$PbI$_{3-x}$Br$_x$ prepared by combined 1- and 2- step deposition: decoupling structure and composition

5.1 Abstract

Chapter 3 and 4 have shown the excellent potential of perovskite solar cells (PSCs) in generating inexpensive solar electricity by a new solution processing method. Two common methods for the preparation of PSCs are based on first, the one-step (1-s) deposition, and second, the two-step (2-s) deposition used nowadays are still lacked behind. This chapter will examine the mixed anion perovskite films which were prepared through the 1 & 2-s method, which is a hybrid method combining both the 1-s and 2-s depositions. Whilst the preparation of methylammonium lead iodide (MAPbI$_3$) films by using the 1 & 2-s method and the effect of co-solvent blends were investigated in Chapter 3 and 4, respectively, we greatly extend that novel approach by preparing the CH$_3$NH$_3$PbI$_{3-x}$Br$_x$ (MAPbI$_{3-x}$Br$_x$) mixed halide films with tuneable competition between the crystal growth and the anion exchange. Here, it was observed that the use of the 1 & 2-s method allowed the decoupling of the MAPbI$_{3-x}$Br$_x$ composition and structure. The composition of the MAPbI$_{3-x}$Br$_x$ films could either be stoichiometrically-controlled or diffusion-controlled based on the reactant addition sequence, hence, a formation mechanism was proposed. Devices with the stoichiometrically-controlled MAPbI$_{3-x}$Br$_x$ film had shown the maximum thermal
stability, device stability, and power conversion efficiency. Thus, the use of 1 & 2-s method offers novel versatility in the device construction and architectural control of perovskite film.

5.2 Introduction

The hybrid lead-halide perovskite solar cells (PSCs) have been shown to be potentially inexpensive and have excellent photovoltaic performance [165, 166]. These features show its potential as the alternatives to silicon-based cells. In this light, there are considerable research interests on methylammonium (MA), formadinium (FA), and hybrid FAMA lead halide perovskite solar cells. Past studies have shown that mixed halide and mixed cation have the highest efficiencies [185] and improved stability [167]. These films were prepared by using preparation methods where both reactants were in the solution, or, the one-step (1-s) deposition [145] where one of the reactants was pre-deposited in a solid phase prior to the second deposition step (2-s) [8]. In the meantime, our previous study (chapter 3 and chapter 4) has presented a hybrid method for the preparation of PSC which combined these two methods. This method creates a new versatility in controlling the composition and structure of the perovskite film. Moreover, this study will extend the earlier approach by investigating mixed anion perovskite films (MAPbI$_{3-x}$Br$_x$) films which were prepared by using this novel approach. A new level of composition and structural control for perovskite films is introduced and mechanistic insights are obtained. In this study, DMSO was used as a co-solvent with DMF (as discussed in Chapter 4) to prepare the MAPbI$_{3-x}$Br$_x$ films using the 1 & 2-s method due to better formation of final morphologies (coverage and properties).

While MAPI is one of the most popular perovskites for PSCs being studied, it has low stability and does not have the optimum band gap for complete absorption of visible light. These limitations have sparked the use of mixed anion and a cation film which allows the narrowing of the band gap [186, 187] and MAPbI$_{3-x}$Br$_x$ have been used to increase the stability of devices [9, 145]. In this regard, Br$^-$ shows smaller ionic radius compared to I$^-$ and this allows facile diffusion through the MAPI matrix, hence, Br$^-$ has been widely
used to create the $\text{MAPbI}_{3-x}\text{Br}_x$ films through the 1-s [9, 145, 188] or exchange anion exchange methods [180, 189]. The 1-s mixed anion method used to produce $\text{MAPbI}_{3-x}\text{Br}_x$ films often have stoichiometrically controlled compositions, which determine the crystal structure [145, 188], on the other hand, the anion exchange approach produces more time-dependent compositions and fixed structures11. Thus, this study investigates the extents of the 1 & 2-s method to decouple the perovskite structure and composition and to determine whether this new approach could provide more versatility than the conventional 1-s and 2-s methods.

It was found that these methods can be adopted by others where only particular preparation variables could be changed systematically. However, this study is not focused on obtaining high PCE devices even though this optimisation could be adopted in future studies, rather, this study is focused on analysing the mixed halide films which are prepared through the 1 & 2-s method and a DMF:DMSO co-solvent blend (Chapter 4). Here, the properties of the mixed halide films prepared using the combined method were compared to single halide (MAPI) prepared through the same method. SEM was used to examine the morphologies of the films, while the UV-visible, photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectroscopies are used to examine the spectroscopic properties. X-ray photoelectron spectroscopy (XPS) was used to probe on the film compositions. These data were then used to propose the structural and composition evolution mechanisms for the $\text{MAPbI}_{3-x}\text{Br}_x$ films prepared through 1 & 2-s method. This study also measured and compared the performance of $\text{MAPbI}_{3-x}\text{Br}_x$ solar devices against the performance of MAPI (1 & 2-s) constructed solar cells. After analysing the stability of the film and the device, this study found that the stoichiometrically-controlled $\text{MAPbI}_{3-x}\text{Br}_x$ films have the best efficiency of 11.3% (average). The 1 & 2-s method allows the separation of structure and composition and shows potential for improving alloy control for other PSCs constructed using solution-based deposition.
5.3 Experimental procedure

The study focuses on incorporating Br⁻ by using the 1 & 2-s combination methods with DMF:DMSO co-solvent blend (Chapter 4) and characterise their optoelectronic properties. The perovskite films were fabricated to investigate their properties and decouple the anion exchange with crystal growth. The key procedure can be separated into materials preparations, perovskite films preparations and device fabrications.

5.3.1 Materials

Isopropanol (IPA, anhydrous, 99.5%), chlorobenzene (CBZ, anhydrous, 99.5%) methylamine (> 98%), HI (99.9%, 57 wt.% solution in water) and HBr (99.95%, 57 wt% solution in water), 4-tert-butylpyridine (96%), lithium bis(trifluoromethanesulfonimido)-date (LiTFSI, 99.95%), PbI₂ (99.999%), N,N-dimethylformamide (DMF, anhydrous, 99.8%), titanium bis[acetyldiacetone) (TDB, 75 wt % in IPA), poly-methylmethacrylate (PMMA, molecular weight 15,000 g/mol) were all purchased from Aldrich and used as received. TiO₂ paste (Dyesol 18NRT) and 2,2’,7,7’-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9’-spirobifluorene (Spiro-MeOTAD, Fenglin Chemicals, 99.5%) were also used as received.

5.3.2 Perovskite film preparation

MAI and MABr were synthesized following established procedures [190] as follows. Briefly, HI (30 mL) was added dropwise into aqueous methylamine (27.9 mL) with a mole ratio of 1:1 into a round-bottom flask in an ice bath for 2 h with stirring [180]. The cold solution was carefully evaporated using a rotary evaporator. The crystals were washed using diethyl ether three times and dried in a vacuum oven. A similar procedure was followed for MABr.

ITO/Glass slides (2.0 cm x 1.5 cm, Ossila Ltd.) were cleaned by sonication in a 1% Hellmanex solution in boiling water for 15 min followed by rinsing with water and IPA and cleaning in ultrasonic for 5 min and dried using a nitrogen stream. TiO₂ paste (70 µL, 1:5 in ethanol) was spin-coated onto the cleaned glass slides at 5000 rpm for 30 s.
5.3 Experimental procedure

to form a mesoporous scaffold (mp-TiO$_2$). The mp-TiO$_2$ film was then annealed at 500 °C for 30 min and had an average thickness of 250 nm. The perovskite was deposited on mesoporous scaffold according to fig. 5.1.

![Figure 5.1: Perovskite films prepared using different anions by the 1 & 2-s method. The MAPI film shown in (a) corresponds to MAPI (1 &-2-s), (b) and (c) depict the preparation of mixed anion films where excess PbI$_2$ and MABr or MAI is used in the first step. Subsequently, MAI or MABr is used in the second step. (d) shows the preparation of MAPB film where MABr was used in both the first and second step. Note that the precursor films for the preparation of MAPI (a) and MAPI-MAPI(B) (c) were the same.](image)

**MAPI films prepared using the 1 & 2-s method**

The precursor film solutions in DMF:DMSO mixed solvent contained PbI$_2$ (1.0 M) and MAI (0.50M) and were prepared in a glove box (humidity ~ 2%). Film fabrication was conducted outside of the glove box (humidity ~ 40%). The solutions (70 µL) were spin-
coated onto the mp-TiO$_2$ layer. The solutions were kept at 70 °C during spin-coating. A two-stage spin-coating procedure was employed for precursor film deposition which was 2000 rpm for 10s and 4000 rpm for 20 s. The precursor films were dried at 100 °C for 10 min. The films were washed with IPA for 10 s. Then, MAI solution in IPA (100 µL, 10 mg/mL) was dripped and spin coated on the precursor film for 30s. This procedure was repeated twice to give the final films. These films were dried at 100 °C for 10 min and immediately placed in a desiccator over P$_2$O$_5$ and stored in the dark until investigation.

*MAPbI$_{3-x}$Br$_x$ films prepared by the 1 & 2-s method*

Mixed anion perovskite films were prepared using the 1 & 2-s method (fig. 5.1b and c) DMF:DMSO co-solvent blends containing a DMSO volume fraction ($\phi_{\text{DMSO}}$) of 60 vol.% were used. The code used for these films identifies the order of preparation. Note that MAPI is MAPbI$_3$. The code MAPI(B)-MAPI indicates that a mixed anion perovskite (in this case MAPbI$_2$Br) would have formed in the first step (fig. 5.1b) along with excess PbI$_2$. In the second step MAPbI$_3$ would have been formed exclusively if no anion exchange occurred. This study investigates the latter possibility as well as the case where one phase MAPbI$_{3-x}$Br$_x$ was formed. The code MAPI-MAPI(B) indicates that MAPbI$_3$ was prepared in the first step (fig. 5.1c) along with excess PbI$_2$. In the second step MAPbI$_{3-y}$Br$_y$ would have been formed exclusively if no anion exchange occurred. Again, this study investigates the latter possibility and whether one phase MAPbI$_{3-y}$Br$_y$ was formed.

To prepare the MAPI(B)-MAPI films the precursor solutions contained PbI$_2$ (1.0 M) and 0.50M of MABr. The films were deposited and annealed as described above. The second-step used MAI (10 mg/mL in IPA) with deposition and annealing as described above.

To prepare the MAPI-MAPI(B) films the precursor solutions contained PbI$_2$ (1.0 M) and 0.50M of MAI. The films were deposited and annealed as described above. The second-step used MABr (10 mg/mL in IPA) with deposition and annealing as described above.
MAPB film prepared by the 1 & 2-s method

These films were prepared as a control system and followed the same method (and concentrations and temperature) described above for the MAPI films except the PbBr$_2$ and MABr were used.

