ENGINEERING CARRIER DYNAMICS IN LEAD HALIDE PEROVSKITES

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ENERGY RESEARCH INSTITUTE @ NTU (ERI@N)

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Interdisciplinary Graduate School
Energy Research Institute @ NTU (ERI@N)

A thesis submitted to the Nanyang Technological University in partial fulfilment of the requirement for the degree of Doctor of Philosophy

2018
Statement of Originality

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

15 Jan 2018
Date

Lim Swee Sien
Student Name
Abstract

Organic-inorganic hybrid perovskites have attracted immense attention primarily due to its outstanding photovoltaic and light emission properties. Specifically, certified power conversion efficiencies exceeding 20% have been demonstrated in perovskite solar cells – attributed to their large absorption coefficients and long, balanced, ambipolar diffusion lengths, large grains and its unique defect tolerance. Careful morphological control is needed to form dense, uniform films essential for high performance devices.

However, the resultant fundamental optoelectronic properties of such process controls are not well understood. In addition, the higher excited states that can aid in breaking the detailed balance limit is also unexplored. This thesis reports on a series of studies using ultrafast optical spectroscopy on the archetypal bulk 3D perovskite, methylammonium lead iodide (MAPI), to provide insights on the photophysics and recombination dynamics of this class of materials.

Here, process controls in fabricating perovskite thin films refers to treatments to the film, in the form of solvent engineering and additives, and to the substrate for hydrophilicity. Our findings reveal that solvent engineering of MAPI, i.e., dripping of toluene during spincoating which is key to improving film morphologies and subsequent solar cell efficiencies, had resulted in increased trap densities. We attribute this anomalous behaviour to an interplay of factors where the improved film morphology had also resulted in the lengthening of the carrier recombination lifetimes. Interestingly, depending on the combination of treatments, the charge extraction interface can go from injecting to non-injecting.

Exceptionally low carrier recombination rates in lead halide perovskites is crucial for its high performance. By careful optimisation of the additive concentration, improvements to device performance were observed when H\textsubscript{2}O was added to MAPI as an additive. Trace amounts of H\textsubscript{2}O passivates the trap states leading to reduced recombination rates, markedly improved carrier lifetimes and \textit{J}_{sc}. At the optimal additive concentration of 1 vol\% H\textsubscript{2}O, higher order carrier recombination is suppressed, and the greatly reduced monomolecular and bimolecular recombination rates was correlated with an
increase in power conversion efficiencies.

Process controls have all but ensured the unprecedented growth in record efficiencies of perovskite solar cells. However, it slows as it approaches the detailed balance limit of solar cells. One way to surpass this limit is to exploit the concept of hot carriers – photoexcited carriers in higher excited states. A technique to directly probe these states is presented, and through this, the broad photoinduced absorption band was revealed to be attributed to the promotion of photoexcited carriers to higher energy states. However, the observed sub-picosecond thermalisation times of these higher excited states may prove difficult for hot carrier extraction. Importantly, our results underscores the importance of judiciously choosing process controls to optimise optoelectronic properties of perovskite devices.
Acknowledgements

*No man is an island*, a giant might be; but giant, I am not – just a man who would like to give his thanks. I am appreciative of everyone and everything around me that, in one way or another, directly or indirectly, has helped me and given me the strength to complete my Ph.D. thesis and journey.

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mind, and heart to appreciate the world around me. You guys taught me a great deal, and for that, I am eternally grateful.

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Ye who seek glory and wealth! Look not to what little you can snatch from your neighbour, but to the boundless wealth of the world beyond! – Raubahn
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Abbreviations

Acronyms

AFM  atomic force microscope
ASE  amplified spontaneous emission
bphen bathophenanthroline
CBM  conduction band minimum
CCD  charge-coupled device
CW   continuous-wave
ESA  excited state absorption
GSB  ground state bleaching
ITO  indium tin oxide
LED  light emitting device
CH₃NH₃⁺ methylammonium
CH₃NH₃I methylammonium iodide
MAPI methylammonium lead iodide
OIHP  organic-inorganic halide perovskite
OPA  optical parametric amplifier
PbI₂ lead iodide
PC₆₁BM [6,6]-phenyl-C61-butyric acid methyl ester
PCE  power conversion efficiency
PEDOT:PSS poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PIA  photoinduced absorption
### Abbreviations

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<td>PL</td>
<td>photoluminescence</td>
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<tr>
<td>PMT</td>
<td>photomultiplier tube</td>
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<tr>
<td>PPP</td>
<td>pump-push-probe</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
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<tr>
<td>SNR</td>
<td>signal-to-noise ratio</td>
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<tr>
<td>spiro-OMeTAD</td>
<td>N2,N2',N2',N7,N7',N7'-octakis(4-methoxyphenyl)-9,9'–spirobi[9H-fluorene]-2,2',7,7'-tetramine</td>
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<td>SPM</td>
<td>self-phase modulation</td>
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<td>TA</td>
<td>transient absorption</td>
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<td>Ti:Sapphire</td>
<td>titanium-doped sapphire</td>
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<td>TRPL</td>
<td>time-resolved photoluminescence</td>
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<tr>
<td>UV</td>
<td>ultraviolet</td>
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<td>VBM</td>
<td>valence band maximum</td>
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<tr>
<td>VI</td>
<td>virtual instrument</td>
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<tr>
<td>WLC</td>
<td>white-light continuum</td>
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<td>XRD</td>
<td>x-ray diffraction</td>
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Chapter 1

Introduction

In this chapter, the motivation and rationale of my research is presented. The objectives and scope will also be defined. Based on the above-mentioned, an overview of my thesis will be laid out.

1.1 Motivation for Research

Irrefutably, the most successful semiconductor platform for commercial solar cells is silicon. The technology to refine and fabricate extremely high purity silicon wafers and solar cells have matured and optimised to the point where materials cost is the factor limiting large scale production[1]. This constrains future expansion of solar technologies, should the market rely solely on silicon.

It then becomes imperative that alternative material systems be explored in order to reduce costs of deployment through cheaper materials or processing. Thin film photovoltaic technologies, such as CdTe, CIGS, and dye-sensitised solar cells, rose to be strong contenders to silicon with their high efficiency and reliability. These technologies gained popularity, coming in second behind silicon photovoltaics due to its cost competitiveness[2, 3]. The organic-inorganic halide perovskites (OIHPs) were fashionably late to the field; but with every right to be so. No other competing material system thus far saw such unprecedented rise of record efficiencies in a short span of 8 years, but have slowed down considerably in recent years. These efforts were largely driven by radical changes and improvements in methylammomium lead iodide (MAPI) fabrication procedures during the perovskite solar cells’ formative years.

More often than not, a comprehensive understanding of the intrinsic photophysics is required to maximise the potential of perovskites for even higher device performance, reliability and stability. However, this are not
are not as well explored, leading to an incomplete understanding of the photophysics in MAPI and the other members of the OIHP family.

Ultimately, the question this Ph.D. thesis serves to answer is: ‘How does morphological changes arising from growth process controls of MAPI influence charge carrier dynamics for improved charge transport and device performance?’ Tackling this problem is indubitably complex and the next section outlines how we attempt to answer it.

1.2 Objectives and Scope

In line with my motivation, the objective of this research is to study charge dynamics and extraction to improve OIHP devices. In this study, we focus on the 3D perovskite, specifically the MAPI as our material system. It is the most well-characterised material sub-system and produces consistently high efficiency devices, although there are multiple reports of increasing the cation count can ultimately serve to increase device performance. Which brings us to our next reason: MAPI is used to avoid complexities and artefacts that can possibly transpire if multiple cation systems were otherwise employed. This allows us to accurately assign any improvements to be solely based on the fabrication changes. In addition, it also provides a cleaner transient spectrum to interpret without extraneous contributions due to multiple photoexcited species interacting with each other because of increased cations.

We use a two-pronged approach to accomplish our objective,

1. By studying how fabrication process controls influence the photophysics and device performance. Specifically, we seek to understand how various film and substrate treatments, and H$_2$O additives affect perovskite film morphology and physical properties. And in turn, how the charge carrier dynamics, recombination kinetics and transport are modulated as a result.

2. By studying the fundamental excited states in perovskites. Specifically, we seek to understand the higher excited states in MAPI, and whether it is possible to extract hot charge carriers as a result. A good understanding of these excited states can help in designing and choosing matching acceptor materials for efficient charge extraction and transport.
1.3 Thesis Overview

Chapter 1 provides the motivation and rationale for the research. It also outlines the objectives and scope of the whole project, and summarises the major findings, outcomes, and implications.

Chapter 2 reviews the relevant seminal and recent literature on the OIHPS thin films and puts the Ph.D. in context.

Chapter 3 describes the experimental setups, the methodology and techniques used in this study. Theory of these techniques will be covered to give the reader sufficient background to understand the data obtained from ultrafast measurements. In addition, the details on sample synthesis and basic characterisation techniques to ensure sample accuracy will be presented.

Chapter 4 presents our results on treating the MAPI film and the substrate it is grown on. Sample morphology is a crucial factor in obtaining high quality thin films and devices. The effects and implications of such treatments on morphology, trap densities and carrier dynamics will be presented and discussed. The origins of these trap densities will also be discussed. In addition, the effect of such treatments on light emission will also be presented.

Chapter 5 presents our new insights into the effect of H$_2$O additives in MAPI. Additives were reported to benefit perovskite devices in a myriad of ways, although their influence on the photophysical properties is severely lacking. The effect on the measured trap density, carrier dynamics recombination will be discussed. The resultant carrier transport and device performance in such perovskites with additives will also be presented.

Chapter 6 focuses on the fundamental photophysics of MAPI, specifically its higher excited states. Understanding these higher excited states, in addition to the fabrication controls used in the previous two chapters, allow for more efficient charge extraction and devices. The experimental setup and methodology employed to directly probe these higher, or ‘hot’, excited states are discussed in detail. The questions on the origins of the broad spectral feature observed in transient absorption will be presented and answered. In addition, the results of hot carrier extraction will also be discussed.
Chapter 7 is devoted to concluding remarks, summarising the major findings and implications arising from this study. Possible future works to extend this research are also outlined.

1.4 Findings and Originality

This research led to several novel findings as summarised below.

1. Through film engineering, our findings reveal new insights into the complex interplay of film morphology and the ensuing carrier recombination dynamics, defect densities, carrier diffusion lengths and light emission properties. We discovered that toluene, commonly used in solvent engineering, adversely increases the defect densities of MAPI in the form of MA vacancies. On the other hand, careful combination of these wet treatments led to more balanced diffusion lengths, paving the way for wet etching of the substrate for large-scale fabrication.

2. Adding trace amounts of H$_2$O as an additive in MAPI improved photovoltaic performance, previously casually attributed to morphological improvements. On the contrary, we found that by adding an optimal concentration of 1 vol% H$_2$O, we observed drastic changes in the photophysics. Higher order carrier recombination were suppressed by one order of magnitude, giving rise to comparatively longer charge diffusion lengths that exceeds the active layer at solar operating conditions. These collectively resulted in higher solar efficiencies compared to the control (0 vol% H$_2$O), with the champion 1 vol% H$_2$O cell exhibiting an efficiency of 12.3%.

3. Employing an elaborate three-pulse ultrafast setup to study the excited states of MAPI revealed exciting photophysics of the higher excited states. We unambiguously discovered that excited state absorption (ESA) of the photoexcited carriers forms the dominant contribution to the photoinduced absorption, contrary to its previous assignment of photoinduced change in the refractive index. We also found that both ESA and band edge recombination transitions involve the same states at the conduction band minimum. These findings were translated to hot carrier extraction, phenomenologically demonstrated when pushed
with 600 nm photons and using a bphen layer. However, the presence of an interfacial barrier, which has a height between 0.6 eV and 1.17 eV, imposes a lower limit to the energy of the push photon required to induce hot carrier extraction. This finding establishes clear design rules for engineering suitable acceptor materials to extract hot carriers in perovskites.