5.3.3 Device fabrication

Laser-patterned, FTO-coated glass substrates (~8 $\Omega$/sq) were cleaned by ultrasonication in a 2% Hellmanex solution, rinsed with deionized water and IPA, and dried. A blocking layer of compact TiO$_2$ (bl-TiO$_2$) was then deposited by spin coating TDB (75 $\mu$L, 0.15 M) solution in 1-butanol at 2000 rpm for 60 s. The procedure was repeated using a TDB solution (0.30 M) and the substrate was heated at 125 °C for 5 min to give an average thickness of 50 nm. A mp-TiO$_2$ layer was then deposited as described above. Perovskite photoactive layers were deposited as described above. The values for MAPI-MAPI(B), MAPI(B)-MAPI and MAPB were ~ 350 nm, 380 nm and 400 nm, respectively. These values were determined by SEM and DEKTAK profilometry. Spiro-MeOTAD was deposited as a hole transport matrix (HTM). The latter (average thickness of 100 nm) was deposited by static spin-coating of Spiro-MeOTAD in CBZ (72.3 mg/mL) at 3000 rpm for 30 s. Li-TFSI salt and TBP in acetonitrile were added to the HTM solution. HTM deposition followed established literature procedures [8, 181]. Finally, a gold layer (80 nm) was deposited on top of the HTM. The active area of the devices was defined using a square aperture within a mask and fixed at 0.025 cm$^2$. The fabrication procedures were performed in ambient atmosphere where ~ 40% relative humidity present. All devices were stored in a desiccator over P$_2$O$_5$ in the dark until investigation.

5.3.4 Physical measurements

The surface morphologies were investigated using a Philips XL30 FEI – SEM. The cross-section microstructure was investigated using a FEI Sigma FEG-SEM. XRD data were obtained using a Bruker D8 Advance diffractometer (Cu-K$\alpha$). The films obtained were scanned with a step size of 0.02°. For these measurements the films were prepared under a
5.3 Experimental procedure

nitrogen atmosphere and were measured using an airtight holder. UV-visible spectra were recorded using a Perkin Elmer Lambda 25 spectrometer. Photoluminescence (PL) spectra were obtained using an Edinburgh Instruments FLS980 spectrometer and time-resolved PL (TRPL) spectra were acquired by using the time-correlate single-photon counting (TCSPC) technique under excitation provided by picosecond diode laser (405 nm) from the ITO side with the repetition frequency of 1 - 10 MHz using the same PL instrument. The perovskite films were prepared on ITO/mp-TiO$_2$ via spin coating (4000 rpm, 20 s) with PMMA dissolved in CBZ (10 mg/mL) prior to measurement [191].

X-ray photoelectron spectroscopy (XPS) measurements were performed with SPECS XPS instrument, equipped with a SPECS Focus 500 monochromated Al K$_\alpha$ X-ray source with photon energy of 1486.6 eV. Emitted photoelectrons were collected using a 150 mm hemispherical energy analyser (SPECS Phoibos 150). Binding energies (BEs) were calibrated to C 1s 248.8 eV from adventitious carbon for all samples and quoted to accuracies of ±0.5 eV and ±0.05 eV, for surveys and high resolution (HR) scans, respectively. Relative atomic ratios were calculated from HRXPS spectra where a Shirley background and GL(30) function (70% Gaussian and 30% Lorentzian) were applied to fit the core level spectra using CasaXPS software. CasaXPS sensitivity factors were used for calculating the stoichiometry of the samples. The films were freshly prepared in nitrogen glovebox and immediately transferred to the XPS vacuum chamber for measurement.

5.3.5 Device characterisation

The current density-voltage (J–V) characteristics were measured using a Keithley 2420 Sourcemeter and 100 mW/cm$^2$ illumination (AM 1.5G) and a calibrated NREL certified Oriel Si-reference cell. An Oriel SOL3A solar simulator was used for these experiments. Forward and reverse direction sweeps were measured with a sweep rate of 0.2V/s in ~ 40% relative humidity. EQE measurements were performed using a 150W Bentham IL1 illuminator as the light source, a Bentham M300 monochromator, a 72 Hz optical chopper, a lock-in amplifier (Stanford Research Corp SR510), and a NIST-certified Si photodiode (Thorlabs FDS 1010-CAL) for calibration. The scan resolution was fixed to 1 nm.
5.4 Results and discussion

This section provides the key findings of CH$_3$NH$_3$PbI$_{3-x}$Br$_x$ films and devices produced by novel combination 1 & 2-s method, with co-solvent blend compositions established in chapter 4. The unique properties of the mixed anionic perovskite films such as improved morphologies, efficient alloying and optoelectronic properties and stability are discussed.

5.4.1 Mixed anionic perovskite films prepared using the 1 & 2-s method

The main aspect investigated in this study is the effect of perovskite films with mixed anions (I$^-$ and Br$^-$) which were prepared using the 1 & 2-s method (See fig. 5.1). MAPI was prepared in this study acted as a control (fig. 5.1a) and the MAPI(B)-MAPI was the first mixed anion films. For the preparation of the precursor film, Br$^-$ was introduced in the first step through MABr while the MAI was included in the second step (fig. 5.1b). Here, it is important to note that the codes used here are reflective of the nominal sequence of perovskite formation.

MAPI-MAPI(B) was the second mixed anion film where during the second step, Br$^-$ was mixed into the MAPbI$_3$ / PbI$_2$ mixture (fig. 5.1c). MAPB, which acted as a second control film, was prepared using PbBr$_2$ and MABr (fig. 5.1d). Here, the concerns for analysing MAPI(B)-MAPI and MAPI-MAPI(B) were to determine whether crystal growth or anion exchange dominated the perovskite formation process. Consequently, both final films would have two phases when growth occurred without exchange (fig. 5.1b and c).

This study used SEM to examine the precursor and final film morphology (fig. 5.2). Figure 5.2i-p illustrates the lower magnification images where the precursor is shown on the left, and the final film is shown on the right of the red reaction arrows. The three precursor films prepared using PbI$_2$ (fig. 5.2a, e and c) all showed the presence of nanometre-scale crystals in contrast to the film precursor film containing MAPbBr$_3$ + PbBr$_2$ (fig. 5.2g) which did not show any presence of nanometre-scale crystals. In this light, it is worth to note that the precursor films (a) and (c) were the same.
5.4 Results and discussion

Figure 5.2: Effect of halide type on the final morphology of perovskite films observed at high magnification (a-h) and lower magnification scale (i-p). The scale bars are shown. Precursor and final films are shown on the left and right reaction arrows, respectively. Note that (a) and (e), (i) and (m) are images of the same precursor film.

For the final films, heterogeneous nucleation of MAPI from the rich surface of the PbI$_2$ [192] caused the MAPI film (fig. 5.2b) to contain a high density of smaller particles. Moreover, there were signs of crystal growth where the MAPI(B)-MAPI (fig. 5.2d) crystals were larger in comparison to the precursor film (fig. 5.2c) while the large crystals in the MAPB film were nucleated (fig. 5.2h). Thus, the three films (MAPI, MAPI(B)-MAPI and MAPB) seemed to experience heterogeneous nucleation while the MAPI-MAPI(B) film (fig. 5.2f) did not show any indication of any significant change in crystal size compared to
the precursor film (fig. 5.2e). The average crystal diameter for the final films for the MAPI was $253 \pm 96$ nm, the MAPI(B)-MAPI was $352 \pm 66$ nm, MAPI-MAPI(B) was $154 \pm 35$ nm and MAPB, was $415 \pm 52$ nm.

High resolution XPS data were measured to identify the compositions for the perovskite films (fig. 5.3). This study found that the MAPB film had the strongest Br 3d peaks (fig. 5.3e) but the peaks were absent for MAPI film. As shown in the table in fig. 5.3e, for the MAPI-MAPI(B) and MAPI(B)-MAPI films, the Br 3d peaks shifted to higher binding energies upon incorporation of I into the films’ matrix. These data and trend are in line with the data for perovskite films [10, 193, 194] reported by several groups. The increase in the binding energy might be due to the changes in the chemical bonding which corresponds to the increase in the lattice spacing for the alloys as shown in the XRD (fig. 5.4). The relative atomic % was calculated from the high resolution scan on the core level spectra (as mentioned in experimental section 5.3.4) and illustrated in fig. 5.3f. From the figure, the films show an expected composition where Pb:N ratio is around 1:1 (however, slightly Pb peak is apparent in XRD analysis (see fig. 5.4(MAPI(B)-MAPI)) and the rest is I. There are substantial amounts of Br in MAPI(B)-MAPI, MAPI-MAPI(B) and obviously MAPB is all Br instead of I. There was an unexpected increase in Br at the surface after MAI dipping, indicating Br migration from inner part of film to the surface. It is worth noting that MAPI(B)-MAPI is MAPI lightly doped with Br. As for MAPI-MAPI(B), the MAPbBr$_3$ is produced but did not fully exchange with I indicating there is perovskites alloy present (fig. 5.1c). The relative atomic ratios can be useful even though it is well known that XPS only quantifies the elements found at less than $\sim 10$ nm from the surface [195].

Table 5.1 shows final films’ atomic% for Pb, N, I and Br; the mol fractions of Br were found in MAPI (B)-MAPI and MAPI-MAPI(B) films. The MAPI(B)-MAPI recorded the (Br and I) of 19 mol.%, while MAPI-MAPI(B) films had 26 mol.%. Hence, the composition for MAPI(B)-MAPI was MAPbI$_{2.4}$Br$_{0.6}$ and for MAPI-MAPI(B), the composition was MAPbI$_{2.1}$Br$_{0.9}$. As shown in table 5.1, the compositions calculated based on the stoi-
Figure 5.3: XPS core level spectra for (a) I, (b) N, (c) Pb and (d) Br for the final films. The binding energies are shown in the table (e). (f) shows the relative atomic % measured and calculated from high resolution scan from (a)-(d). The legend shown in (a) also applies to (b)-(d).
5.4 Results and discussion

### Table 5.1: Composition of the films determined from XPS.a

<table>
<thead>
<tr>
<th>Code</th>
<th>% Pb meas. (Calc.)</th>
<th>% N meas. (Calc.)</th>
<th>% I meas. (Calc.)</th>
<th>% Br meas. (Calc.)</th>
<th>Mol frac. x_{Br}</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPI</td>
<td>23.2 (20.0)</td>
<td>18.5 (20.0)</td>
<td>58.3 (60.0)</td>
<td>0 (0)</td>
<td>0</td>
</tr>
<tr>
<td>MAPI(B)-MAPI</td>
<td>23.3 (20.0)</td>
<td>18.1 (20.0)</td>
<td>47.5 (50.0)</td>
<td>11.1 (10.0)</td>
<td>19</td>
</tr>
<tr>
<td>MAPI-MAPI(B)</td>
<td>22.7 (20.0)</td>
<td>18.8 (20.0)</td>
<td>43.4 (50.0)</td>
<td>15.1 (10.0)</td>
<td>26</td>
</tr>
<tr>
<td>MAPB</td>
<td>26.6 (20.0)</td>
<td>15.4 (20.0)</td>
<td>0 (0)</td>
<td>58.0 (60.0)</td>
<td>100</td>
</tr>
</tbody>
</table>

*Data obtained from analysis of the data shown in fig. 5.3. The calculated values were determined from the stoichiometry used for preparation.*

*Mole fraction of Br determined from the measured %I and %Br values shown in columns 4 and 5, respectively.*

The XRD analysis was used to examine the structures of the precursor and final films (fig. 5.4). In term of the precursor films prepared with PbI$_2$ (fig. 5.4), the study found that the PbI$_2$ (001) peak at $2\theta = 12.7^\circ$, for all precursors film (except for MAPB + PbBr$_2$). It is noted that same precursor film was used for MAPI and MAPI-MAPI(B), hence the same PbI$_2$ peak (see fig. 5.1.) The precursor film with MAPI also had major peaks as a result of the peaks exhibited by the (110)t, (112)t and (220)t planes which shows the tetragonal [90, 196] MAPI [64, 197]. In contrast, the MAPI (B) precursor film (fig. 5.4(MAPI(B) + PbI$_2$)) showed strong (100)c and (200)c peaks due to the cubic structure of MAPbBr$_3$ [145, 198]. The latter two peaks can also be seen in the diffractogram for the MAPB precursor. The latter data also showed a peak due to PbBr$_2$ at $2\theta = 18.5^\circ$ [199].
Figure 5.4: X-ray diffractograms for the precursor and final films (labelled). Key peaks ((110)t, (100)c, (220)t and (200)c) associated with the perovskite structure for the final films have been expanded in (b) to show the shift occurred when increasing mol% Br are used. Note that the diffractograms for MAPI and MAPI-MAPI(B) are the same because the same precursor films were used (refer fig. 5.1).

Meanwhile, the XRD data for the final films indicated that the diffractograms for MAPI and MAPB have similar features to those reported in previous studies [200]. As noted above the MAPI diffractogram had a small amount of residual PbI$_2$. The MAPI-MAPI(B) diffractogram has five peaks which were also present in the MAPI. However, these peaks were at higher angles compared to the MAPI peaks. This is visible in the expanded views of the (110)t and (220)t peaks as shown in fig. 5.4b. Upon inclusion of Br into MAPI, the phase undergoes transition from tetragonal to cubic phase [201, 202]. Meanwhile, there were only two significant peaks in the diffractogram for MAPI(B)-MAPI. These peaks were attributed to (100)c and (200)c caused by a cubic phase. None of the diffractograms for MAPI(B)-MAPI or MAPI-MAPI(B) showed multiple peaks which represent two or more different phases. Consequently, the XRD data show that efficient alloying occurred for MAPI(B)-MAPI and MAPI-MAPI(B).
Noh et al. and Park et al. examined alloyed MA-based perovskites which contain I and Br [145, 188]. In each case, there were transitions from tetragonal (at low x values) to cubic (at high x values) structures when x was greater than or equal to 0.2 to 0.3. In this case, the MAPI(B)-MAPI (x = 0.19) and MAPI-MAPI(B) (x = 0.26) formed cubic and tetragonal structures, respectively. Here, the perovskite with the lower x (0.19) had a more densely packed structure compared to those with a higher x. This result is counter-intuitive because Br\(^-\) has a smaller ionic radius (1.96 Å) than that of I\(^-\) (2.2 Å) which the potential of the 1 & 2-s method in controlling the perovskite structure while the final structure in each case was determined by that of the precursor film. The 1 & 2-s method could separate the perovskite growth into the first step (structure forming stage) and the second stage (alloying stage).

5.4.2 UV-visible and PL spectroscopy

Figure 5.5a presents the digital photographs of the films. A further inspection into the film colours has shown that visible light absorption has decreased in the order MAPI > MAPI(B)-MAPI > MAPI-MAPI(B) > MAPB as supported by the films’ UV-visible spectra measured (fig. 5.5b). Tauc plots were used to determine the \(E_g\) values (fig. 5.5c) while fig. 5.5d presents the variation of \(E_g\) where the mole fraction of Br in the films was estimated based on the XPS compositions (table 5.1). The data reported for the MAPbI\(_{3-x}\)Br\(_x\) films prepared using the conventional 1-s method are also presented for comparison [145]. Here, the \(E_g\) values obtained for MAPI(B)-MAPI and MAPI-MAPI(B) are almost similar to those reported for the conventional films with the same overall Br content. This shows that despite the use of the 1 & 2-s method for the formation of the films (fig. 5.1), the mixed anion 1 & 2-s films have transformed to a uniform composition. This observation agrees with the XRD data reported above and confirms that MAPI(B)-MAPI and MAPI-MAPI(B) films comprised of alloys that are compositionally uniform.
5.4 Results and discussion

Figure 5.5: (a) Digital photographs of the final films (1.5 cm × 2.0 cm). (b) UV-visible spectra for the films from (a). (c) Variation of the energy gaps calculated via Tauc plots. $E_g$ values calculated using the equation given in Ref. [145] are also shown. (d) Variation of the energy gaps with mole fraction of Br in the films in comparison with those from literature [145].

This study also measured the PL spectra for films deposited onto ITO/mp-TiO$_2$ (fig. 5.6a) and the peak wavelength of the MAPB was the lowest at 543 nm while the MAPI-MAPI(B), MAPI(B)-MAPI and MAPI recorded 735, 748 and 780 nm, respectively. This trend is in line with those of UV-visible spectra (fig. 5.5a) while the PL intensities for the iodide-containing films have decreased in the order MAPB > MAPI(B)-MAPI > MAPI > MAPI-MAPI(B). Moreover, the thicknesses of the capping layer for these films were 400, 380, 330 and 350 nm, respectively. In general, as observed for MAPI, the PL intensity increased in linear manner as the thickness of the capping layer improves (fig. 5.6b) as more of the perovskites was further from the mp-TiO$_2$, preventing the quenching.
5.4 Results and discussion

Figure 5.6: (a) PL spectra for the films. The excitation wavelength was 480 nm for all films except MAPB. For the latter film an excitation wavelength of 390 nm was used. (b) The effect of capping layer thickness, $CL_{thick}$ with respect to maximum PL intensities gained for perovskite films. (c) Time-resolved photoluminescence data measured for the films (labelled). (d) The table shows the time constants extracted from bi-exponential fits to the data in (c).

We also conducted time-resolved PL measurements (fig. 5.6c) and two time constants were used to fit the data, as shown. In general, it is believed that the short (fast) and long (slow) time constants from the fits are related to the carrier recombination at the grain surfaces and / or the related carrier diffusion; while the longer time relates to these processes within the bulk material [203]. Hence, as the Br content decreased, the time constants will also decrease, i.e., in the order MAPB >MAPI(B)-MAPI > MAPI-MAPI(B) > MAPI. This trend similar to the observed steady-state PL data which can be attributed to the thickness of the capping layer.
5.4 Results and discussion

5.4.3 Proposed mechanism for mixed anion perovskite film growth by the 1 & 2-s method

A proposed mechanism has been put forward based on the results discussed above. This mechanism will help to explain the changes that have happened when preparing the MAPI(B)-MAPI and MAPI-MAPI(B) films. In regard to MAPI(B)-MAPI (fig. 5.7a), the initial step produced a 2-phase precursor film that contained MAPbI$_2$Br, and PbI$_2$ crystals. The subsequent reaction could lead to the growth of MAI crystal growth in response to the presence of PbI$_2$ and anion exchange. The crystal growth was relatively fast compared to I$^-$ diffusion (and exchange) within the perovskite lattice. This is because of the relatively large I$^-$ ionic radius [197]. Furthermore, the smaller Br$^-$ ions could rapidly diffuse from the perovskite into the new crystal phase. We propose this process uniformly distributed Br$^-$ in the crystals giving a one-phase material (MAPbI$_2$$_4$Br$_{0.6}$) with a stoichiometry that was limited by the initial concentration of MABr used in the first step. The growth of new cubic crystals during the formation of the final film was determined by the initial seed perovskite crystals in the precursor film.

In the case of MAPI-MAPI(B) (fig. 5.7b), the first step produced a two phase MAPbI$_3$ and PbI$_2$ precursor film. The second step involved competition between very fast Br$^-$ diffusion into MAPbI$_3$ (and anion exchange), as well as the fast crystal growth by reaction with PbI$_2$ to form MAPbI$_{3-x}$Br$_x$. It is also likely that fast Br$^-$ exchange occurred between the two crystal types which resulted in a uniform Br$^-$ distribution within the one-phase final film of MAPbI$_{2.1}$Br$_{0.9}$. Moreover, the composition was limited due to the time available for diffusion of the Br$^-$ into the crystals during the final film formation. In this case, the new crystal growth that occurred was tetragonal and was directed by the first (perovskite) phase in the precursor film (MAPbI$_3$).
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Figure 5.7: Proposed mechanism for mixed anion preparation via the 1 & 2-s method for the (a) MAPI(B)-MAPI and (b) MAPI-MAPI(B) films. The former film composition is limited by the stoichiometry used in the first (precursor forming) step; whereas, the latter film composition is limited by diffusion that occurs in the second (final film forming) step.

5.4.4 Device performance and stability

This study has examined the performance of solar cells produced using the films. Figure 5.8a illustrates the cross-section for the best performing device, MAPI(B)-MAPI. The architecture used to fabricate the solar cell also shown to illustrate the layer arrangement. Comparing to widely used PSCs configuration, the perovskite active layer thickness is deposited to be about 400-500 nm (which is a little bit thinner compared to other conventional system) to warrant for efficient light diffusion and carrier transfer. In this light, fig. 5.8b illustrates the EQE data that shows that the device has harvested light over much of the UV-visible range while the integrated EQE data provided a $J_{SC}$ value of 20.6 mA/cm$^2$, which is close to the value obtained from the J-V data (20.4 mA/cm$^2$). Figure 5.8c shows
representative J-V curves for all the devices and fig. 5.9 presents the key parameters from the device measurements act as function of Br mole fraction while table 5.2 presents the data from the device. Here, the MAPI(B)-MAPI showed the highest $J_{SC}$ values while MAPB had the lowest $J_{SC}$. This is caused by the lack of light harvesting at higher wavelength (fig. 5.5b). As expected, the increasing Br content caused an increase in the $V_{OC}$ values as the band gap widened (fig. 5.5c while the FF values for all devices were comparable. Here, the PCEs ranged from 4.20 to 11.33 $\pm$ 0.47 % and MAPI(B)-MAPI had the maximum PCE. The latter value was relatively lower than those of high performance PSCs as methods such as anti-solvents [64] or solvent-mediated granular coarsening [204] were not used in this study, and instead, the processing was kept simple in this study to help increase the fundamental understanding of structure, composition and device performance.