References


Figure 1.1: Roadmap of my thesis.
Chapter 2

Literature Review

The past years have seen an explosive growth in halide perovskite research in the exploration of their optoelectronic properties, exploiting their facile fabrication methods, and striving for high quality films. This chapter presents the relevant seminal and recent literature on the perovskites, focusing on thin films.

The material in this chapter is adapted from Ref. [1] with permission from World Scientific Publishing.

2.1 Organic-Inorganic Halide Perovskites

The organic-inorganic halide perovskites were not products of a miracle. In fact, it was a once-forgotten child; first synthesised by Weber in 1978, who replaced the inorganic cesium with methylammonium (CH$_3$NH$_3^+$) [2] forming the first 3D organic-inorganic halide perovskite (OIHP), the methylammonium lead iodide (MAPI). This particular perovskite has a chemical formula CH$_3$NH$_3$PbI$_3$ that can be generalised to ABX$_3$ for other OIHPs and its crystal structure is shown in Figure 2.1. The A site is usually occupied by organic or inorganic cations (e.g. MA:CH$_3$NH$_3^+$, FA:[CH(NH$_2$)$_2$]$^+$, Cs), the B site is usually occupied by divalent metal cations (e.g. Pb$^{2+}$, Sn$^{2+}$), and the X site is usually occupied by the halides (e.g. I$^-$, Br$^-$, Cl$^-$). The [BX$_6$]$^{4-}$ inorganic octahedral gives the perovskite is responsible for charge transport. Partially substituting the different molecules at their respective sites (e.g. using a combination of [CH(NH$_2$)$_2$]$^+$ and CH$_3$NH$_3^+$) allows for tunability of the physical characteristics and optoelectronic properties of the resultant perovskite.

The perovskite field was left pretty much undisturbed until 1994 when Mitzi incorporated organic alkylammonium cations between tin iodide sheets, revealing its fascinating optoelectronic properties. It was not until
Figure 2.1: OIHP crystal structure with the chemical formula ABX$_3$. The organic or inorganic cations occupy the A site, with divalent metals occupying the B site. The X site contains the halides.

2009 when Kojima made the first functional MAPI solar cell that is merely 3.81% efficient. This discovery, coupled with its highly abundant, low cost materials, low temperature and highly scalable solution processing methods, paved the way for the explosive growth in this field. Progressive efforts to address the stability of perovskite cells led to the modifications of liquid electrolytes [3] and eventual fabrication of an all-solid state device [4].

Fast forward to recent years, OIHPS became the new darling of the solution-processed photovoltaics community, and have been extensively researched on. The main advantage OIHPS has over incumbent Si and CdTe photovoltaic technologies is its low-temperature solution-processability which gives it immense cost efficiency. But when metallisation of the OIHP cells is factored in, its cost per m$^2$ becomes borderline comparable to Si and CdTe only when silver is used as the electrode[5]. Therefore, to increase the cost competitiveness of OIHP cells, a clear understanding of the photophysical processes and charge transfer mechanisms in these novel light-harvesting semiconductors is required. This aids in engineering more efficient charge extraction layers and device architectures that ultimately drive the performances. From early photophysical studies on the archetypal MAPI perovskite thin films, many novel optoelectronic properties of halide perovskites that are favourable for high performance photovoltaics were uncovered. For example, these include their high absorption coefficients, low direct bandgaps, balanced ambipolar carrier diffusion lengths, high carrier
mobilities, and low exciton binding energies etc. [6, 7, 8, 9] In this study, we focus on the archetypal MAPI perovskite, as the 3D perovskites still produces the highest performing devices albeit at the cost of stability. Furthermore, MAPI is the most well characterised sub-system and we use it to avoid complexities and artefacts that can possibly transpire if multiple cation systems were otherwise employed.

2.1.1 Optoelectronic Applications

Presently, record perovskite solar efficiencies have exceeded 22% [10, 11]. The rapid surge in photovoltaic efficiencies seen in the early years have now slowed down considerably. Figure 2.2 shows the various optoelectronic applications of OIHPs. Apart from its obvious application in photovoltaic technologies, its versatility enables high degrees of bandgap tunability via cation and halide substitutions. Its wide spectral tunability and low amplified spontaneous emission (ASE) threshold [12] is realised in lasing [12, 13] and light emitting devices (LEDs) [14, 15] applications. Recently, OIHPs have also found its use in photodetectors [16, 17, 18] and phototransistors [19, 20]. A complete photophysical picture would also spur the development of emerging areas in perovskite optoelectronics.

2.1.2 OIHP Thin Film Fabrication

The photovoltaic performance of the perovskite solar cell is strongly influenced by the active layer morphology, crystallinity, and stoichiometry, etc. Early solution processing approaches utilise drop-casting [22] and one-step [4] methods, which simply involves dropping, and spincoating a prepared perovskite solution on a substrate. The single step spin-coating forms voids in the perovskite film due to uncontrolled crystallisation of the perovskite and this resulted in poorer performance due to lower light absorption and shunting paths [23, 24]. An improvement is the sequential method [24], that allows for better morphological control over the perovskite film by first preparing the lead iodide (PbI2) layer and then dipping it into a solution of MAI. OIHPs can also be produced with mixed dimensionality, depending on how the [BX6]4− octahedrons connect [25]. As researchers aim for even tighter morphological controls, other methods such as vapour-assisted solu-
Various optoelectronic applications of OIHPs, e.g. (a) solar cells using OIHPs, typically 3D variants, as the active layer. Figure adapted from Ref. [21]. (b) Low threshold and broadband spectral tunability of the ASE in OIHPs (Ref. [12]) enables versatile light emitting applications such as (c) LEDs (Ref. [15]) and (d) observation of lasing from drop-casted MAPI crystal (Ref. [12]) and (e) thin films (Ref. [13]). (f) Photodetectors made using MAPI, figure adapted from [17].

Regardless of the approaches used, Figure 2.3 shows the importance of MAPI film morphology on high device performance [23], underscoring the need to achieve dense, uniform perovskite films.

Achieving good control over the morphology of the perovskite film is non-trivial as its morphology could be influenced by many factors during fabrication. These include: variation in the compact TiO$_2$ thickness in planar cells [23], influence from the underlying PbI$_2$ film in mesoscopic cells fabricated using the two-step approach [24], and the presence of additives such as acids [22, 28, 29] and water [30, 31, 32, 33]. The efficacy of H$_2$O additives turned out to be a surprise, considering that the perovskite is inherently weak against water, rapidly degrading into hydrated compounds [34] and PbI$_2$ [35]. In mid-2014, Jeon et al. and Xiao et al. found that by employing solvent engineering during the spincoating, dense and uniform films could be obtained [36, 37]. This approach involves introducing an anti-solvent (e.g., toluene which perovskite has poor solubility). The ensuing toluene drip during spincoating removes the excess 'good' solvent from the film. Consequently, this
Figure 2.3: Perovskite film coverage dependence of the photovoltaic parameters and PCE. (a) Short-circuit current density and (b) PCE dependence on perovskite film coverage. (c) Current-voltage curve of optimised perovskite film coverage devices. All devices were measured under simulated AM1.5, 100 mW cm\(^{-2}\) sunlight. Figure adapted from [23].
decreases the solubility of the perovskite and results in the rapid crystallisation of the perovskite crystals. Although solvent engineering significantly improves the morphology, it also increases the trap density of perovskite films as revealed by transient spectroscopy [38]. Direct experimental evidence into the identity of the specific traps from optical spectroscopy is highly challenging, though first principles calculations could offer us some insights about their possible identities. The influence of process controls via toluene solvent engineering and water additives are explored in Chapters 4 and 5, respectively.

2.2 Defects in OIHP

Early density functional theory calculations have shown that the defects in MAPI are generally shallow point defects occurring near to the conduction and valence bands due to their lower formation energies unlike deep defects [39]. Further theoretical studies revealed that benign perovskite grain boundaries, i.e., in crystalline thin film samples do not form any gap states, suggesting that the former samples have single crystal-like behaviour [40]. Defects deep in the band gap are detrimental for photovoltaic performance as they significantly increase non-radiative recombination of charge carriers and the minority carriers via the Shockley-Read-Hall process. Predicted shallow point defects include vacancies (\(V_{\text{MA}}\), \(V_{\text{Pb}}\), \(V_{\text{I}}\)), interstitials (\(\text{MA}_i\), \(\text{Pb}_i\), \(\text{I}_i\)), cation substitutions (\(\text{MA}_{\text{Pb}}\), \(\text{Pb}_{\text{MA}}\)) and antisite substitutions (\(\text{MA}_{\text{I}}\), \(\text{Pb}_{\text{I}}\), \(\text{I}_{\text{MA}}\), \(\text{I}_{\text{Pb}}\)) [39]. These studies have also shown that the perovskite could be changed from n-type, to intrinsic, and to p-type depending on the type of defects introduced during film fabrication – intentional or otherwise. Fortunately, halide perovskites possess a tolerance for such defects, which are also described as benign defects. This beneficial characteristic is found not only in the archetypal MAPI thin films [40, 41, 42], but also in nanocrystals [43], as well as their fully inorganic counterpart CsPbBr\(_3\) [44].

The defect tolerance of OIHPs stems from its unique electronic band structure, shown in Figure 2.4, where the conduction band minimum is predominantly bonding and the valence band maximum is predominantly antibonding; a direct opposite compared to most semiconductors. The conduction band is formed by the hybridisation of the Pb 6p orbitals, and the
valence band from Pb 6s and I 5p orbitals. Specifically, Brandt et al. suggested that the interactions between the atomic orbitals in the conduction and valence bands serve to increase the width of the electronic bands. Pb 6s and I 5p orbitals interacts to form two valence bands, and the antibonding orbitals within the band pushes the valence band maximum upwards. Their calculations also revealed that relativistic spin-orbit coupling effects increase the width of the conduction band by about 2 eV. As such, due to the relative position between the valence orbitals and the bonding/antibonding bands, any dangling bonds that are created due to vacancies will appear as resonances in the bands, rather than forming deep gap trapping states [41].

![Diagram of electronic bands in MAPI](image)

**Figure 2.4:** (a) Formation of electronic bands in MAPI from interactions between the Pb (red) and I (blue) bonding ($\sigma$) and antibonding ($\sigma^+$) orbitals. (b) Computed density of states (DOS) from density functional theory showing the metal cation and halide anion contributions, and the absence of band edge states by CH$_3$NH$_3^+$. Figures adapted from Ref. [41].

A key challenge would be to find a suitable less toxic replacement that possesses similar characteristics afforded by Pb. Alternatively, if defects are inevitable in the Pb-free or Pb-less (i.e., reduced Pb) systems, more efficient charge extraction pathways that bypass the defects states (e.g., efficient hot carrier extraction [45] – see Section 2.3.2 and Chapter 6) could be a viable approach to high efficiency Pb-free cells. One way to understand and search for current and alternative OIHPs is through optical spectroscopy.
2.3 Optoelectronic Properties of OIHPs

To date, detailed photophysical studies have revealed the intrinsic optical properties of MAPI perovskite thin films that make them highly favourable for solar cells i.e., trap-mediated monomolecular recombination, low bimolecular recombination, long diffusion lengths, low exciton binding energy, high carrier mobility. Seminal reports on the long carrier diffusion lengths, i.e., $>100\text{ nm}$ [6] and $1\text{ µm}$ [7], were independently reported by our group and Snaith’s group, respectively in 2013. By fitting the time-resolved photoluminescence (TRPL) lifetimes of the neat perovskite films and comparing them against films with electron and hole quenchers, the diffusion lengths were also estimated using a 1D diffusion model (see Equation 4.14; further discussed in Section 4.4.3). Although the exact values would differ due to the dependence on film quality and thickness, these long diffusion lengths bear testament to perovskites’ unique advantage over organic and dye-sensitised solar cells. However, the origins of these long carrier diffusion lengths in halide perovskites remain a subject of intense debate, where large polarons [46, 47] and photon recycling [48] concepts were recently proposed as plausible causes.