**Figure 5.8:** (a) SEM cross-section (with device architecture). and (b) EQE data for the MAPI(B)-MAPI device. The scale bar is 200 nm. The integrated current density as a function of wavelength for a MAPI(B)-MAPI device is also shown. (c) Representative J-V curves for all of devices.
5.4 Results and discussion

The PCE for MAPI(B)-MAPI was 11.33 ± 0.47 % (table 5.2), which is 30% larger than the highest value reported for a PSC prepared using the 1 & 2-s method (see Chapter 3 section 3.4.4). This high PCE is due to the larger crystal size (and consequently, less grain boundaries31) which causes a higher $J_{SC}$ value. Moreover, the predominantly long (and large) crystals have extended through the film thickness as shown in the SEM cross-section (fig. 5.8a). In contrast, fig. 5.10 shows smaller crystals were observed in the SEM cross-section for the MAPI-MAPI(B) which has led to more grain boundaries. This study found that the inclusion of Br (within MAPI(B)-MAPI) lead to much improved PCE value compared to the control Br-free system (MAPI), as shown in fig. 5.9d. This result differs from an earlier report for mixed anion PSCs prepared using the 1-s method [145]. This

**Figure 5.9:** Variation of (a) $J_{SC}$, (b) $V_{OC}$, (c) FF and (d) PCE with mol fraction of Br/% for the devices. The legend in (a) applies to all.
5.4 Results and discussion

Table 5.2: Photovoltaic performance data for all devices measured in this study. The data shown were obtained using the reverse scan\(a\).

<table>
<thead>
<tr>
<th>Device</th>
<th>(J_{SC}) (mA/cm(^2))</th>
<th>(V_{OC})</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPI</td>
<td>15.6 ± 0.8</td>
<td>850 ± 20</td>
<td>57.7 ± 4.4</td>
<td>7.59 ± 0.84</td>
</tr>
<tr>
<td>MAPI(B)-MAPI</td>
<td>20.4 ± 1.0</td>
<td>860 ± 10.0</td>
<td>64.5 ± 2.7</td>
<td>11.33 ± 0.47</td>
</tr>
<tr>
<td>MAPI-MAPI(B)</td>
<td>14.8 ± 1.6</td>
<td>930 ± 10.0</td>
<td>60.8 ± 3.1</td>
<td>8.35 ± 1.14</td>
</tr>
<tr>
<td>MAPB</td>
<td>7.9 ± 0.6</td>
<td>980 ± 10.0</td>
<td>54.8 ± 2.9</td>
<td>4.20 ± 0.34</td>
</tr>
</tbody>
</table>

\(a\) The ± values are standard deviations.

improvement seen here could be due to the larger crystal size as a result of using the 1 & 2-s method as shown by the SEM images (fig. 5.2, higher magnification).

Figure 5.10: SEM cross-section for the MAPI-MAPI(B) film. The scale bar is 200 nm.

As the MAPI(B)-MAPI system has a higher PCE, this study examined the stability for this system. Figure 5.11a shows the thermal stability test whereby data are compared to the MAPI film. Comparing to MAPI, the MAPI(B)-MAPI film had higher thermal stability and only minor degradation was evident after 8 h of heating at 150 °C in humid atmosphere. The enhanced stability is caused by tighter binding of the MA\(^+\) cations \([145, 205]\), within the lattice due to the cubic morphology (fig. 5.4) and this slows the rate of H\(_2\)O hydration which is a main step in the moisture based degradation process. On the other hand, the MAPI film had a tetragonal structure (fig. 5.4) and was less thermally stable. The device stability was assessed through using the un-encapsulated devices in ambient air to probe for relative PCE as a function of time (fig. 5.12). In this regard, the MAPI(B)-MAPI device
showed a superior stability compared to the control MAPI device where it only lost 30% of its PCE after 30 days compared with other MAPI system (1 & 2-s, conventional MAPI 1-s and 2-s reported earlier in Chapter 4 section 4.4.4). Other J-V data such as $J_{SC}$, $V_{OC}$ and FF are presented in fig. 5.12b-d. This is a result of the cubic morphology and good capping layer properties (fig. 5.2) which is in good agreement to the result of the MAPbI$_{2.4}$Br$_{0.6}$ device [145] reported by Noh et al. Here, the higher stability is aided by the improved morphology in the films produced by the 1 & 2-s method.

Figure 5.11: (a) Heat stress images for MAPI(B)-MAPI and MAPI. The films were heated on ITO/mp-TiO$_2$ at 150 °C (with humidity of ~60%).
5.4 Results and discussion

Figure 5.12: (a) Normalised power conversion efficiency (PCE) for 31 days. (b) – (d) show other normalised device characteristics: $J_{SC}$ (mA/cm$^2$), $V_{OC}$ (mV) and FF (%), respectively. The PSCs were exposed to $\sim$40% humidity at room temperature. The devices were stored in the dark between measurements and were not encapsulated.
5.5 Conclusion

This study has investigated the preparation of a novel combined 1 & 2-s method for mixed anions perovskite films. It was observed that the MAPbI$_{3-x}$Br$_x$ films prepared using the 1 & 2-s method showed unexpected thermal and device stability improvement compared to MAPI, which could be attributed to an enhanced capping layer morphology and the nature of Br. Concurrently, the mixed anion study illustrated that the MAPI(B)-MAPI and MAPI-MAPI(B) corresponded to MAPbI$_{2.4}$Br$_{0.6}$ and MAPbI$_{2.1}$Br$_{0.9}$. The MAPI(B)-MAPI has a cubic structure while the MAPI-MAPI(B) has a tetragonal structure and despite the combined approach used to prepare the films, the XRD, UV-visible and PL data showed the presence of efficient alloying in these films. This study proposes two mechanisms to explain how one-phase perovskites are formed from two parent phases. In this regard, it is notable that the final crystal phase was different for both mixed anion perovskites prepared using the 1 & 2-s method as it was determined by the first (seed) stage. Furthermore, the inclusion of MABr in the first or second steps could change the composition from being stoichiometrically controlled or diffusion controlled where the 1 & 2-s method allows structure formation and composition for mixed anion perovskites to be separated. In the meantime, the MAPI(B)-MAPI recorded the highest PCE (11.3%), which was the highest recorded for any device prepared using the 1 & 2-s method. The MAPI(B)-MAPI film also had the best thermal stability due to the combination of enhanced morphology (from the 1 & 2-s method) and cubic structure. Elaborated XRD patterns and study would be interesting to be discussed further in future study. All in all, this study has found that the mixed anion perovskite films could efficiently create alloys despite the radical changes of their processing methods. The 1 & 2-s method allows the preparation of the composite perovskite films using either stoichiometric or diffusion control that can be switched conveniently. This method offers a new dimension to the synthesis of perovskite, in term of decoupling structure and composition, and is worthy of further study.
6.1 Summary of conclusions

This study was conducted to investigate the new perovskite morphologies by using a novel solution-processing method. Here, we have elucidated how perovskites morphology affects the performance and stability of perovskite solar cells (PSCs).

A new CH$_3$NH$_3$PbI$_3$ (MAPI) film preparation method (1 & 2-s) has been introduced in Chapter 3. Moreover, three novel mixed morphology perovskite photoactive films ($x = 0.33, 0.50$ and $0.66$) were investigated. We found that the new 1 & 2-s deposition method produced MAPI films with tunable morphologies, crystal size and optoelectronic properties linked to those in conventional 1-s and 2-s films. Furthermore, this study found that the use of different values of $x$ precursor (PbI$_2$ + $x$MAI) solutions during the film preparation could systematically change the morphology. As a result, a combined 1D and 3D crystal morphologies were produced by the combination method where each proportion was considered as tuneable. This study observed that the morphology significantly affects the primary properties of MAPI films and devices. Here, when the new combined method was used, the new MAPI films produced have had enhanced light scattering, stronger absorption and better device performance compared to control devices.
Chapter 4 presented an extension of the new combination method which was introduced in Chapter 3. Here, the co-solvent blends were introduced and their effect on the properties of the final film was studied. We compared the perovskite absorbing layer with the well-established conventional depositions methods (1-s and 2-s) to see their optoelectronic properties, stability and device characteristics. Consequently, using the DMSO as a co-solvent with DMF could strongly affect the film’s properties and final morphology. This process also resulted in a tuneable morphology. In this light, when DMSO volume fraction ($\phi_{DMSO}$) was increased, an enhance coverage and larger crystal size was observed. We found that 60 vol % of DMSO was the best solvent blend that gave better film properties and solar cell performance. The presence of $\phi_{DMSO}$ in the solvent preparation method controls the morphology of the perovskite films and crystalline grain size. We also observed that the MAPI films prepared using the 1 & 2-s method had enhanced thermal and device stability due to improved morphology structure.

In Chapter 5, both approaches in Chapter 3 and Chapter 4 were greatly extended. This was done by adding Br$^-$ into the system. An improvement in the PCE and stability was observed as a result. The MAPI(B)-MAPI (through halide diffusion and exchange method by 1 & 2-s deposition) had highest average PCE (11.3%) and max PCE of 12.08%, which were the highest recorded for any device prepared using the 1 & 2s method. In this regard, the combination of mixed morphology and cubic structure had caused the MAPI(B)-MAPI film to have the most optimum thermal stability. We also investigated how the presence of Br anion (halide) affects the optoelectronic and device properties of CH$_3$NH$_3$PbI$_{3-x}$Br$_x$. Subsequently, we found a mechanism that explains the decoupling of exchange and growth in perovskite-forming stage. The XRD, XPS, UV-visible and PL data demonstrated that these combined deposition films had efficient alloying.

All in all, the 1 & 2-s deposition method presented in this study enabled perovskite films to be prepared using either stoichiometric or diffusion control and this can be switched conveniently. This new deposition method adds an additional dimension to perovskite synthesis and PSC device fabrication in terms of tuning morphology, crystal growth,
decoupling structure and composition and should be applicable to the processing of other hybrid organic-inorganic perovskites thin film.

6.2 Future work and recommendations

The present research investigated the growth of perovskite crystal and explored the prospect of using architectural control of perovskite particles and morphologies to achieve high performance, efficient and stable perovskite solar cell. Because this study was not aimed to fabricate devices with high efficiencies, several strategies, as highlighted below are suggested can be used in future studies to increase PCE.

**Use planar P-I-N junction for combination 1&2-s method.** Preliminary SEMs (not shown) indicated that more perovskite nucleation could be obtained through a planar configuration and a uniform layer could be fabricated. A study by Yun et al. observed the higher presence of photovoltage at the grain boundaries compared to the interior part of perovskite (within TiO$_2$) [206]. This creates a higher short-circuit current collection adjacent to the grain boundaries without the need of mesoporous layer. Furthermore, the planar P-I-N structure is deemed to suit large-scale production [62]. This approach is worthy to be pursued with the 1 & 2-s method.

**Use FA or mixed MA-FA cations alloy.** Our study in Chapter 5 has demonstrated that ‘X’ site anions of MAPI can be chemically modified by halide exchange (substituting I with Br) through the 1 & 2-s method. The energy bandgaps can be tuned to be between 1.5 eV and 2.3 eV by including Br$^-$ which created different film properties and device characteristics (see Chapter 5 section 5.4.2). On the other hand, we can also modify the ‘A’ site of the ABX$_3$ perovskite structure, to contains formamidinium (FA$^+$) cations with the bandgap of $\sim$1.48 eV and the absorption edge of 840 nm [207, 208]. It is expected that this smaller bandgap may allow photons to be absorbed over a broader solar spectrum and maximise the light harvesting capacity which in turn, help improve the power conversion efficiency (PCE).
Anti-solvent method. One of the study aims was to investigate how device performance of similarly prepared devices could be affected by crystal growth and morphologies; hence we did not optimise the device. It is suggested that the application of anti-solvent method can help achieve better PCE in the future. Chapter 2, section 2.6.3 has discussed the advantage of this anti-solvent method. A preliminary SEM study (not shown) indicates that the 1 & 2-s method with anti-solvent procedure can be used to obtain highly homogenous perovskite coverage. This shows good opportunity for future application and should be pursued.
Appendix

A.1 NREL efficiency chart

Since the mid 1980s, the National Renewable Energy Laboratory (NREL) has develop an openly accessible chart of the most astounding detailed of the various form of research grade photovoltaics (PV) solar cells in all major PV advancements. From fig. A.1, it can be observed that perovskite solar cells (yellow dot with red outline) as one of the third-generation solar cells progressively paving their efficiencies that are comparable to crystalline Si solar cells.
Figure A.1: NREL efficiency chart 2017 [1].
A.2 Scherrer equation

In x-ray diffraction and crystallography, the Scherrer equation, is a formula that relates the size of sub-micrometre particles, or crystallites, in a solid to the broadening of a peak in a diffraction pattern. It is used in the determination of crystallite particle size in the form of powder. In this study, the Scherrer equation was used to calculate the average grain size for the MAPbI$_3$ and PbI$_2$ crystals. Following Jeong et al [146] the full-width at half-maximum height (FWHM) for the (001) peak was used in the case of PbI$_2$ and FWHM of peaks (110), (202) and (220) peaks were used for the MAPbI$_3$ for these calculations. The Scherrer equation can be written as eq. (A.1) as follow:

$$t = \frac{K \lambda}{\beta \cos \theta} \quad \text{(A.1)}$$

Where,

- $t$ is the mean size of the ordered (crystalline) perovskite domains, which may be smaller or equal to the grain size.
- $K$ is a dimensionless shape factor, with a value close to 1. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite.
- $\lambda$ is the X-ray wavelength used for XRD.
- $\beta$ is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians.
- $\theta$ is the Bragg angle.

In this calculation, we used $K = 0.94$ assuming the crystallite to be round in shape, $\lambda = 0.154$ nm and the $\beta = 1$ assuming it was negligible. Both $\lambda$ and $\beta$ were determined from the instrument. From the calculation, the average crystallite size, $t$ was determined as table below.
Table A.1: Average crystallite size, $t$ calculated according to Scherrer equation for PbI$_2$ present on precursor films (PbI$_2$ + xMAI).

<table>
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<tr>
<th>$x$</th>
<th>$2\theta/\degree$</th>
<th>FWHM/$\degree$</th>
<th>FWHM / rad</th>
<th>$t$ / nm</th>
<th>$t_{\text{perov}}$ / nm</th>
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<td>0</td>
<td>13.1308</td>
<td>0.1771</td>
<td>0.00309</td>
<td>47.1362</td>
<td>56.4</td>
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<td>0.33</td>
<td>12.711</td>
<td>0.1968</td>
<td>0.0034353</td>
<td>42.40</td>
<td>61.1</td>
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<tr>
<td>0.5</td>
<td>12.6739</td>
<td>0.1968</td>
<td>0.0034353</td>
<td>42.40</td>
<td>68.2</td>
</tr>
<tr>
<td>0.66</td>
<td>12.754</td>
<td>0.1968</td>
<td>0.0034353</td>
<td>42.40</td>
<td>65.7</td>
</tr>
</tbody>
</table>

$^a$ Data obtained from Scherrer analysis of final perovskite film for comparison.
References


References


References


References


[150] Lingling Zheng, Yingzhuang Ma, Saisai Chu, Shufeng Wang, Bo Qu, Lixin Xiao, Zhijian Chen, Qihuang Gong, Zhaoxin Wu, and Xun Hou. Improved light absorption


[187] Ik Jae Park, Seongrok Seo, Min Ah Park, Sangwook Lee, Dong Hoe Kim, Kai Zhu, Hyunjung Shin, and Jin Young Kim. Effect of rubidium incorporation on the


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Perovskite solar cells continue to attract strong attention because of their unprecedented rate of power conversion efficiency increase. CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) is the most widely studied perovskite. Typically one-step (1-s) or two-step (2-s) deposition methods are used to prepare MAPbI$_3$ films. Here, we investigate a new MAPbI$_3$ film formation method that combines 1-s and 2-s deposition (termed 1 & 2-s) and uses systematic variation of the stoichiometric mole ratio ($x$) for the PbI$_2$ + xMAI solutions employed. The PbI$_2$ + xMAI solutions were used to deposit precursor films that were subsequently dipped in MAI solution as a second step to produce the final MAPbI$_3$ films. The morphologies of the 1 & 2-s MAPbI$_3$ films consisted of three crystal types: tree-like microcrystals ($x\approx 1$ μm), cuboid meso-crystals ($\sim 0.1–1$ μm) and nanocrystals ($\sim 50–80$ nm). Each crystal type and their proportions were controlled by the value for $x$. The new 1 & 2-s deposition method produced MAPbI$_3$ films with tuneable optoelectronic properties that were related to those for the conventional 1-s and 2-s films. However, the 1 & 2-s film properties were not simply a combination of those for the 1-s and 2-s films. The 1 & 2-s films showed enhanced light scattering and the photoluminescence spectra displayed a morphologically-dependent red-shift. The unique morphologies for the 1 & 2-s films also strongly influenced PbI$_2$ conversion, power conversion efficiency, hysteresis and recombination. The trends for the performance parameters and hysteresis were compared for devices constructed using spiro-MeOTAD and P3HT and were similar. The 1 & 2-s method should apply to other perovskite formulations and the new insights concerning MAPbI$_3$ crystal growth conditions, morphology and material properties established in this study should also be transferable.

**Introduction**

The interest in perovskite solar cells has dramatically accelerated in recent years$^{4,5}$ which is driven in large part by the remarkable increase of their power conversion efficiency. A certified value of 22.1% has recently been achieved.$^3$ Whilst there are many challenges to overcome,$^4$ excellent progress continues to be made$^{5,7}$ and there is good reason to believe that these new solar cells may one day contribute to low carbon electricity generation.$^8$

Here, a new (combined) method is investigated for the preparation of CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) perovskite films. The latter is the most commonly studied perovskite.$^9$ There are two main deposition methods used to prepare MAPbI$_3$ photoactive layers. The 1-step deposition (abbreviated as 1-s) method uses a solution containing a (normally) stoichiometric ratio of PbI$_2$ and MAI.$^{10}$ Alternatively, the 2-step deposition (2-s) method involves the sequential deposition of PbI$_2$ onto a mesoporous TiO$_2$-coated substrate (mp-TiO$_2$) followed by dipping into a MAI solution.$^{11}$ The latter approach may also involve anti-solvent additives to control crystallisation.$^{12}$ The morphologies of MAPbI$_3$ prepared by the 1-s and 2-s methods can differ greatly. The 1-s and 2-s preparation methods have been reported to produce tree-like and cuboid MAPbI$_3$ crystal morphologies, respectively.$^{13,14}$ The ability to tune the morphology of perovskites is important both for improving the fundamental understanding of the relationship between morphology and optoelectronic properties as well as for the practical optimisation of solar cell performance.$^{15}$ In the present fundamental study we investigate a new approach for MAPbI$_3$
preparation that combines the 1-s and 2-s methods (abbreviated as 1 & 2-s) and uses reaction stoichiometry control. The aims of the study were to (1) investigate whether such films had morphologies and optoelectronic properties that were combinations of those for films prepared by the conventional 1-s and 2-s routes and (2) broaden the understanding of the relationships between formulation conditions and properties.

Whilst the 1-s method has been successfully used to prepare perovskite films\textsuperscript{[16-18]} and is known to provide stoichiometric MAPbI\textsubscript{3} compositions, uncontrolled crystallisation may result in films with low surface coverage. Generally, the 2-s method provides fewer pinholes and higher efficiencies for devices.\textsuperscript{[14,19]} However, the 2-s method is susceptible to incomplete conversion of PbI\textsubscript{2}.\textsuperscript{[20]} Remnant PbI\textsubscript{2} results in decreased light absorption and photocurrent. On the other hand remnant PbI\textsubscript{2} can reduce recombination\textsuperscript{[21]} and even increase the power conversion efficiency (PCE).\textsuperscript{[22]} Here, we investigate films prepared using our new 1 & 2-s method and also the effect of preparation conditions on PbI\textsubscript{2} conversion.

The film deposition sequence (Scheme 1a) involved reaction of PbI\textsubscript{2} + xMAI solutions as the first step, where x is the stoichiometric ratio of MAI used. The x values of 0 and 1.0, respectively, correspond to 2-s (Scheme 1b) and 1-s (Scheme 1d). The x values of 0.33, 0.50 and 0.66 correspond to 1 & 2-s (Scheme 1c).

The proportions of MAPbI\textsubscript{3} prepared in the first and second steps of the 1 & 2-s process were tuned using x. As x increased a higher proportion of the total MAPbI\textsubscript{3} was formed during the first step (in precursor films) and less additional MAPbI\textsubscript{3} was formed during the second step which produced the final films.

There have been relatively few MAPbI\textsubscript{3} studies where reaction stoichiometries of the precursor solutions have been investigated. Zhang \textit{et al.} prepared planar MAPbI\textsubscript{3} films by mixing PbI\textsubscript{2} and MAI solutions at specific mole ratios of MAI and then deposited those films before dipping the films into MAI solution.\textsuperscript{[23]} That work differed from the present study because they used lower x values than used here, did not use a mesoporous TiO\textsubscript{2} coated substrate and did not form a perovskite prior to dipping in the MAI solution. By contrast our approach involved formation of an initial (precursor) perovskite film with excess PbI\textsubscript{2} before a MAI dipping step (Scheme 1c). Roldán-Carmona \textit{et al.}\textsuperscript{[22]} used a 1-s method and non-stoichiometric ratios of PbI\textsubscript{2} to MAI combined with an anti-solvent to obtain high efficiency devices. However, they used relatively low x values compared to those used here and did not dip their films into a MAI solution as a second step.