The recombination dynamics of these carriers can be quantified through the monomolecular, bimolecular and Auger rate constants obtained by fitting pump fluence dependent transients with the differential rate equation (Equation 5.1 in Section 5.4.1. The monomolecular recombination, typically around $10^6\text{ s}^{-1}$, is trap-mediated [49] and plays a vital role in limiting the solar cells performance [50]. Surprisingly, the bimolecular recombination rate in OIHPs is extremely low ($\approx 10^{-9}\text{ cm}^3\text{s}^{-1}$), which is about four orders of magnitude lower than theoretically predicted using the Langevin model [51]. The Auger recombination constants in halide perovskites ($\approx 10^{-28}\text{ cm}^6\text{s}^{-1}$) were also found to be surprisingly large and are comparable with strongly confined colloidal inorganic quantum dots (e.g., CdSe). Amazingly, stimulated emission still outcompetes the Auger processes in halide perovskites with amplified spontaneous emission and lasing first demonstrated in 2014 [12]. Figure 2.5 shows a summary of the photophysical processes in MAPI polycrystalline thin films. The relatively high mobility of carriers, together with low monomolecular and bimolecular recombination rates make per-
ovskites highly attractive for photovoltaic applications. Although MAPI is now the model system for halide perovskites, a full picture of its photophysical mechanisms is still far from complete.

![Diagram of photophysical processes in MAPI](image)

**Figure 2.5**: Different photophysical processes in MAPI and its dependence of excitation intensity. Figure adapted from [25].

### 2.3.1 Excitons and Charge Carriers in OIHPs

Following the ground-breaking reports on the long carrier diffusion lengths, the nature of the primary photoexcited species being excitons or free carriers became the subject of intense research activities in early 2014. The
answer to this puzzle has important ramifications on the light harvesting concept, the design and architecture of the solar cell to cater to the transport of energy (i.e., excitons or free charges). One approach is to accurately determine the binding energy of the excitons in the perovskite. Its value would provide valuable clues on whether the primary photoexcited species are excitons or free carriers at room temperature ($k_BT \approx 25\text{ meV}$). A small binding energy ($\ll 25\text{ meV}$) means that a larger population of the excitons will spontaneously dissociate and carrier transport is dominated by free carriers. On the other hand, a large binding energy ($> 25\text{ meV}$) will mean that charge transfer interfaces (like in organic photovoltaics) are required to facilitate exciton dissociation and charge separation. Early studies revealed that exciton binding energies can be as small as 2 meV or as large as 50 meV [52, 53, 54]. This large discrepancy arises because of the presence of a phase transition, variation in sample quality, and different techniques used: e.g., temperature-dependent PL, absorption, and magneto-absorption. Sheng et al. performed ultrafast polarisation memory measurements and proposed that an estimated exciton to free carrier branching ratio in MAPI to be approximately 1:10 [55].

Eventually, Miyata et al. resolved this controversy in 2015 by performing temperature- and field-dependent magneto-absorption experiments [8]. Fittings of the Landau levels transitions in the magneto-absorption spectra yielded an effective mass of $m^* \approx 0.1\text{ m}_e$, which is in excellent agreement with computational calculations [56, 57]. The accuracy of the calculations were improved greatly because of the identification of a $2s$ transition, which imposes strict constraints on the exciton binding energy. By determining the effective mass precisely, the authors accurately deduced the exciton binding energy to be only $16\text{ meV}$ at 4 K, which is significantly lower than the aforementioned range. Furthermore, there is a critical collapse of the binding energy to a few meV at room temperature, which is attributed to the frequency-dependent dielectric constant, as predicted by Even et al [58]. A similar behaviour was also observed by Yamada et al. with temperature-dependent absorption where they reported an exciton binding energy of $30\text{ meV}$ at 13 K which similarly collapses to $6\text{ meV}$ at 300 K [59]. These findings independently suggests the free carrier nature of MAPI.

The small, non-zero exciton binding energy could support a small exci-
ton population, which were indeed detected by Simpson et al. in the same year. As shown in Figure 2.6, the authors used transient absorption (TA) microscopy to spatially resolved positive and negative TA signals coexisting in crystal grains of MAPI thin films. The high excitation fluence used (mJ cm\(^{-2}\)) allows direct probing of exciton-exciton annihilation and Auger recombination nonlinear dynamic processes [60].

Since the respective differential absorption signals are proportional to the exciton and free carrier population respectively (\(\Delta A(t) \propto n(t)\)), they can be extracted by fitting them with equations governing the nonlinear processes:

\[
\frac{1}{n_{ex}(t)} - 1 = \gamma_{ex}t 
\]

\[
\frac{1}{[n_{ex}(t)]^2} - 1 = \gamma_{eh}t, 
\]

where \(\gamma\) is the rate constant of the respective processes. As shown in Figure 2.6b, The linear dependence of ROI 2 on Equation 2.1 suggest exitonic behaviour. On the other hand, Figure 2.6c reveals a linear dependence of ROI 1 on Equation 2.2 suggests free carrier behaviour. Their results established the spatially separated coexistence of exitonic and free carrier heterogeneity in MAPI [60].

Nah et al. extended their work by spectrally resolving TA signals, revealing that red and blueshifts of the bandedge absorption are responsible for the heterogeneities (Figure 2.6d,e). The measured shifts are in the range larger than 20 meV, higher than the room temperature thermal energy, reinforcing that excitons and free carriers can potentially coexist. The decay and rise of the red and blueshifting features shows strong anti-correlation, suggesting that both effects are due to thermalisation of hot carriers screening the excitonic transitions. The fluence dependence of the redshift and blueshift shown in Figure 2.6g-i shows a null and a linear dependence, indicative of free carrier and excitonic behaviours, respectively. Their results shed further insights on the coexistence of free carriers and a minority exciton population in MAPI [61].
Figure 2.6: Free carrier and exciton coexistence revealed by spatial heterogeneities in MAPI (a) revealed by TA microscopy distinctly showing opposing signs depending on which part of the film is probed (ROIs 1 and 2). (b) The time linear dependence of the modelled TA signal revealing excitonic behaviour in ROI 2. (c) TA signal squared reveals the free carrier behaviour in ROI 1. Figures (a-c) adapted from Simpson2015. (d) Illustration of how a red or blueshift of the Gaussian absorption peak results in a derivative $\Delta T$ TA signal. (e) Measured derivative features at specific time slices that has both positive and negative $\Delta T$ signals. (f) Plot showing the strong anticorrelation of the redshift and blueshift data. (g-h) Pump fluence dependence of the redshifts and blueshifts. (i) Plot illustrating the linearity of the blueshifts, revealing excitonic behaviour, whereas the null dependence of the redshifts are indicative of free carrier behaviour. Figures (d-i) adapted from [61].
2.3.2 Slow Hot Carrier Cooling

The first report on 0.4 ps hot hole cooling in MAPI (shown in Figure 2.7) was reported by Xing et al. in 2013 [6]. The authors observed a concomitant rise and fall in the TA signals (shown in Figure 2.7a) monitoring the state-filling of a pair of interacting valence band states – i.e., depletion of a lower valence level (black squares: 480 nm) and the concurrent repletion of an upper valence level (red circles: 760 nm) upon 400 nm pulsed excitation. The hot-phonon bottleneck effect were independently reported by Price et al. [62] and Yang et al. [63] to be a possible cause for the slow hot carrier cooling.

More recently, Li et al. successfully slowed down the cooling by a further 2 orders in MAPbBr$_3$ nanocrystals and efficiently (83%) extracted their hot carriers [45]. They also found that there are in fact two fluence dependent origins for the slow hot carrier cooling phenomenon: the hot-phonon bottleneck at lower fluence and Auger heating at higher fluence. These are also present in polycrystalline thin films [64]. Clarifying the underlying mechanisms for slow hot carrier cooling has important consequences for both light harvesting and lasing applications. The demonstration of efficient 83% extraction of hot carriers exemplifies the potential of perovskites for hot carrier photovoltaics; while optical gain onsets (and thresholds) are highly dependent on the thermalisation processes at high carrier densities. The challenge would be to utilize these knowledge and translate them to practical opto-electronic devices.

2.4 My Ph.D. in the Context of the Literature

There is still great potential in OIHP-based devices, as long as high quality perovskite active layers can be produced. The perovskite community has known since 2014 (conservatively, but probably earlier) that film morphology is of utmost importance. Thus, the initial efforts were focused on exploring different radical fabrication techniques to boost photovoltaic performance. Film treatment via solvent-engineering with toluene remains the most ubiquitous approach due to its facile nature and surprising effectiveness that does not require elaborate growth schemes. The differing requirements in morphology, specifically perovskite grain size, for light emission raises
Figure 2.7: Seminal reports of MAPI carrier dynamics showing the early time normalised bleaching kinetics at 480 nm and 760 nm reveals the hot-hole cooling across the valence bands in MAPI after 400 nm photoexcitation (pump fluence = 1 µJ cm$^{-2}$). (b) Energetics illustration of hot-hole cooling and charge recombination in MAPbI$_3$ and charge separation at the MAPI/PC$_{61}$BM and MAPI/spiro-OMeTAD interfaces. VB1 and VB2 energy levels were approximated from the TA measurements.
question on how carrier dynamics will be affected as a result. Furthermore, the inclusion of H$_2$O, which by itself is the arch nemesis of OIHPs, was surprisingly effective and prompts further investigation on its effects on carrier transport. Both techniques involve direct interaction of the solvent and MAPI crystal grains which would impact the carrier dynamics and resultant charge transport properties.

While the predominantly free carrier nature of MAPI already allows for high photocurrent generation, coexisting excitonic pockets in the perovskite grains can impose limits on device efficiency [61]. This raises the question of whether charge generation can be induced through higher excited states in MAPI, previously demonstrated in highly excitonic organic photoactive systems [65]. In addition, to help in engineering and choosing appropriate acceptor materials for efficient charge extraction and transport, it is therefore first necessary to obtain a deeper understanding of the fundamental excited states in OIHPs.

Ultimately, for new breakthroughs in device efficiencies, it is essential to carefully examine the fundamental optical properties of OIHPs in its totality: i.e., correlating the charge kinetics and the structure-function relations where defects, morphology, and surface effects have a dominant influence; and understanding the higher excited state dynamics in perovskites to enable more efficient charge transport.

References


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Chapter 3

Experimental Methodology

In this thesis, various steady-state and time-resolved techniques were used in the spectroscopic characterisation of MAPI, including steady-state and time-resolved photoluminescence, and transient absorption spectroscopy. These experiments serve to reveal the carrier dynamics and relaxation of excited charge carriers. Knowledge of the excited state lifetimes gained from these measurements allows us to interpret the spectroscopic data. As such, careful optimisation of the components in the experimental setup is crucial. In this chapter, I will describe the experimental methods and discuss the aspects for these experiments. The samples, lasers used, the various optical setups, and data acquisition schemes will be explained.

3.1 Sample Fabrication

The organic-inorganic hybrid perovskite, MAPI, is spincoated on transparent substrates using the one-step solution process in collaboration with Prof. Subodh’s and Prof. Nripan’s group. The thin film samples used in this work consists of

1. MAPI on plasma-cleaned quartz
2. MAPI on piranha-etched quartz
3. MAPI with H$_2$O-additives on plasma-cleaned quartz
4. MAPI with electron transport layer (i.e. PC$_{61}$BM)
5. MAPI with hole transport layer (i.e. spiro-OMeTAD)

The quartz substrates were cleaned with an ultrasonic bath in a beaker of deionised water, followed by acetone, and finally isopropyl alcohol for 15 min.
each. The substrates were blown dry and placed in an oven overnight to dry off residual moisture. Prior to spincoating, the substrates are treated to improve wettability. This allows the solution to stick on the substrate during spincoating; without it, the solution will be flung away during spincoating. In this work, plasma-cleaning was primarily used, and is ubiquitous in the field. We also use piranha solution, a cleaning agent commonly used in the silicon industry, as an alternative substrate treatment technique (courtesy of Assoc. Prof. Chen Hongyu, CBC, SPMS, NTU). The substrates are either plasma-cleaned for 10 min or etched in piranha solution (3 parts H$_2$SO$_4$ to 1 part H$_2$O$_2$) for 30 min, rinsed with deionised H$_2$O and dried.

The single-step stoichiometric solution was prepared in an N$_2$-filled glovebox (O$_2$ < 0.5 ppm, H$_2$O < 0.1 ppm) by mixing 78.3 mg ml$^{-1}$ methylammonium iodide (CH$_3$NH$_3$I) (Dyesol) and 27.0 mg ml$^{-1}$ PbI$_2$ (Acros Organics, 99%) in anhydrous N,N-dimethylformamide (Sigma Aldrich, 99.9%) to form a clear, yellow solution. The solution was stirred for 30 min and filtered with a 0.45 µm polytetrafluoroethylene filter before spincoating. When water additives were used, deionised H$_2$O was added to the perovskite solution as additives at this preparation stage. The perovskite solution is heated at 70°C prior to spincoating. The samples were fabricated by spincoating 20 ml of the one-step perovskite solution on the treated substrates at 2000 RPM for 60 sec. For samples that were solvent engineered, 60 ml of toluene was dripped 5 s from the start of the spincoating procedure. These conditions yielded a 10 wt% perovskite film, suitable for transmission measurements using pump-probe spectroscopy (see Section 3.4 for details).

When required for diffusion length or quenching measurements, charge transport layers were spincoated either below (in contact with the substrate) or above (in contact with atmosphere) the perovskite layer depending on experimental requirements. The [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM) electron transport layer was spincoated at 1200 RPM for 45 sec, and N2,N2,N2’,N2’,N7,N7,N7’,N7’-octakis(4-methoxyphenyl)-9,9’-spirobi[9H-fluorene]-2,2’,7,7’-tetramine (spiro-OMeTAD) hole transport layer was spincoated at 4000 RPM for 30 sec.

To minimise sample exposure to moisture and oxygen during optical measurements, the samples were mounted in a sample chamber (Figure 3.1) in the glovebox. The sample chamber consists of two stainless steel high-
vacuum flanges clamped together, and this allows us to keep the samples in a dry $\text{N}_2$ environment.

Figure 3.1: Photograph of the sample chamber used for optical spectroscopy. The samples are loaded into the chamber and sealed in the glovebox.

3.2 Lasers

In our optical experiments, we primarily use a femtosecond laser amplifier. The gain medium is a titanium-doped sapphire (Ti:Sapphire) crystal that has a broad wavelength bandwidth. This allows for the generation of ultrashort pulses in accordance to the uncertainty principle. Using these femtosecond pulses allows us to interrogate processes that occur in the sub-picosecond timescales with high accuracy.

3.2.1 Femtosecond Pulse Generation

In order to generate a femtosecond pulse, the many continuous-wave (CW) lasing modes of the Ti:Sapphire medium is present in the laser cavity. By itself, these CW lasing modes oscillate in the cavity independent of each other and their relative phase is random. Should we use this output, we will get a noisy beam, since the intensity is the squared of the electric field at any point. Through mode locking, a more useful output can be generated - the laser pulse. This process is illustrated in Figure 3.2.
A common modelocking technique is Kerr lens modelocking. The technique uses the optical Kerr effect; a nonlinear effect which occurs when an intense light passes through the Ti:Sapphire crystal. The nonlinearity results in a change in the intensity-dependent refractive index, $n(I)$,

$$n(I) = n_0 + n_2(I)$$  \hspace{1cm} (3.1)

where $n_0$ is the linear refractive index, and $n_2$ is the nonlinear refractive index coefficient. As a result, the modelocked pulse train then self-focusses to a smaller diameter, as compared to a larger CW one. By placing a slit at a suitable location within the cavity, the larger CW beam can be partially blocked, thus introducing huge losses to the CW mode (Figure 3.3). It is important to eliminate the CW beam as it is competing with the femtosecond pulses for subsequent amplification in the regenerative amplifier cavity.

Another crucial consequence from the Kerr effect is self-phase modulation (SPM) which arises from the time-dependent intensity of the pulse as it passes through the medium [1]. SPM will cause a time-dependent phase shift.
of the pulse, thus changing the frequency components of the pulse without affecting the pulse envelope, an effect also known as ‘chirp’. Either the front or back of the pulse will be red- or blue-shifted depending on the shift induced by SPM, generating new frequency components and broadening the spectral bandwidth of the pulse. However, a chirped pulse is temporally broadened, and is unsuitable for ultrafast spectroscopy as it will continue to spread due to dispersion. In order to exploit the increased spectral bandwidth, the chirp must be compensated by using, for example, negative dispersion mirrors, such that the faster wavelength components will be delayed, and the slower wavelength components will be advanced.

3.2.2 Pulse Amplification

The femtosecond pulse generated thus far may not be intense enough for spectroscopic applications. To produce even higher intensity pulses, we use the Coherent Libra, a one-box laser system, that operates at 1 kHz with a pulse energy of 4 mJ per pulse and it contains a few critical components:

1. Seed laser (Coherent Vitesse™ oscillator)
2. Pump laser (Coherent Evolution™)
3. Stretcher and compressor
4. Regenerative amplifier

Using the above-mentioned techniques for pulse generation (Section 3.2.1), low intensity femtosecond pulses is emitted from the Vitesse at a
repetition rate of 80 MHz and routed to the stretcher/compressor and regenerative amplifier module for amplification. The pump beam from the Evolution is a high intensity nanosecond pulse with a repetition rate of 1 kHz is used to excite the Ti:Sapphire gain medium.

However, if the seed beam is allowed to propagate freely in the regenerative amplifier cavity, it will extract large amounts of energy from the Ti:Sapphire crystal. This leads to extremely high peak intensities that can cause undesirable nonlinear distortion or even destruction of the delicate optical components in the laser. The Libra utilises an ubiquitous technique known as chirped pulse amplification to mitigate this problem. Prior to amplification, the seed pulse is temporally stretched to increase its pulsewidth up to 500 ps, significantly reducing its peak intensity.

The broadened pulse is then injected into the regenerative amplifier, where it is contained by a pair of synchronised Pockels cells and passes through the Ti:Sapphire gain medium multiple times for even greater amplification ($> 10^6$) as compared to just a single pass. When sufficiently amplified, Pockels cell 2 is switched on and this rotates the polarisation of the amplified beam from $p$ to $s$-polarised. Switching the pulse polarisation causes the pulse to reflect off a reflective polariser and into the compressor module for compression back to a femtosecond pulse. The emitted 800 nm pulse from the Libra has an energy of $\approx 4 \text{ mJ per pulse}$, with a pulsewidth of $\approx 50 \text{ fs}$ at a repetition rate of 1 kHz.

### 3.2.3 Optical Parametric Amplifier

While the 800 nm fundamental beam can be used for certain experiments and samples, a large fraction of the Libra output is split and used to pump two Coherent OPerA™ Solo OPAs. Using an OPA greatly improves the spectral versatility of the excitation beam used in our spectroscopic techniques (240 nm to 2600 nm).

Optical parametric amplification exploits the $\chi^{(2)}$ nonlinearity of crystals to produce wavelengths of different frequencies via frequency-mixing, $\omega_p = \omega_s + \omega_i$, where $\omega_p$ is the pump frequency, $\omega_s$ is the signal frequency, and $\omega_i$ is the idler frequency. This allows us to generate frequencies that are below the pump frequency. By using a combination of mixer crystals just before the OPA output port, the tunable range can be extended up to the
ultraviolet (UV) region (240 nm to 800 nm) by means of second harmonic, second harmonic-second harmonic, and sum/difference frequency generation of the signal and idler beams. The excitation wavelength can be set in the computer software (WinTOPAS 3) controlling the OPAs, and depending on the input wavelength, the software will automatically adjust the optics within the OPA.

Collectively, the pulses, either directly from the Libra or OPerA Solo, will be termed as from the femtosecond laser. In our experiments, we use an excitation wavelength of 600 nm (second-harmonic signal), at varying pump fluences. The term ‘pump fluence’ to describe the pump energy per unit area, described in units of μJ cm$^{-2}$, and is analogous to pump intensity used to describe CW beams. Since the 50 fs laser pulses are strongly affected by air currents, the Libra, OPAs and majority of the beamlines are enclosed by a plastic enclosure. This helps to keep the average pump power stable over a longer period of time.

### 3.3 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy, one of the most straightforward optical spectroscopic technique, involves the direct detection of emitted light following photoexcitation of the semiconductor sample. Important information about the excited states and their recombination behaviour can be extracted by spectrally and/or temporally resolving the decay of the excited states. In the simplest case of a two-level system, a photoexcitation event is an optically allowed transition from the ground state to the excited state. Subsequently, the excited carrier will, after some time as described by the Einstein A coefficient, $\tau_2 = \frac{1}{A_{21}}$, eventually relax back to the ground state by emitting a photon of a certain energy.

If we consider an ensemble of such excited systems in a semiconductor, the probabilistic relaxation of the excited population results in a time distribution of the PL. In real semiconductors where it is much more complex, multiple relaxation channels from the initial excited state to the ground state can exist. In addition, there can also be intermediate levels where the carriers can relax to, or get trapped before relaxing back to the ground state. The transitions to and from these levels may not be radiative, resulting in
weakly emitting samples.

In this thesis, we use two PL setups that can be used with the femtosecond laser; one specifically for steady-state measurements, and the other for time-resolved measurements. Due to space constraints, the setups share a majority of the beam path and the difference lies in the detection equipment. Although the time-resolved section has its own spectrometer to spectrally resolve the kinetics, the steady-state setup offers much greater spectral resolution. Correlating the data from both setups allow us to accurately determine the kinetics of the PL.

Figure 3.4 shows the schematic of the PL setups. Since the setups are fundamentally similar, they share majority of the beam path. The femtosecond laser pulses from the femtosecond laser is incident on the sample chamber in a backscattering geometry after passing through a focussing lens. This minimises the amount of pump scattering, and allows us to place the collection optics nearer to the sample chamber for maximum PL collection efficiency. The collection optics form a collimating lens pair that refocusses the PL into the corresponding detectors for steady-state or time-resolved photoluminescence (TRPL) measurements, detailed below.

For steady-state measurements, a flipper mirror is placed after the collimating lens pair to guide the focussed PL into an UV optical fibre. The fibre is coupled to a Princeton Instruments 2500i spectrometer equipped with an air-cooled PIXIS 400 charge-coupled device (CCD) camera. By using a CCD, we can simultaneously measure the PL intensity across a wavelength range determined by the grating used. A grating with low lines per mm (300 lines/mm) allows measurement over a larger range compared to a grating with higher lines per mm (1200 lines/mm); the former results in rapid acquisition, whereas the latter provides high spectral resolution that is useful for identifying lasing modes and other narrow linewidth features. The configuration of the gratings and CCD acquisition parameters were set in a computer software, WinSpec32. Depending on how intense the PL from the sample was, the capture exposure was adjusted accordingly to prevent the CCD pixels from saturating.

Although the basic spectrometer and CCD setup allows us to measure the full wavelength spectrum of the PL, we are unable to resolved any of that PL in time. As such, we utilise a streak camera to capture the PL
Figure 3.4: Schematic of PL setup. The optical parametric amplifiers (OPAs) offers high degree of tunability for photoexciting the sample. A collimating lens pair then collects the photoluminescence and gets collected by either a fibre coupled to a spectrometer, or a streak camera, for steady-state and TRPL measurements, respectively.
decay as a function of time. Using the fast streak unit, allows us to measure PL lifetimes down to 10 ps, however at the expense of measurement time window. Reducing the time resolution allows us to increase the measurement time window up to seconds.