In the present study stoichiometry variation during the formation of precursor films was employed as a form of intermediate engineering to control the morphology of the final
MAPbI₃ films. Other approaches to control MAPbI₃ morphology have used solvents such as DMSO, which is a high boiling point and strongly coordinating solvent, to form intermediate complexes that decreased the rate of MAPbI₃ crystallisation. DMSO delays MAPbI₃ crystallisation because of the formation of strong PbI₂(DMSO) adducts.²⁴⁻²⁶ In contrast, DMF forms weaker adducts with Pb, i.e., PbI₂(DMF), and the replacement of DMF with MAI results in MAPbI₃ formation.²⁷ Here, we used DMF as the solvent to encourage rapid crystallisation of the MAPbI₃ phases and enable morphological differences due to reaction stoichiometry to be clearly revealed.

In this study we introduce and investigate a new and versatile combined deposition approach that provides widely tunable MAPbI₃ morphologies. The study focusses on understanding the relationships between the film morphology and optoelectronic properties. The morphology of MAPbI₃ films is investigated using optical microscopy and SEM. The spectroscopic properties are studied using UV-visible, photoluminescence (PL) and transient absorption spectroscopies. Because this study focussed on establishing relationships between crystal growth and properties it did not aim to obtain high performance devices. Nevertheless, the effect of preparation conditions on device performance is investigated. The 1 & 2-s method had a major effect on nucleation and growth and generally provided systematic control over film morphology, optoelectronic properties and device performance. We show that the distinct morphology that resulted from the 1 & 2-s approach was not simply a combination of those from the 1-s and 2-s methods and resulted in important differences in the physical chemistry underpinning the MAPbI₃ films. Our new and simple combined approach to MAPbI₃ film preparation should apply to other perovskites and is expected to provide enhanced versatility for morphological and property control.

**Experimental**

**Materials**

Isopropanol (IPA, anhydrous, 99.5%), methylamine (≥98%), HI (99.95%, 57 wt% solution in water), 4-tert-butylpyridine (96%), lithium bis(trifluoromethanesulfonimide) (LiTFSI, 99.95%), PbI₂ (99.999%), N,N-dimethylformamide (DMF, anhydrous, 99.8%), and poly(3-hexylthiophene) (P3HT, M₉, 54 000–75 000) were all purchased from Aldrich and used as received. Dyesol 18NRT titania paste (TiO₂) and 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]9,9'-spirobifluorene (spiro-MeOTAD, Fenglin Chemicals, 99.5%) were also used as received.

**Perovskite film preparation**

MAI was synthesized according to the method reported elsewhere.²⁸ This involved the dropwise addition of 30 mL of aqueous HI solution (57 wt%) to 27.9 mL of an aqueous solution of methylamine (40 wt%) in an ice bath with stirring. The cold solution was stirred for 2 h, and the solvent was evaporated using a rotary evaporator. The crystals were washed using diethyl ether three times and dried in a vacuum oven. ITO/glass slides (2.0 cm × 1.5 cm) were cleaned by sonication in a 1% Hellmanex solution in boiling water for 15 min followed by rinsing with water and IPA and cleaning in ultrasonic for 5 min and dried using a nitrogen stream. Titania paste (70 µL, 1 : 5 in ethanol) was spin-coated onto the cleaned glass slides at 5000 rpm for 30 s to form a mesoporous scaffold (mp-TiO₂) with an average thickness of 250 nm. The films were then annealed at 500 °C for 30 min. Next, solutions of PbI₂ + xMAI in DMF containing PbI₂ (1.0 M) and x = 0, 0.33, 0.50, 0.66, 1.00 M of MAI were prepared in a glove box (humidity ~2%). Film fabrication was subsequently conducted outside of the glove box (humidity ~40%). The solutions were spin-coated onto the mp-TiO₂ layer (Scheme 1). Note that x = 0 and 1.0 correspond to the 2-s and 1-s methods, respectively. The values x = 0.33, 0.50 and 0.66 correspond to 1 & 2-s films. The solutions were kept at 70 °C during spin-coating. The spin-coating conditions employed were 2000 rpm for 40 s for the 1-s and 1 & 2-s methods; whereas, 6500 rpm for 60 s was used for the 2-s method. The films were dried at 100 °C for 15 min (or 30 min for 1-s, x = 1.0). The dried films (with the exception of the 1-s film) were washed with IPA for 3 s and then dipped in 20 mL MAI (10 mg mL⁻¹) for 15 min. The films were dried at 100 °C for 15 min and immediately placed in a desiccator over P₂O₅ and stored in the dark until investigation. The 1s and 1 & 2-s film layer thicknesses were in the range 550–700 nm. The thickness for the x = 0 film was 350 nm.

**Device fabrication**

Laser-patterned, ITO-coated glass substrates (20 Ω sq⁻¹) were cleaned by ultrasonication in a 2% Hellmanex solution, rinsed with deionized water and IPA, and dried. A blocking layer of compact TiO₂ (bl-TiO₂) was then deposited by spin coating TDB (75 µL, 0.15 M) solution in 1-butanol at 2000 rpm for 60 s. The procedure was repeated using a TDB solution (0.30 M) and the substrate was heated at 125 °C for 5 min to give an average thickness of 50 nm. A mp-TiO₂ layer was then deposited as described above. Perovskite photoactive layers were then deposited as described above. P3HT was deposited as a hole transport matrix (HTM). The latter (average thickness of 100 nm) was deposited by dynamic spincoating of P3HT in toluene (15 mg mL⁻¹) at 4000 rpm for 20 s. Following Heo et al., Li-TFSI salt and t-BP in acetonitrile were added to the P3HT solution.²⁸ Finally, a gold layer (70 nm) was deposited on top of the HTM. The fabrication procedures were performed outside the glovebox in ~40% relative humidity. Devices were also prepared using spiro-OMeTAD as the HTM with an average thickness of 100 nm. In that case HTM deposition followed established literature procedures.²⁹,³⁰ All devices were stored in a desiccator over P₂O₅ in the dark until investigation.

**Physical measurements**

The surface morphologies were investigated using a Philips XL30 FEI-SEM. The device cross section was prepared with Ar ion polishing at 6 kV and cleaned at 1 kV using Ilion system from Gatan (France). The cross-section microstructure was investigated using a FEI Magellan FEG-SEM and the local composition probed via energy dispersive X-ray spectroscopy (EDX). XRD data were...
obtained using a Bruker D8 Advance diffractometer (Cu-Kα). The films obtained were scanned between 10 and 50° with a step size of 0.02. For these measurements the films were prepared and measured under a nitrogen atmosphere. UV-visible spectra were recorded using a Perkin Elmer Lambda 25 spectrometer. Optical images were obtained using an Olympus BX41 polarizing microscope with an Olympus U-AN360-3 rotatable analyser and polariser filter. PL spectra were obtained using an Edinburgh Instruments FLS980 spectrometer. Pump–probe microsecond to millisecond transient absorption spectroscopy (TAS) measurements were conducted on mp-TiO₂/MAPbI₃/spiro-MeOTAD films excited by a dye laser (Photon Technology International GL-301, sub-nanosecond pulse width) pumped by a pulsed nitrogen laser (Photon Technology International GL-3300). A quartz halogen lamp (Benthalm IL1) was passed through a monochromator and used to probe changes in the absorption characteristics of the films as a function of time after the laser excitation. The probe light was detected using home-built silicon (≤1000 nm) or InGaAs (≥1000 nm) photodiodes and an oscilloscope. Perovskite films were kept under flowing N₂ during the measurements. All TAS measurements employed 567 nm laser pulses (25 μJ cm⁻²).

Device characterization

The current density–voltage (J–V) characteristics were measured using a Keithley 2420 Sourcemeter and 100 mW cm⁻² illumination (AM 1.5G) and a calibrated NREL certified Oriel Si-reference cell. An Oriel SOL3A solar simulator was used for these experiments. The active area of the devices was defined using a square aperture within a mask and fixed at 0.16 cm². Forward and reverse direction sweeps were measured with a sweep rate of 100 mV s⁻¹.

Results and discussion

Effects of preparation conditions on MAPbI₃ morphology

Three MAPbI₃ film types were prepared using our new method that utilised combined 1 & 2-s (x = 0.33, 0.50 and 0.66) deposition and control of the stoichiometric ratio (x) for the reaction of PbI₂ + xMAI (see Scheme 1a and c). The first step involved spin-coating mp-TiO₂ using a PbI₂ + xMAI solution and drying the film at 100 °C to give a precursor film. The second step involved dipping the precursor film in MAI solution to convert excess PbI₂ to the final MAPbI₃ film. The 2-s (x = 0) system was prepared as a control (Scheme 1b). The 1-s (x = 1.0) system was another control and was prepared as a final film in one step (Scheme 1d). The precursor films prepared using PbI₂ + xMAI solutions with x = 0.33, 0.50 and 0.66 turned black prior to the final dipping step in MAI solution (films shown in middle column of Scheme 1c). The precursor films appeared more black (and less yellow) as x increased due to decreased PbI₂ in the films. After subsequent MAI solution dipping, the final films were dark black (films shown in right hand column of Scheme 1) due to conversion of the excess PbI₂ to MAPbI₃.

The precursor films and final films were examined using SEM (Fig. 1). The images for the precursor films are shown in Fig. 1a and reveal that dramatic changes in the morphology occurred as x increased. Tree-like micrometer-sized crystals (termed here as microcrystals) appeared and were most pronounced for x = 0.66. Because the microcrystals were absent for the x = 0 precursor film (which was PbI₂), they are attributed to MAPbI₃. The highest magnification image insets (Fig. 1a, right hand column) show that the surfaces of the microcrystals were covered by smaller crystals which had a comparable appearance to the nanocrystals evident for PbI₂ (x = 0) and are proposed to have been excess PbI₂. This proposal was supported by EDX data which probed the compositions of the microcrystals for the 1 & 2-s precursor prepared using x = 0.66 (see Fig. S1, ESI†). The data show that the microcrystals (with nanocrystals at the surface) had a relatively high Pb²⁺ content compared to the theoretical value for x = 0.66 and the background perovskite signal.

To prepare the final films (x < 1.0) the precursor films were dipped in MAI solution and heated (see Scheme 1b and c). This MAI dipping step converted the excess PbI₂ to MAPbI₃ according to the right hand side of the equation shown in Scheme 1a. (Because there was only a final film produced by the 1-s method (x = 1.0, Scheme 1d) the SEM images for that film are shown in Fig. 1b.) The 1-s (x = 1.0) film consisted of interconnected micrometer-sized tree-like microcrystals. These microcrystals had fewer branches compared to the films prepared using x = 0.33, 0.50 and 0.66, which implies a decrease in nucleation occurred as x increased. These morphology differences in the films were also apparent using polarised light optical microscopy (Fig. S2, ESI†). Interestingly, the higher magnification SEM images of Fig. 1b showed that cuboid crystals with average sizes in the range of 140–460 nm were present. These crystals became smaller with increasing x (see Fig. S3, ESI†). We term the crystals as meso-crystals because they had dimensions (~0.1–1 μm) that were between those for the MAPbI₃ microcrystals (≥1 μm) present in the capping layer and the smaller nanocrystals (~50–80 nm) within the mp-TiO₂ layer (later). The % coverage by the capping layer was calculated using image analysis from the lower magnification images (Fig. 1a and b). (An example SEM image and a description of the method used to calculate the % coverage values are given in Fig. S4, ESI†) The variation of % coverage as function of x is shown in Fig. 1c. The % coverage was highest for the precursor 2-s film (x = 0), which was PbI₂, and decreased with increasing x. The % coverage for the precursor and final 1 & 2-s films (x = 0.33, 0.50 and 0.66) were not able to be distinguished because the meso-crystals were about an order of magnitude smaller than microcrystals. Consequently, the meso-crystals were too small to influence the % coverage values which were dominated by the relatively large microcrystals.