Figure 3.5 illustrates how a streak camera works in a simplified manner using three PL photons. The collected PL from the sample is first spectrally separated by a spectrometer (Princeton Instruments 2300i) coupled to the streak camera, thereby spreading the PL in space. Since there is no integration of the PL happening within the spectrometer, the output of the spectrometer - i.e., the input to the streak camera - is spread in both space and time. The PL then strikes a photocathode which generates a number of electrons that is proportional to the intensity of incident light at each wavelength and time unit.

While moving through the photocathode, the electrons are accelerated and pass through a pair of sweep electrodes which applies a rapidly time-varying electric field that is synchronised to the femtosecond laser and controlled by the Timing and Delay Controller. The time-varying field causes the electrons, which are temporally separated, to deflect at various angles in the vertical axis depending on the time they pass through the sweep electrode. These electrons then pass through the micro-channel plate where they are multiplied depending on the gain setting and strike against the phosphor screen, converting them back to light and forming a streak image.

The streak image formed on the phosphor screen corresponds to the pulse arriving the earliest is imaged at the top, with subsequent pulses arriving later imaged further down towards the bottom, i.e., the time axis. The spatial location of the pulses is imaged horizontally, giving the wavelength axis. The intensity of the image is proportional to the respective incident pulses. These streak images are captured by a coupled CCD rotated 90°, such that the image displayed on the computer screen corresponds to the time axis along the horizontal axis, and the wavelength axis along the vertical axis.

The acquired raw data from the steady-state and time-resolved data acquisition computers were exported in ASCII for subsequent analysis in OriginLab’s Origin Pro graphing software.
3.4 Transient Absorption Spectroscopy

The main advantage of PL spectroscopy, in providing quick, direct spectroscopic information on the emissive species, can also be its limitation. If the sample is poorly or non-emissive, such as indirect semiconductors, PL spectroscopy will not be useful. In such situations, we use another technique: transient absorption (TA) spectroscopy. Since it is sensitive to non-emissive species, it is far more spectroscopically rich but at the same time more difficult to interpret, as compared to PL measurements. As such, PL and TA measurements serve to complement each other and help spectroscopists gain a better insight in the optical transitions of the sample.

3.4.1 Two-pulse Time-Resolved Pump-Probe Spectroscopy

TA spectroscopy is one type of pump-probe measurement, and as its name suggest, involves at least two laser pulses, a stark contrast from PL which requires only one pulse. In TA spectroscopy, one pulse acts as a pump that will generate photoexcited carriers within the sample. While the other act as a probe that will interrogate the change in sample absorbance (Figure 3.6). The nature of the pump-probe experiment does not call for extremely fast detectors in order to measure femtosecond events because we are not
measuring the whole decay event at once, instead an delay is introduced to
the pump and probe pulses by means of a high-precision motorised linear
delay stage.

The delay stage plays a key role in the technique because the optics on
the stage is positioned in such a way that the probe beam will be reflected
back to its starting plane. In turn, a path difference is introduced between
the pump and probe pulses. Although, in theory either pulses can be passed
through the delay stage, it is more convenient to delay the probe because the
probe alignment is usually fixed; whereas the pump wavelength will change
frequently depending on experimental considerations, and thus affect the
alignment. Another issue that can arise from delaying the pump, especially
if it is poorly collimated, is the change in pump spot size over long delay
times. This has a big impact on the resultant pump fluence which can be
disastrous for data interpretation if left unchecked. Varying the optical path
difference between the two pulses introduces temporal delay between them,
and is calculated by path difference divided by the speed of light. The
pump and probe pulses are then steered by mirrors to overlap spatially on
the sample.

Monitoring the change in sample absorbance (typical absorption exper-
iment) with time (transient), is how the name transient absorption comes
about. The change in sample absorbance (and hence, the change in how
much light is transmitted through the sample), is a nonlinear effect stem-
ming from the $\chi^{(3)}$ nonlinearity, and it arises from the light-matter interaction of the sample with the intense laser pulse. This effect is observed by the probe when the pump perturbs the electronic population sufficiently. This implies that:

1. the pump must be more intense than the probe,
2. the probe must arrive after pump perturbation.

As such, the fluence of the pump pulse is typically 10 times higher than that of the probe. Furthermore, the probe pulse is typically smaller in diameter than the pump pulse to ensure we are probing a homogeneously excited region, and this also helps with improving signal-to-noise ratio (SNR). The pump-probe signal is first observed when the pump and probe pulses overlap; both spatially by using mirrors, and temporally by fine adjustments of the delay stage. The special term for this state is called ‘time zero’, and we will see an obvious increase in the magnitude of the pump-probe signal.

This transient change of the absorbance is made observable by chopping the pump beam with an optical chopper. However, the physical quantity we measure is the probe transmittance by means of a photodetector. Taking the difference with and without pump excitation, yields one form of TA data representation: the so-called differential transmission pump-probe signal, $\Delta T$:

$$\Delta T = T_{\text{pump}} - T_{\text{nopump}},$$

where $T_{\text{pump}}$ is the transmittance of the probe when pump beam is present, and $T_0$ is the transmittance of the probe light when pump beam is absent (i.e., chopped or before time zero). Another form of representation is the change in absorbance, $\Delta A$:

$$\Delta A = -\log\left(\frac{I_{\text{pump}}}{I_{\text{nopump}}}\right),$$

where $I_{\text{pump}}$ is the intensity of the probe when pump beam is present, and $I_0$ is the intensity of the probe light when pump beam is absent (i.e., chopped or before time zero).

In addition, a white-light continuum (WLC) probe can be used to scan across a range of wavelengths. This is particularly useful if the sample has
multiple relaxation The WLC is generated by focussing the probe beam (that has the fundamental wavelength of 800 nm) onto a transparent optical medium, such as sapphire (Al₂O₃). At sufficiently high laser intensities, the nonlinear effects (SPM and self-focussing) converts the fundamental wavelength into a WLC [2], and the pulse energy is distributed across the different wavelength components of the WLC. The resultant TA spectrum generally contains contributions from a few major processes:

1. The first is known as ground state bleaching (GSB). Following initial pump photoexcitation, the non-equilibrium ground state has a smaller population. As a result, the absorption of the probe pulse is reduced in the excited sample as compared to the non-excited one. Consequently, this is revealed as a negative transient absorption signal, or in other words, a positive transient absorption signal in the wavelength region of the ground state absorption.

2. The second is known as stimulated emission of the probe pulse. This arises when the probe spectrum overlaps with the PL spectrum of the material. From the Einstein’s relations, stimulated emission occurs when the probe pulse of similar wavelength passes through the excited sample, inducing the excited carriers to relax at this wavelength assuming it is optically allowed. The photons from the stimulated emission and the probe are collinear, which results in them being detected. Consequently, an increase in light intensity brings about an associated increase in transmission, hence a positive differential transmission signal, or a negative differential absorption signal.

3. The third is known as photoinduced absorption (PIA). Apart from downward transitions, excited states in the material can have optically-allowed upward transitions to higher excited states as well. As these wavelengths, absorption of the probe pulse can occur, leading to a positive differential absorption signal, or negative differential transmission signal.

After the TA data is collected at one time delay, the computer instructs the delay stage to move to the next position to acquire the TA following data point, and so on. Since ultrafast processes can complete within a couple of
picoseconds, a large number of the data points collected are around time zero to allow accurate measurement of any fast early time processes.

The transmitted probe pulse in TA experiments can be detected by either CCD or a photomultiplier tube (PMT). As mentioned in Section 3.3, a CCD allows us to collect data across a wide wavelength range rapidly. But using a point detector, such as a PMT, allows the experimenter to utilise lock-in detection to further improve SNR. Lock-in detection requires modulation of the excitation beam at a chosen frequency, and through the lock-in amplifier’s internal phase-sensitive detection circuits, allows extraction of the signal of interest and rejecting the noise.

3.4.2 Three-pulse Time-Resolved Pump-Push-Probe Spectroscopy

In typical pump-probe spectroscopy, the excited state can be sufficiently measured using two pulses. An introduction of a second excitation pulse – which we will call the ‘push’ or ‘dump’ (depending on the wavelength relative to the absorption) – after initial photoexcitation opens the opportunity to further manipulate and probe that excited state. By controlling the length of time the push or dump arrives after the pump, we are able to further excite or deplete the excited state carrier population. Further details on the design considerations and concepts will be discussed in Section 6.2.2.

3.4.3 Optical Setup: Pump(-Push)-Probe Transient Absorption

Figure 3.7 shows our home-built TA experimental set up. The fundamental output from the Libra is split into three beams: two beams goes into one OPA each for wavelength mixing, and will be the pump and push beams; the last is being used as the probe, and directed to the motorised delay stage (miCos LS-180). The pump passes through an optical chopper to be modulated for lock-in detection before hitting the sample.

The probe beam is focussed onto a 2 mm thick sapphire crystal for WLC generation, spanning from 450 nm to 850 nm. Since WLC generation is not an efficient process, there is a large fraction of a residual beam having the fundamental wavelength that is collinear with the WLC. We have shown that this residual is strong enough to cause artefacts in TA measurements and misinterpretation of results [3]. In order to minimise this issue, we placed a
Figure 3.7: Schematic of a simplified TA setup. The beam from the Libra is split three ways, to obtain the pump (orange), probe (red) and push beams (green). In typical two-pulse TA measurements, only the pump and probe beams are used. The push beam is useful for interrogating higher excited states after initial photoexcitation.
750 nm short pass filter after the sapphire crystal to attenuate the residual fundamental beam. When the push beam is used for pump-push-probe experiments, the other OPA is used to generate the required wavelength depending on the energy required for the higher excited state transition.

The WLC probe is then collimated and focused onto the sample using a pair of Al parabolic mirrors. Parabolic mirrors are used in place of lenses because they do not introduce dispersion into the incident beam which causes additional chirp. After passing through the sample, the probe is then focused by a lens into a spectrometer, where the wavelength of interest is resolved, and collected by a PMT. The output of the PMT is first amplified by a pre-amplifier and sent to the lock-in amplifier. A data acquisition computer with a home-built LabVIEW virtual instrument (VI), a custom written program, then reads the signals and processes it. This computer is responsible for automation of the experiment – from accepting user inputs for the pump-probe time delays, moving the motorised delay stage appropriately, and subsequent data collection.

3.5 Miscellaneous Methods in Laser Spectroscopy

The beams generated by the femtosecond laser (CW laser) can result in very high laser fluences (intensities) when focused on the sample. As such, the laser fluence and intensity must be quantified in order for meaningful discussion and interpretation of the data as a result of intensity-dependent studies.

3.5.1 Spot Size Measurement

The incident laser beams are focussed through a lens, and its spatial intensity, \( I \), with radius from the beam axis, \( r \), can be well-approximated to a Gaussian profile,

\[
I(r) = I_0 \exp\left(-\frac{2r^2}{w^2}\right), \tag{3.4}
\]

where \( w \) is the spot size, defined to be the radius at which the intensity is reduced to \( \frac{1}{\exp(2)} \) of its maximum value.

One method to determine the spot size of the beam is to measuring the power as a function of \( r \), and the total power of the beam, and this can be
done by using a pinhole placed in the path of the beam. The power, \( P(r) \), of the beam within an arbitrary radius (e.g. pinhole), \( R \), can be obtained by integrating Equation 3.4 from 0 to \( R \),

\[
P(r) = \int_0^R \int_0^{2\pi} I_0 \exp \left( -\frac{2r^2}{w^2} \right) d\theta \, dr
\]

\[
= \frac{I_0\pi w^2}{2} \left[ 1 - \exp \left( -\frac{2r^2}{w^2} \right) \right],
\]

where \( da = d\theta \, dr \) is the infinitesimal area element.

Recalling that the Gaussian beam extends to infinity, in the limit as \( r \to \infty \), the exponential term reduces to zero, and Equation 3.6 gives us the total power of the beam, \( P(\infty) \),

\[
P(\infty) = \frac{I_0\pi w^2}{2}
\]

The beam diameter, \( 2w \), can then be expressed as,

\[
d = 2r = 2R \sqrt{-\frac{2}{\ln \left( 1 - \frac{P(r)}{P(\infty)} \right)}}
\]

In our experiments, we use a 50 \( \mu \)m pinhole, and we generally use a spot size of about 400 \( \mu \)m for TA measurements, and about 800 \( \mu \)m for PL measurements.

### 3.5.2 Pump Fluence Measurement

The pump fluence, a pulsed laser analogue of the intensity used to describe CW beams, is measured in a similar way, with an additional factor for the repetition rate of the pulsed laser,

\[
\text{pump fluence} = \frac{P}{f \pi r^2},
\]

where \( P \) is the average power of the laser measured by a Coherent power meter, \( f \) is the repetition rate of the laser, and \( r \) is the beam radius as measured by the pinhole method (Section 3.5.1).
3.6 Basic Characterisation

In this section, other complementary characterisation techniques used in this work are described here. They are often used to screen good samples from the bad ones, and can be used to explain certain recombination phenomena, especially when sample morphology is involved.

3.6.1 UV/vis Linear Absorption Spectroscopy

UV/vis absorption spectroscopy is one of the most, if not the most, basic optical technique available to researchers and it offers very important information about the electronic band gap and presence of any other optically allowed states. Being aware of the carrier population’s nature opens up opportunities to study said properties with the abovementioned optical techniques described in the previous sections.

In modern laboratories, measuring the absorption spectrum has become very much simplified with commercial systems such as the Shimadzu UV-3600-UV-vis-NIR (240 nm to 2.6 µm), the light from a broadband source (D2 for UV regime, and tungsten for the visible and IR) is split into two beams, one for the sample, and the other for the reference. The sample under test would be placed in the sample beam, and a blank substrate (e.g. quartz, glass etc.). The beams are then incident on 2 set of detectors, one for the sample, one for the reference: PMT for the UV and visible regime, InGaS for the near-IR, and PbS for the mid-IR. In the event where the films are rough and highly scattering or reflecting, an integrating sphere attachment should be used to ensure as much of these scattered light is captured by the detectors. Failing to do so might otherwise result in artefacts in the absorption spectra, such as spurious absorption peaks or bands.

By using two set of detectors and a single light source, the sample beam can be normalised with respect to the reference, allowing for accurate and stable measurement of the absorption (or reflection, and transmission) spectrum.

3.6.2 Scanning Electron Microscopy

In material characterisation, using a scanning electron microscope (SEM) is arguably the most ubiquitous technique for imaging nanoscale devices. This
technique offers a resolution that surpasses optical microscopy since the ability to image an object is directly related to the wavelength, or energy, of the incident beam. As its name suggest, it uses electrons instead of electromagnetic radiation, raster-scanned across an area to image microscopic down to nanoscale objects.

The JEOL JSM6700F field emission scanning electron microscope is used in this work. The electrons are emitted from a field-emission gun when a strong potential is applied between the extraction electrode and cathode. These electrons incident on the sample illuminates it and causes secondary electrons, backscattered electrons, transmitted electrons, and characteristic x-rays to be emitted. However, detection of only the secondary electrons is sufficient for imaging the sample morphology.

Prior to placing the sample in the SEM chamber, a thin layer of gold is sputtered using a JFC-1600 Auto Fine Coater onto the perovskite thin film to improve surface electrical conductivity. A narrow continuous strip of carbon tape is then placed on the sample to electrically ground the sample surface to the sample holder. This is crucial for our samples, as they have low electrical conductivity and is susceptible to charging artefacts.

### 3.6.3 Atomic Force Microscopy

Another technique to investigate sample morphology and topology is with the help of a atomic force microscope (AFM). The technique uses a cantilever with a very sharp tip, also called a probe, to scan the sample surface and provides information on the surface roughness, distribution and homogeneity. When the tip is in close proximity with the sample, forces between the tip and sample causes the cantilever to deflect. A laser beam reflecting off the cantilever into a photodiode then measures the intensity of the reflected beam. The modulations in the reflected laser intensity is converted into an electrical signal that is proportional to the displacement of the cantilever.

Although there are a number of different scanning modes, i.e. contact, non-contact, and tapping mode, contact mode involves the fragile AFM tip dragging across the sample, while it is acceptable for atomically smooth and clean surfaces, it is undesirable for atomically rough samples which can cause the tip to crash and cause damage to both the tip and sample. In non-contact mode, the tip oscillates at its resonance frequency without touching
the sample at all, but can be heavily influenced by surface contaminants, such as water. As such, tapping mode, which is a hybrid of contact and non-contact mode, where the resonantly oscillating tip comes into contact very briefly with the sample. This minimises sample damage while avoiding any influences from liquid contaminants on the sample surface.

In this work we use an Asylum Research MFP-3D Classic AFM to image our MAPI samples. Prior to characterisation, the samples are briefly cleaned with a burst of clean and dry $N_2$ to remove as much dust and contaminants as possible. The images are then taken in tapping mode to minimise tip and sample damage.

### 3.6.4 X-ray Diffraction

X-ray diffraction (XRD) is another commonly used analytical technique in material characterisation. It is used for unit cell dimension and phase identification in crystalline solids, such as thin films, powders, and single crystals. The crystal structure causes the incident collimated x-ray beam to diffract at specific directions. A detector scans a range of angles and measure the intensities of these diffracted beams, yielding an x-ray diffractogram. The diffractogram is compared against a database of known materials or literature to determine the phases present in the material. However, in order to obtain a good diffractogram, care must be taken to ensure that the sample is placed flatly on the goniometer stage.

The working principle of XRD is based on Bragg’s model of diffraction. In this model, collimated X-rays incident on crystalline sample constructively interferes with the lattice planes which as a spacing $d$. The x-rays are diffracted in accordance to Bragg’s Law, $n\lambda = 2d\sin \theta$, where $n$ is an integer, $\lambda$ is the wavelength of the x-ray, and $\theta$ is the angle between the x-ray and the lattice plane. Traditional methods of XRD measurements using a high $\theta$ angle results in a weak thin film signal, with a strong substrate signal. As such, for our thin film samples, we utilise the grazing incidence XRD method, with the incident beam $\theta \approx 2^\circ$, and the detector scans across an angle $2\theta$ from $10^\circ$ to $60^\circ$. The x-ray diffractometer used in this work is a $D8$ Bruker Advance with a CuK$\alpha$ source ($\lambda = 1.54180$ Å).
3.7 Overview of Methodologies

In this chapter, the experimental methodologies used in this work is presented. The freshly prepared samples using the procedures in Section 3.1 are first examined using the basic characterisation techniques described in Section 3.6. After they were deemed to be of sufficient quality, they were then further investigated for their charge dynamics and behaviour following femtosecond laser excitation, as described in Section 3.3 and 3.4.

References


Chapter 4

Modulating Carrier Dynamics Through Perovskite Film Engineering

Morphological control has always been an important part of perovskite research, and there are many ways to modify the morphology of perovskite thin films. This chapter presents the results of our work on treating the substrate and film. The effects and implications of such treatments will be presented and discussed.

The material in this chapter is adapted from Ref. [1] with permission from the PCCP Owner Societies.

4.1 Introduction

The versatility of OIHPs spurred development in optoelectronic applications such as light harvesting and emission. In both cases, photovoltaic and LED applications require dense, uniform films [2], but they also have contrasting morphological criteria (i.e., large crystals in the former but small nanograins in the latter) [3]. Detailed insights into the intricate relationship between substrate and film treatments on morphology and the ensuing charge kinetics are still severely lacking.

Careful morphological control needed to form dense, uniform films essential for high performance photovoltaics and LEDs. Poor film coverage would result in decreased light absorption and increased shunting pathways in photovoltaics [4]; while resulting in current leakage and poor exciton confinement in LEDs [3] that leads to adverse device performance. A myriad of factors can affect perovskite film morphology ranging from: the deposition method (single [5, 6] vs. two-step [7] deposition), substrate wettability, and subsequent film modifications. Substrate treatment is necessary since the perovskite solution does not readily wet the substrate’s surface. Typical semiconductor processing approaches to improve surface hydrophilicity include plasma-cleaning and piranha-etching of substrates; where the former is commonly used in perovskite devices, and the latter in the silicon industry. Researchers employ these different process controls including
humidity control and additives, e.g. H$_2$O (presented in Chapter 5), with the ultimate goal of improving sample morphology for higher device performance.

This chapter will present my work on a comprehensive ultrafast optical spectroscopy study of various substrate/film-treated perovskite thin films (i.e., plasma-cleaned vs piranha-etched quartz substrates and with toluene drip) in a bid to investigate the structure-functional relationship by correlating the effects of morphology with the carrier dynamics. Insulating quartz substrates were used in this study for a non-injecting interface to avoid influence on the charge kinetics. Surprisingly, our findings reveal that film treatments, i.e. dripping of toluene during spincoating, of perovskites which is key to improving film morphologies and subsequent solar cell efficiencies, had resulted in increased trap densities. We attribute this anomalous behaviour to an interplay of factors where the improved film morphology (after film treatment of the perovskites on the plasma-cleaned substrates) had also resulted in the lengthening of the carrier recombination lifetimes.

4.2 Experimental Details

4.2.1 Samples

In this chapter, stoichiometric 10 wt% MAPI perovskite films were used and synthesised according to the procedures detailed in Section 3.1. As illustrated in Figure 4.1, the samples were spincoated either with or without toluene drip (film treatments; suffix T and S, respectively), and on either plasma-cleaned or piranha-etched (substrate treatments; prefix Plas and Pir, respectively) quartz substrates.

The fabricated samples are summarised below,

1. MAPI on plasma-cleaned quartz (Plas-S)
2. MAPI on piranha-etched quartz (Pir-S)
3. MAPI on plasma-cleaned quartz with toluene drip (Plas-T)
4. MAPI on piranha-etched quartz with toluene drip (Pir-T)
5. samples 1 to 4 with PC$_{61}$BM
6. samples 1 to 4 with spiro-OMeTAD

4.2.2 X-ray Diffraction

Grazing-incidence XRD spectra of the samples were measured using a D8 Bruker Advance with a CuK$\alpha$ source (\(\lambda = 1.54180 \text{Å}\)) in ambient conditions, with an
Cleaned quartz substrates are first treated, and subsequently spincoated with the perovskite solution and annealed. Incident angle of $\theta \approx 2^\circ$ to minimise signals reflected from the underlying quartz substrate.

**4.2.3 Scanning Electron Microscopy**

Top-view SEM images of the samples were taken after completing the spectroscopic studies. A JEOL JSM6700F field emission scanning electron microscope was used at an accelerating voltage of 10.0 kV, emission current of 10 µA, and working distance of 6.0 mm.

**4.2.4 Atomic Force Microscopy**

Sample topology of the samples were taken with an Asylum Research MFP-3D Classic AFM with a raster scan size of 20.0 µm by 20.0 µm, with 250 scan lines.

**4.2.5 Optical Spectroscopy**

For PL and TA spectroscopy, a Ti:Sapphire femtosecond regenerative amplifier based setup is described in Section 3.3 and 3.4, respectively. The perovskite samples were excited with 600 nm pulses generated by an OPA that is well above
its bandgap. Concurrently, the absorption coefficient at this wavelength is sufficiently low ($\approx 0.2\ OD$) to cause reabsorption of the probe pulse. All optical measurements are done with the samples in a sample holder sealed in a $N_2$ gas glovebox.

### 4.3 Sample Characterisation

#### 4.3.1 Sample Morphology

Figure 4.2 shows the SEM and AFM images of the MAPI films with various film and substrate treatments, collectively referred to as film engineering. Substrate treatment describes the methods used for preparing the substrate for spincoating. Film treatment, also known as solvent engineering, involves the dripping of toluene at a specific time into spincoating and was previously shown to markedly improve film morphology [8, 9]. To directly investigate the smoothness of the resultant films, the AFM images were processed and analysed using the WSxM software [10] to estimate Root-Mean-Squared roughness, $R_q$. The perovskite spincoated on plasma-cleaned quartz (Plas-S, Figure 4.2a, e, $R_q = 19.5\ nm$) will be used as the reference for comparison. The addition of toluene during the spincoating evidently decreases surface roughness (Plas-T, Figure 4.2b, f, $R_q = 10.3\ nm$) of the perovskite film. As expected, the perovskite film covers the surface of the substrate very well, as observed from the SEM image in Figure 4.2b.