As x increased the tree-like microcrystals became longer, tended to interpenetrate less and had fewer branches, which indicates a decrease in the number-density of nucleation sites. This trend is best seen from lower magnification images of Fig. 1a and b. The growth of the cuboid meso-crystals, which occurred during MAI dipping, was likely governed by homogeneous nucleation and growth with a contribution from dissolution and crystallisation. As x increased the proportion of unreacted PbI₂ decreased. We speculate that the apparent high nucleation density for lower
x values was due to a higher extent of supersaturation in the PbI₂-rich deposition solutions. The microcrystals of the precursor films were covered by PbI₃ nanocrystals (discussed above) which were converted to MAPbI₃ upon MAI solution dipping. These features are captured in the mechanism depicted in Fig. 2.

Achieving complete conversion of PbI₂ to MAPbI₃ can be challenging for films prepared using the conventional 2-s deposition method⁶,²⁰,²¹ and PbI₂ peaks have been frequently observed in X-ray diffractograms.³²,³³ We investigated the effect of the MAI dipping time for the final 2-s (x = 0) films using XRD. The conversion was probed using the %amplitude of the MAPbI₃(110) peak with respect to the PbI₂(001) peak, using

$$\% \text{Amplitude} = \frac{100A_{(110)}}{A_{(110)} + A_{(001)}} \quad (1)$$

where $A_{(110)}$ and $A_{(001)}$ are the amplitudes for the MAPbI₃(110) and PbI₂(001) peaks, respectively. The %amplitude increased rapidly for dipping times less than 2 min and then increased more slowly for dipping times between 2 and 30 min [Fig. S5, ESI †]. A dipping time of 15 min was used in this study because it was in the middle of the region where conversion increased slowly. This value corresponded to %amplitude = 87%. The diffractograms were recorded under a nitrogen atmosphere which rules out post-preparation degradation involving moisture as the origin of PbI₂. Consequently, residual PbI₂ is attributed to incomplete conversion of PbI₂ which was buried within the mp-TiO₂ layer.

X-ray diffractograms for all of the final films are shown in Fig. 3a. The (110) peak at 2θ = 14° was dominant for the MAPbI₃ films. However, there was also evidence for PbI₂ in the diffractograms for the 1 & 2-s (x = 0.33, 0.50 and 0.66) films at 2θ = 12.8°. By contrast, the 1-s film (x = 1.0) had negligible PbI₂.

Fig. 1  SEM images showing morphologies of precursor (a) and final (b) MAPbI₃ films. The variation of coverage with stoichiometric ratio (x) (Scheme 1) for the precursor and final films is shown in (c) and was determined from the images shown in (a and b), respectively. The scale bars for SEM images on the left and right hand sides of (a and b) are 20 μm and 200 nm, respectively. Note that the precursor film for x = 0 was PbI₂.
Fig. 3b shows the variation of %amplitude with x for the final films. Interestingly the %amplitude value increased linearly with x for the 1 & 2-s (x = 0.33, 0.50 and 0.66) and 2-s (x = 1.0) films. The precursor MAPbI₃ microcrystals are proposed to have restricted MAI ingress into the mp-TiO₂ layer (see below). As x increased the % coverage of the mp-TiO₂ surface decreased (Fig. 1c). Also, there was less excess PbI₂ in the precursor films as x increased according to Scheme 1a. Both of these effects (decreased coverage and less excess PbI₂) were responsible for increased conversion as x increased. However, the %amplitude for the 2-s (x = 0) film did not fit the linear trend established for the other films which might be due to the absence of MAPbI₃ at the precursor stage.

To identify the location of the residual PbI₂ discussed above a cross-section of an ITO/bl-TiO₂/mp-TiO₂/MAPbI₃/spiro-MeOTAD/Au device containing a final 1 & 2-s (x = 0.5) film was examined using SEM and EDX (see Fig. S6, ESI†). Whilst the atomic% of Pb near the surface was close to the observed in other studies for MAPbI₃, the data also show that the atomic% of Pb was highest deep within the mp-TiO₂ layer. These data indicate that PbI₂ was located deep within the mp-TiO₂ layer and supports the proposal above of restricted MAI access.

The Scherrer equation was used to calculate the average grain size for the MAPbI₃ and PbI₂ crystals present (Fig. 3c). Following Jeong et al. the full-width at half-maximum heights (FWHM) for the MAPbI₃(110), (202) and (220) peaks were used for these calculations. In the case of PbI₂ the FWHM for the (001) peak was used. These data and analysis gave average MAPbI₃ sizes in the range of 56 to 73 nm. These species originated in large part because more of the PbI₂ was converted to MAPbI₃ at the precursor stage. Evidence for MAPbI₃ can be seen from the band-edge absorption from MAPbI₃ at 775 nm, which was most pronounced for the 1 & 2-s (x = 0) film which was PbI₂. The latter suggestion is confirmed by the spectrum for the 2-s (x = 0) film which was PbI₂. The relative size of the absorption at 520 nm decreased as x increased which is expected because more of the PbI₂ was converted to MAPbI₃ at the precursor stage. Evidence for MAPbI₃ can be seen from the band-edge absorption from MAPbI₃ at 775 nm, which was most pronounced for the x = 0.33 film (see inset of Fig. 4a).

Once the precursor films were converted to the final MAPbI₃ films several features of the spectra changed considerably (see Fig. 4b). Firstly, for each final 1 & 2-s films the MAPbI₃ absorption at 775 nm (inset of Fig. 4b) increased compared to the respective precursor film (inset of Fig. 4a) which is due to greater PbI₂ conversion. This absorbance increase was strongest for the x = 0.33 and 0.50 films. Secondly, the spectra for the 1 & 2-s films (x = 0.33, 0.50 and 0.66) became relatively flat; whereas, the spectra of mp-TiO₂ measured from SEM (Fig. S7, ESI†). The average MAPbI₃ size likely increased with increasing x (Fig. 3c) due to an increase in the proportion of MAPbI₃ that was present in the capping layer as relatively large microcrystals and/or meso-crystals. Because the microcrystals and meso-crystals had dimensions that were much larger than 100 nm (Fig. S3, ESI† and Fig. 1) it is likely that (smaller) MAPbI₃ nanocrystals within the mp-TiO₂ were the majority MAPbI₃ species present for all of the films. The Scherrer analysis also showed that the average size for the residual PbI₂ nanocrystals present was 42–47 nm.

Effects of morphology on the film spectroscopic properties
The UV-visible spectra for the precursor films and final MAPbI₃ films were measured and are shown in Fig. 4a and b, respectively. The spectra for all of the precursor films (Fig. 4a) contained an absorption maximum (or shoulder) at 520 nm, which was due to PbI₂. The latter suggestion is confirmed by the spectrum for the precursor 2-s (x = 0) film which was PbI₂. The relative size of the absorption at 520 nm decreased as x increased which is expected because more of the PbI₂ was converted to MAPbI₃ at the precursor stage. Evidence for MAPbI₃ can be seen from the band-edge absorption from MAPbI₃ at 775 nm, which was most pronounced for the x = 0.33 film (see inset of Fig. 4a).

Once the precursor films were converted to the final MAPbI₃ films several features of the spectra changed considerably (see Fig. 4b). Firstly, for each final 1 & 2-s films the MAPbI₃ absorption at 775 nm (inset of Fig. 4b) increased compared to the respective precursor film (inset of Fig. 4a) which is due to greater PbI₂ conversion. This absorbance increase was strongest for the x = 0.33 and 0.50 films. Secondly, the spectra for the 1 & 2-s films (x = 0.33, 0.50 and 0.66) became relatively flat; whereas, the spectra
for the 2-s ($x = 0$) and 1-s ($x = 1.0$) films had absorbance values that increased strongly with decreasing wavelength. The flat type of spectrum was noted by Jain et al.\textsuperscript{33} Here, the flat spectrum is due to scattering from microcrystals within the capping layer. Particles that are much larger than the nanometre size range scatter light in a complex manner according to Mie theory.\textsuperscript{38} The present spectra indicate that the nature of the light interaction with the films was fundamentally changed for the 1 & 2-s films as compared to the 2-s ($x = 0$) and 1-s ($x = 1.0$) films.

The extent of light scattering for the 1 & 2-s ($x = 0.33, 0.50$ and $0.66$) final films was greater than or equal to that for the 2-s ($x = 0$) and 1-s ($x = 1.0$) films as judged by the absorbance values at $900 \text{ nm}$ ($A_{900}$, see Fig. 4c). The value for $A_{900}$ was dominated by Mie scattering\textsuperscript{39} and light scattering was strongest for the films containing microcrystals ($x > 0$). Interestingly, there was a linear decrease for $A_{900}$ with increasing $x$ for both the precursor and final 1 & 2-s films ($x = 0.33, 0.50$ and $0.66$). This is most likely the result of a decreased coverage by the microcrystals with increasing $x$ (Fig. 1c). Whilst other workers have included scattering particles within perovskite photoactive layers,\textsuperscript{40,41} the data shown in Fig. 4c demonstrate that light scattering tuning can be achieved using morphology control of MAPbI$_3$ within the capping layer. Enhanced light scattering within photoactive layers is potentially beneficial for maximising light harvesting within solar cells because it can increase the path length.\textsuperscript{40-42}

The PL spectra of the final MAPbI$_3$ films were measured (Fig. 5a). All of the spectra showed a strong band-edge emission peak at $776$ to $784 \text{ nm}$. The signals indicate incomplete non-radiative recombination due to inefficient quenching by the mp-TiO$_2$ scaffold. The PL intensity for the 1 & 2-s films ($x = 0.33, 0.50$ and $0.66$) decreased with increasing $x$ and was highest for the film prepared using $x = 0.33$ (see Fig. 5b). The PL intensities for the 1 & 2-s films ($x = 0.33, 0.50$ and $0.66$) films were significantly higher than those for the 2-s ($x = 0$) and 1-s ($x = 1.0$) films. It follows that more of the photogenerated charges within the 1 & 2-s films were greater than a distance corresponding to the exciton diffusion length ($\sim 100 \text{ nm}$\textsuperscript{43}) from the mp-TiO$_2$ surface. The higher PL intensity for those films is due to a combination of increased MAPbI$_3$ in the capping layer (Fig. 1b) and stronger absorption (Fig. 4b).