The perovskite spincoated on piranha-etched quartz (Pir-S, Figure 4.2c, g, $R_q = 16.0\ nm$) reduced surface roughness slightly, with no obvious improvement in coverage as compared to Plas-S. Even the addition of toluene drip (Pir-T, Figure 4.2d, h, $R_q = 16.0\ nm$) did not seem to reduce surface roughness (under similar experimental conditions) and had no observable improvements to the surface morphology, as observed in Figure 4.2d. This is in stark contrast to the perovskite film morphology grown on plasma-cleaned sample (top row of Figure 4.2). This indicates that piranha-etching of the substrates affected the film formation, and prevented the perovskite crystals from forming a continuous film during spincoating.

#### 4.3.2 Sample Crystallinity

Figure 4.3 shows the XRD spectra of engineered MAPI samples. The main MAPI peaks (labelled in Figure 4.3a) are largely invariant across all samples, regardless of the type of modulation used. This strongly suggests that the film quality
and crystallinity of the samples are not severely degraded as a result of film or substrate engineering.

4.3.3 Optical Properties

The absorption spectra of the various MAPI films are shown in Figure 4.4a. The absorption onset of the films are very similar, around 790 nm. To better estimate the band gap of our representative perovskite, Plas-S, the Tauc plot is calculated from the absorption spectra, with the following relation $(h\nu)^2 \propto (E_g - h\nu)$. The Tauc plot, as shown in Figure 4.4b, shows that our films have a band gap of about 1.6 eV ($\approx 775$ nm), which is consistent with values reported in literature. With a band gap that is close to that of the current commercial silicon solar cells, this is one major reason why the MAPI perovskite has attracted much interest. Various studies, ranging from temperature-dependent PL to measurements using high magnetic fields, it was found that the exciton binding energy of MAPI is about a few meV. A binding energy of such a small value implies that at room temperature, a large population of the photoexcited species are statistically free carriers.
Figure 4.3: XRD spectra of the engineered perovskite samples with different treatments Plas-S (black), Plas-T (red), Pir-S (green), Pir-T (blue), and quartz (cyan).

Figure 4.4: (a) Linear absorption spectra of the engineered perovskite samples with different treatments Plas-S (black), Plas-T (red), Pir-S (green), and Pir-T (blue). (b) Tauc plot of the representative Plas-S MAPI film, estimated to have a band gap of 1.598 eV.
4.4 Carrier Dynamics in Engineered Perovskite Films

4.4.1 Spectral Features

Investigating the carrier dynamics are crucial for understanding the electronic and charge transport properties in semiconductor systems such as MAPI perovskite films. Seminal spectroscopic papers have suggested interesting electronic band structure and also how morphology plays a role in influencing the carrier lifetimes within the perovskite. Here, we use a combination of TA and PL spectroscopy as our primary techniques.

As mentioned in Section 3.4, in pump-probe TA spectroscopy, the pump pulse incident on the sample photogenerates a population of carriers in an excited state. This results in a smaller population in the ground state, which can be termed as ‘non-equilibrium ground state’. A weaker probe pulse passing through the sample has its intensity modulated as a result of the transient photoexcited population, which gives rise to a differential transmission (or absorption) signal. If interrogated with a WLC probe pulse, we get a differential transmission (or absorption) spectrum.

Using Plas-S in Figure 4.5a as the representative sample for the engineered samples, three distinct spectral features typical of photoexcited MAPI perovskite films are observed, (i) the strong photobleaching band around 770 nm (PB2), (ii) the broad PIA band spanning the majority of the visible regime, (iii) a weak photobleaching band around 480 nm (PB1). By convention, a positive differential transmission denotes photobleaching, whereas a negative differential transmission denotes PIA.

Since PB2 coincides very well with the absorption onset, this lead to the consensus that PB2 is related to the GSB, and stimulated emission. Both of these processes give rise to the phenomenon where there is an increase in probe transmittance; bleach, the former process, is a result of reduced absorption of the probe beam due to state filling of the band edge states, and the latter is the probe beam stimulating emission of more photons that corresponds to that optical transition. Unfortunately in most instances, it is difficult to accurately distinguish the contributions of either processes at the GSB band.

While PB2 was straightforward to assign, on the contrary, the origins of PB1 is still an open debate, with interpretations of the origins from the dual valence band/dual conduction bands [11, 12], overlapping contributions from PbI$_2$ [13], and charge transfer states to iodo-plumbate complexes [14]. Furthermore, the broad PIA band, which can be generically assigned to excited state absorption
(ESA) of photoexcited carriers, was largely ignored in earlier photophysical studies. A recent work by Price et al. attributed it to originate from a photoinduced change in the refractive index [15]. We discuss this in detail in Chapter 6, and present unambiguously that ESA is the major contributor to the PIA band.

The TA spectra at different time delays for the various engineered samples are shown in Figure 4.5. While some of the spectra have poorer signal-to-noise than the others due to differences in collection efficiency, the similarities in the TA spectra highlights further corroborates that the MAPI film still forms unhindered regardless of the differences in fabrication methods.

4.4.2 Recombination Kinetics

MAPI was reported to have observable cooling of hot carriers, first looking at how the TA signals decay in the early time regime (< 2 ps) can help us understand if any of the treatments affect the fundamental photophysical charge relaxation properties. Figure 4.6 shows the early time evolution of the decay, where probing at 480 nm revealed an ultrafast relaxation, and a slow simultaneous rise of the signal was observed when probing at 770 nm for all samples. This concomitant rise and and decay of the TA signal was attributed to hot carrier cooling [11],
and further studies showed that a hot phonon bottleneck might be responsible for such phenomena in MAPI [15, 16, 17, 18] (Section 2.3.2). The slow cooling of hot carriers can possibly aid in hot carrier extraction, but a deeper understanding of these excited states are crucial for designing and engineering appropriate quenchers. We explore the rich photophysics of higher excited states in MAPI and demonstrate evidential hot carrier extraction later in Chapter 6.

![Figure 4.6: Early time TA kinetics (−1 ps to 4 ps) of engineered perovskite samples with different treatments, the samples are pumped at 600 nm, and probed at 480 nm (PB1) denoted by blue squares, and at 770 nm (PB2) denoted by red triangles.](image)

To assess the carrier recombination as a result of substrate/film modification, bandedge (PB2) TA kinetics of the photoexcited samples as a function of pump and probe delay is extracted and shown in Figure 4.7. A pump wavelength of 600 nm at a relatively low fluence (5 µJ cm⁻²) was used to excite the carriers across the bandgap and avoid multi-particle interactions, while still maintaining good signal-to-noise ratio. The TA signal was fitted with a multi-exponential function (with the system response deconvolved) to account for both the rise, and the mono-exponential decay for the carrier relaxation.

\[
y \propto \sum_i A_i \exp \left[ -\frac{t - t_0}{\tau_i} \right] \left\{ 1 - \text{erf} \left[ -\frac{t - t_0 - s}{a \cdot t_0} \right] \right\}, \tag{4.1}
\]
where $i$ is the number of components chosen to fit the data satisfactorily, $A_i$ is the amplitude of each lifetime component, $\tau_i$, $t$ is the current probe delay, $t_0$ is the time zero, and $s$ is a coefficient related to the instrument response.

Such mono-exponential decay (i.e. $i = 1$) obtained at low pump excitation is typical of a trap-dominated recombination. The rise in the $\Delta T$ signal is attributed to the hot-carrier cooling and state-filling of the bandedge states [12]. A comparison of the TA signals from the four samples would allow us to gain insights into the time evolution of the population of the photoexcited states within the perovskites films that have undergone different film and substrate treatments.

![Figure 4.7: Normalised TA kinetics of engineered perovskite samples with different treatments, Plas-S (black squares), Plas-T (red circle), Pir-S (green triangle), and Pir-T (blue inverted triangle)](image)

The marked improvement of morphology in Plas-T when compared to Plas-S accounts for the lifetime lengthening evident in Figure 4.7, where $\tau\text{Plas-T} = 9.9 \pm 0.2$ ns vs $\tau\text{Plas-S} = 8.6 \pm 0.1$ ns. As the measurement window of our delay stage is limited to about 5 ns, these fitted values should not be taken with absolute certainty. Nonetheless, one can still qualitatively compare the influence of the substrate/film treatments on the trend of the recombination lifetimes. Such lifetime lengthening is in agreement with past reports that films with better morphology exhibits longer lifetimes [19].

Comparatively, the films with piranha-etched substrates yielded a faster recombination over those with plasma treatment. Despite the slight improvement in morphology that Pir-S has over Plas-S, the former’s lifetime is still considerably quenched. Surprisingly, the recombination lifetimes in toluene-washed films on
piranha-etched substrates are severely quenched (Figure 4.7, \(\tau_{\text{Pir-S}} = 7.0 \pm 0.1\) ns as compared to \(\tau_{\text{Pir-T}} = 4.1 \pm 0.1\) ns); in contrast to films on plasma-treated substrates. Given that the piranha-etched samples (i.e. Pir-S and Pir-T) are largely similar in surface morphology, evident from both AFM and SEM images (bottom row of Figure 4.2), we posit that the lifetime quenching is not solely a consequence of the induced morphological changes, but could possibly arise from the introduction of additional non-radiative recombination channels following the addition of toluene during the spin-coating.

### 4.4.3 Inadvertent Introduction of Trap States

To ascertain the cause for the quenching, we performed power dependent steady-state photoluminescence in the low fluence regime (where there is negligible Auger recombination) to estimate the trap densities. The trap densities of the samples are estimated using a rate equation model [20], and the results are summarized in Figure 4.8. In this model, the relation between the photoexcited carrier density and the recombination intensity can be used to determine the trap states density, \(m_i\). The relation is described with the following differential rate equation which governs the photoexcited carrier density and the non-radiative (trapping) and radiative recombination,

\[
\frac{dn(t)}{dt} = -\sum_i a_i m_i(t)n(t) - \frac{n(t)}{\tau_0}, \tag{4.2}
\]

where \(a_i(t)\) is the product of trapping cross-section and carrier velocity, \(i\) is the \(i^{th}\) trapping pathway, and \(\tau_0\) is the radiative recombination lifetime. We assume that the trapping rate and is much larger than the detrapping rate, such that the density of carriers that become trapped remain trapped for a significant length of time. As more carriers get trapped, the rate of change of trap density, first time on the right hand side, decreases proportionally and can be expressed by the expression,
\[
\frac{dm_i(t)}{dt} = -a_i m_i(t) n(t) \quad (4.3)
\]
\[
\int_0^t \frac{dm_i(t)}{dt} = -a_i \int_0^t m_i(t) n(t) dt \quad (4.4)
\]
\[
\ln \left( \frac{m_i(t)}{m_i(0)} \right) = -a_i \int_0^t m_i(t) n(t) dt \quad (4.5)
\]
\[
m_i(t) = m_i(0) \exp \left[ -a_i \int_0^t m_i(t) n(t) dt \right] \quad (4.6)
\]

By integrating the second term, which describes the radiative recombination of carriers, the PL intensity, \( I_{PL} \), can be obtained,

\[
I_{PL} = \frac{E}{\tau_0} \int_0^t n(t) dt, \quad (4.7)
\]

where \( E \) is the detection efficiency arbitrary constant. Substituting Equations 4.6 and 4.7 into 4.2 in the limit where \( t \to \infty \),

\[
\frac{dn(t)}{dt} = \sum_i \frac{dm_i(t)}{dt} = \frac{n(t)}{\tau_0} \quad (4.8)
\]
\[
\int_0^\infty \frac{dn(t)}{dt} dt = \sum_i \int_0^\infty \frac{dm_i(t)}{dt} dt - \int_0^\infty \frac{n(t)}{\tau_0} dt \quad (4.9)
\]
\[
n(\infty) - n(0) = \sum_i (m_i(\infty) - m_i(0)) - \frac{I_{PL}}{E} \quad (4.10)
\]
\[
n(0) = -\sum_i (m_i(\infty) - m_i(0)) + \frac{I_{PL}}{E} \quad (4.11)
\]
\[
= -\sum_i \left[ m_i(0) \exp \left( -a_i \tau_0 \frac{I_{PL}}{E} \right) - m_i(0) \right] + \frac{I_{PL}}{E} \quad (4.12)
\]
\[
n(0) = \frac{I_{PL}}{E} + \sum_i m_i(0) \left[ 1 - \exp \left( -a_i \tau_0 \frac{I_{PL}}{E} \right) \right], \quad (4.13)
\]

where \( n(\infty) = 0 \) and \( m_i(\infty) = m_i(0) \) because the number of excited carriers in the system will all relax, regardless of being them being trapped or not.