The position of the wavelength corresponding to the maximum PL intensity ($\lambda_{\text{max}}$) is plotted as a function of $x$ in Fig. 5c. It can be seen that a red-shift of $8.0 \text{ nm}$ occurred as $x$ increased from $0$ (2-s) to $1.0$ (1-s). Interestingly, after an initial sharp increase of $\lambda_{\text{max}}$ when $x$ increased from $0$ to $0.33$, the $\lambda_{\text{max}}$ values gradually increased linearly with $x$. Whilst band gap tuning has been achieved by using anion\textsuperscript{35} or cation\textsuperscript{44} substitution in perovskites, the ability to achieve tuning using combined deposition control is new. An expanded view of the maxima (see Fig. S8, ESI) shows that their positions (and specifically $\lambda_{\text{max}}$) could be generally approximated using a superposition of the signals due to 2-s ($x = 0$) and 1-s ($x = 1.0$) systems (below). Consequently, the PL signals for the 1 & 2-s films originated from combinations of the signals found in the MAPbI$_3$ films prepared using 1-s and 2-s deposition.

In a study of cuboid MAPbI$_3$ crystals deposited using a 2-s method D’Innocenzo et al.\textsuperscript{45} showed that increased crystal size caused a $\lambda_{\text{max}}$ red-shift.\textsuperscript{45} The meso-crystals present for our systems are similar to those for D’Innocenzo et al.\textsuperscript{et al.} However, here the size decreased with increasing $x$ (Fig. S3, ESI) which rules out the possibility that their size dominated the $\lambda_{\text{max}}$ red shift. PbI$_2$ is known to cause a blue-shift for the PL spectra of MAPbI$_3$ due to passivation.\textsuperscript{46} The XRD data (Fig. 3a) showed that all of the films with blue-shifted $\lambda_{\text{max}}$ values ($x < 1.0$) contained residual PbI$_2$. However, the $\lambda_{\text{max}}$ value for the $x = 0$
film (Fig. 5c) does not agree with this trend because that film had a PbI₂ content that was similar to those present in the x = 0.50 and 0.66 films based on the %amplitude values (Fig. 3b) but had the most strongly blue shifted $\lambda_{\text{max}}$ value.

Microcrystals were present for films containing x = 0.33 to 1.0. They were also located on top of the mp-TiO₂ layer and fluorescence from those species should have been less quenched. As a first approximation, the PL maxima for the 1 & 2-s (x = 0.33, 0.50 and 0.66) films could be generally matched using a weighted spectrum for a hypothetical x = 0.75 film calculated using 75% weighting of the measured spectra for the 1-s (x = 1.0) film and a 25% weighting of the 2-s (x = 0) film (Fig. S8, ESI†). In contrast, the measured spectra for x = 0.33, 0.50 and 0.66 could not be matched to the respective hypothetical spectra calculated using x = 0.33, 0.50 and 0.66 (not shown). Moreover, those hypothetical spectra were all significantly blue shifted compared to the respective measured spectra for those films. Therefore, the PL spectra of the 1 & 2-s (x = 0.33, 0.50 and 0.66) films were not a straightforward linear combination of those for the 1-s and 2-s systems; rather they were preferentially weighted with x = 1.0 species. Hence, the data suggest that the microcrystals were mostly responsible for the PL spectra.

Transient absorption spectroscopy (TAS) was employed to investigate the effect of x on photo-induced separation. These experiments were conducted using a glass/mp-TiO₂/Perovskite/spiro-MeOTAD architecture (Fig. S9, ESI†) and probed the yield of photo-generated [spiro-MeOTAD]⁺ polarons as a function of time after pulsed laser irradiation (567 nm) by measurement of the change in absorption ($\Delta$OD) at 1600 nm. The decay kinetics data indicate that upon increasing x, and moving from 2-s (x = 0) through 1 & 2-s (x = 0.5) to 1-s (x = 1.0), a shorter charge separation lifetime was observed. For x = 0, the charge recombination was within a timescale of 5–50 μs. In comparison, increasing x accelerated the recombination kinetics, where a significant fraction of the decay appears to have occurred on a timescale faster than instrument response of the transient spectrometer (i.e., <1 μs). The data indicate that the extent of recombination and hence recombination kinetics for the 1 & 2-s film (x = 0.5) was between those for the 2-s (x = 0) and 1-s (x = 1.0) films.

**Effects of MAPbI₃ preparation conditions on device performance and hysteresis**

Solar cells were fabricated using P3HT or spiro-OMeTAD as the HTM. (The device architecture used is shown in Fig. 2.) We included P3HT in this study because at present it is the most likely HTM to be used to scale up perovskite solar cells. The aim of the present work was to investigate the effect of the preparation conditions and hence morphology on the device performance. Values for all of the device parameters are shown in Table S1 (ESI†). It can be seen from Fig. 6 that $J_{\text{sc}}$ and the PCE systematically decreased with increasing x. These values decreased by a factor of about two as x increased from 0 (2-s devices) to 1.0 (1-s devices) for both cell types studied. This trend follows that reported previously for related 2-s and 1-s devices.44 The ability to systematically tune the $J_{\text{sc}}$ and PCE values between the values for the 2-s and 1-s values is new. The importance of these results is that the morphology control demonstrated here provides a new route for tuning device performance which may be potentially useful for longer term tandem cell applications of perovskites. The performance of the latter cells can rely on careful adjustment of $J_{\text{sc}}$ values for the subcells.45

The values for $V_{\text{oc}}$ and FF were not significantly affected by x which is expected because the photodevice layer compositions were the same and the devices were prepared using similar conditions. The highest PCE values obtained were 10.32% and 4.23% for the 2-s (x = 0) devices prepared using spiro-OMeTAD and P3HT, respectively. This difference is likely due to slower recombination for the devices containing spiro-MeOTAD.43 J–V Curves for the best 1 & 2-s devices (x = 0.33) are shown in Fig. S10a (ESI†). Comparison of the data showed that the main parameter affecting the PCE was $J_{\text{sc}}$. Indeed, it can be seen from Fig. S10b (ESI†) that the PCE values were proportional to $J_{\text{sc}}$.

Consideration of the SEM data (Fig. 1) indicated that the decrease of $J_{\text{sc}}$ and the PCE with increasing x was likely due to an increase in the area of pinholes within the capping layer. This proposal was tested by plotting each parameter as a function of the % coverage determined from the SEM data. The results show that both $J_{\text{sc}}$ (Fig. 6b) and the PCE (Fig. 6c) increased with increasing % coverage. Whilst it is well accepted that high efficiency and capping layer coverage are correlated we are not aware of any studies that have quantified the relationship for MAPbI₃ solar cells. Thus, the 1 & 2-s (x = 0.33, 0.50 and 0.66) capping layer morphologies which provided the best coverage gave the highest $J_{\text{sc}}$. These values, i.e., a high number-density of smaller microcrystals with relatively large meso-crystals. In terms of PCE and $J_{\text{sc}}$, x = 0.33 gave the best results obtained using the 1 & 2-s deposition approach for each cell type (spiro-MeOTAD and P3HT). The PCE values for those cells were 8.64% and 3.04%,
respectively. To obtain increased PCE values using the 1 & 2-s approach higher % coverage values are required.

Whilst PCE hysteresis is an important topic governing perovskite solar cell performance\(^{50-52}\) its origin is not fully understood. Here, we calculated the hysteresis index, \(H\), using:

\[
\%H = 100 \left( \frac{A_F}{A_R} - 1 \right)
\]

where \(A_F\) and \(A_R\) are the integrated areas under the forward and reverse \(J-V\) curves, respectively. Fig. 7 shows the variation of %\(H\) with \(x\) for the devices prepared in this study (see also Table S1, ESI\(^*\)). Irrespective of the HTM the %\(H\) value decreased with increasing \(x\) and was tuneable. Migration of iodide ions is believed to play a key role in hysteresis\(^{51}\) and this phenomenon is believed to include accumulation of ions at the perovskite/TiO\(_2\) interface.\(^{54}\) Interfacial contacts and perovskite morphology have also been shown to affect hysteresis.\(^{26,53}\) Fig. 7 shows the %\(H\) values for the spiro-MeOTAD and P3HT-based devices were not significantly different. This indifference to HTM type supports the view that the morphology at the perovskite/TiO\(_2\) interface was responsible for the hysteresis.\(^{56}\)

An explanation for the trend shown in Fig. 7 is that %\(H\) was controlled by the MAPbI\(_3\) capping layer morphology. Consideration of the SEM images shown in Fig. 1b reveals that the total surface area of the perovskite crystals decreased as \(x\) increased, \(i.e.,\) the high surface area-to-volume ratio meso-crystals were progressively replaced with lower surface area-to-volume ratio microcrystals. Fig. 7 shows that the %\(H\) decreased with increasing \(x\). Consequently, it can be suggested from our results that the hysteresis decreased as \(x\) increased because of the decrease of the interfacial area at the capping layer MAPbI\(_3/\)mp-TiO\(_2\) interface that occurred.

**Proposed conceptual model for 1 & 2-s morphologies**

Based upon the results of this study we propose a schematic model for the 1 & 2-s photoactive layer structures (Fig. 8). There were three MAPbI\(_3\) crystal environments; microcrystals (\(>1\ \mu\text{m}\)), meso-crystals (\(~0.1-1\ \mu\text{m}\)) and nanocrystals (\(~50-80\ \text{nm}\)). Each of these crystal environments controlled different parts of the optoelectronic properties. The mp-TiO\(_2\) layer also contained remnant PbI\(_2\) nanocrystals and this was more prevalent at the deepest regions of the mp-TiO\(_2\) layer. As \(x\) increased the average size of the microcrystals increased and their number-density decreased; whereas, the average size of the meso-crystals decreased. The MAPbI\(_3\) nanocrystals were the majority MAPbI\(_3\) species based on the Scherrer analysis. The microcrystals and meso-crystals were responsible for light scattering. The microcrystals also determined the extent of coverage which, in turn, controlled the PL signal as well as \(J_{sc}\) and PCE.

![Fig. 7 Variation of the hysteresis index with x for various perovskite devices. See Scheme 1 for the meaning of x.](image-url)
Conclusions

In this study we have introduced and investigated a new MAPbI$_3$ film preparation method (1 & 2-s) and studied three novel mixed morphology perovskite photoactive films ($x = 0.33, 0.50$ and $0.66$). SEM data showed evidence of a change in the nucleation and growth mechanism that controlled the morphologies for the 1 & 2-s films. The morphologies were not simply a combination of the 1-s and 2-s morphologies and indicated that a change in nucleation kinetics occurred. The SEM and XRD data showed that the 1 & 2-s films had three MAPbI$_3$ species: micro-, meso- and nanocrystals. The proportion of each crystal type in the final films was controlled by $x$ and dominated device performance.

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References