By fitting Equation 4.13 on a plot of excited carrier density against PL intensity, the trap densities can be estimated. From Figure 4.8a, we observe the trap densities \( m \): Plas-S has the lowest trap density \( m_{\text{Plas-S}} = 3.3 \pm 0.3 \times 10^{17} \text{ cm}^{-3} \); followed by Pir-S, \( m_{\text{Pir-S}} = 5.6 \pm 0.2 \times 10^{17} \text{ cm}^{-3} \). Interestingly, the film treated samples exhibited higher trap densities, with Plas-T having a trap density of \( m_{\text{Plas-T}} = 4.5 \pm 0.3 \times 10^{17} \text{ cm}^{-3} \) and; Pir-T, \( m_{\text{Pir-T}} = 6.6 \pm 0.2 \times 10^{17} \text{ cm}^{-3} \).
Although our model can discern between bulk and surface traps, the data could be well-fitted by just considering only one type of trap. The traps are primarily surface-related, possibly MA vacancies [21], since the dripping of toluene is expected to have a larger impact on the surface of the perovskite [22] and may preferentially dissolve the more volatile MA cation. This does not imply that bulk traps do not exist, but the density may be much smaller than that of surface traps. Based on the work by Jeon et al. and Xiao et al., it has been generally accepted that solvent engineering (film treatment with toluene drip) results in better film morphology [8, 9]. Surprisingly, our findings reveal that toluene dripping actually increases the trap densities in the perovskite films regardless of substrate treatments which leads to quenching of the carrier lifetimes. Although film morphology is not indicative of sample lifetimes, it certainly plays a key role.

For piranha-etched substrates, although the perovskite film morphology remains unaltered with toluene dripping, the carrier dynamics become significantly quenched. For plasma-cleaned substrates, the perovskite film morphology is significantly improved with toluene dripping and the carrier dynamics were improved in stark contrast to piranha-etched substrates. Although the addition of toluene during the spincoating process introduces traps into the perovskite film, this is counteracted by the large improvement in film morphology. This explains why there is only a small improvement in the carrier lifetime, as the effects of film...
morphology and trap density are competing with each other and the interplay of these two factors heavily influence carrier relaxation mechanisms within films.

Another important parameter for assessing the impact of sample engineering is the diffusion length of charge carriers in the presence of electron and hole quenching layers, PC$_{61}$BM and spiro-OMeTAD respectively. The electron and hole diffusion lengths were estimated by calculating the density and distribution of excited carriers, $n(x, t)$ in the perovskite film using a one-dimension diffusion model,

$$\frac{\partial n(x, t)}{\partial t} = D \frac{\partial^2 n(x, t)}{\partial x^2} - kn(x, t)$$  \hspace{1cm} (4.14)

where $D$ is the diffusion coefficient, and $k$ is the rate of PL decay in the absence of quenchers. The effect of quenching layers is included by assuming all carriers that reach the perovskite-quenching layer interface are quenched completely, $n(x = L, t) = 0$, where $L$ is the thickness of the perovskite active layer. The samples are excited from the substrate side, and the initial distribution of carriers along the thickness is given by, $n(x < L, 0) = n_0 \exp(-\alpha x)$, where $\alpha$ is the absorption coefficient of the sample. By considering a hard wall boundary condition, $\frac{dn}{dx}igg|_{x=0} = 0$, and integrating across the whole active layer, the number of carriers inside perovskite active layer is described by the expression,

$$N(t) = \frac{2n_0 L}{\pi} \exp \left( \frac{t}{\tau_0} \right) \sum_{m=0}^{\infty} \frac{(-1)^m \alpha L + \pi (m + \frac{1}{2}) \exp(-\alpha L)}{\alpha^2 L^2 + \pi^2 (m + \frac{1}{2})^2 (m + \frac{1}{2})} \times \exp \left[ - \left( m + \frac{1}{2} \right)^2 \frac{\pi^2}{L^2} Dt \right] = A \exp \left( - \frac{t}{\tau_D} \right),$$  \hspace{1cm} (4.15)

where $\tau_0$ and $\tau_D$ is the carrier lifetime in the absence and presence of quenchers, respectively. At higher indices of $m$, the coefficient would be small, and exponent would be large, implying a large decay rate. As such, Equation 4.15 can be
approximated to only have the first term,

\[
\exp \left( -\frac{t}{\tau_D} \right) \approx \exp \left\{ -\left[ \frac{1}{\tau_0} + \frac{\pi^2}{4} \left( \frac{L_D^2}{L} \right) \right] t \right\} \tag{4.16}
\]

\[
\frac{t}{\tau_D} = \frac{t}{\tau_0} + \frac{\pi^2}{4} \left( \frac{L_D}{L} \right)^2 \left( \frac{t}{\tau_0} \right) \tag{4.17}
\]

\[
\frac{\tau_0}{\tau_D} = 1 + \frac{\pi^2}{4} \left( \frac{L_D}{L} \right)^2 \tag{4.18}
\]

\[
\frac{L_D}{L} = \frac{2}{\pi} \sqrt{\frac{1}{\tau_D/\tau_0} - 1} \tag{4.19}
\]

Figure 4.9: Normalised TA kinetics of engineered perovskite samples with different treatments, Plas-S (black squares), Plas-T (red circle), Pir-S (green triangle), and Pir-T (blue inverted triangle).

By using the fitted TRPL lifetimes with and without quenchers with Equation 4.19, the diffusion lengths of the electrons and holes in the samples can be obtained and is summarised in Figure 4.9. It is important to note that the estimated diffusion lengths are strongly influenced by the actual thickness of the sample. The estimated diffusion lengths are reasonable since our samples are roughly 50 nm thick. One should not expect micron diffusion lengths like in large mm-sized perovskite single crystals [23, 24] and it would be highly unreliable to extrapolate our results.

Figure 4.9 illustrates the diffusion lengths of the perovskite samples that are normalized to the thickness of the samples for comparison. The dashed line corresponds to Equation 4.19. In the case of Plas-S and Plas-T, the electron and
hole diffusion lengths remain relatively invariant after toluene dripping. Comparing the Plas-S and Pir-S samples, the electron and hole diffusion lengths in the piranha-etched substrates are more balanced. As in the case for Pir-S and Pir-T, the combination of substrate and film treatments strongly influences charge dynamics and the diffusion lengths. The electron diffusion length is considerably shortened by $\frac{1}{3}$ with toluene drip in Pir-T over Pir-S. However, the hole diffusion length cannot be estimated because of the absence of any lifetime quenching from the Pir-T sample. Due to the non-conductive nature of the quartz substrate, we were unable to measure the energy band alignments using x-ray photoelectron spectroscopy. As mentioned earlier, quartz substrates were used here in this study as a non-injecting interface. The piranha-etching, together with toluene-drip may have modified the substrate/film interface and formed an interfacial barrier [25] between the perovskite film and the spiro-OMeTAD hole quencher which prevents extraction of the holes. This is evident when we consider the lengthening of PL lifetime and enhancement of PL in Pir-T spiro-OMeTAD samples.

A recent work by Cohen et al. found that toluene-treated perovskite films were slightly more intrinsic (i.e., more p-type with the Fermi level less negative by 0.1 eV) than non-treated films based on surface photovoltage measurements [21]. The n-type perovskite film allows extraction of holes under normal circumstances, but as piranha-etching and toluene dripping of the films likely induce p-type behavior, the Fermi level is then shifted to be equal or below that of the spiro-OMeTAD, leading to poor/non-injecting scenarios, as illustrated in Figure 4.11. This shift in the Fermi level can be a result of CH$_3$NH$_3^+$ defects (vacancies, interstitials and substitutions) that was previously shown with density functional theory calculations by Yin et al. A lower defect formation energy indicates a higher probability of the defect existing and dripping with toluene increased the density of MA vacancies which are acceptors in nature [26]. These vacancies possibly exist as a result of MA and halide ions forming complexes with toluene [21].

While we are not able to identify the specific type of defects introduced in our samples, the observed increase in trap density in toluene-dipped films and the poor/non-injecting behavior of Pir-T suggests that MA vacancies may be responsible, and agrees well with literature. The non-injecting behavior makes the combination of piranha-etching and toluene dripping unfavorable for both PV and LED applications. On the other hand, the electron and hole diffusion lengths are more balanced on piranha-etched substrates, which is also beneficial in other optoelectronic applications like phototransistors.
Figure 4.10: PL quenching observed in kinetics of engineered perovskite samples with different treatments, (a) Plas-S, (b) Plas-T, (c) Pir-S, and (d) Pir-T without quenchers (black line), with electron quencher PC$_{61}$BM (red line), and hole quencher spiro-OMeTAD (green line). PL enhancement was observed in Pir-T/spiro-OMeTAD.
Carrier Dynamics in Engineered Perovskites

Figure 4.11: Proposed energetic alignment of MAPI perovskite in contact with spiro-OMeTAD hole quencher after different treatments: (a) Plas-S; (b) Pir-S slightly shifts the perovskite towards more p-type behaviour; and (c) Pir-T that makes the perovskite heavily p-type resulting in poor/no injection of holes with different Fermi level positions of the perovskite film. Energetic alignment of MAPI having different Fermi level positions of the perovskite film, (a) heavy n-type, (b) n-type, (c) p-type, in contact with spiro-OMeTAD hole quencher. The different doping behaviour of the perovskite film may be a consequence of substrate/film treatment.
4.4.4 Enhanced Light Emission

As seen in the preceding sections, the influence of sample engineering does in fact play a significant role in characteristics immediately observable, i.e. sample morphology, and those that require spectroscopic interrogation, i.e. carrier lifetimes and trap densities. Apart from these charge transport and trapping properties, light emission properties are also affected by sample engineering.

To characterise the light emission performance of the samples, its PL is collected as a function of excitation fluence, as illustrated in Figure 4.12. Note that this fluence range far exceeds that of the one used in the estimation of trap density. The samples without film treatment do not exhibit any amplified spontaneous emission (ASE) and its PL started to saturate. On the other hand, the film treated samples were observed to have a clear superlinear behaviour at the observed ASE peak position, and ASE thresholds, \( P_{th} \) were obtained by taking the intercept of both linear regimes that were fitted linearly. The ASE thresholds were found to be very similar, with \( P_{th,Plas-T} = 49 \pm 3 \mu \text{J cm}^{-2} \) and \( P_{th,Pir-T} = 44 \pm 3 \mu \text{J cm}^{-2} \).

![Figure 4.12: Light emission properties of engineered samples. (a) Graph of PL intensity against fluence of engineered samples Plas-S (black square), Plas-T (red circle), Pir-S (green triangle), Pir-T (blue inverted triangle) showing the ASE threshold of Plas-T and Pir-T.](image)

It can be straightforward to attribute an improvement in morphology to be
the reason why Plas-T exhibits ASE but not Plas-S, considering both surface roughness and coverage (Figure 4.2). This is known from literature, where morphology strongly influences the ASE threshold [27]. Strangely, both Pir-S and Pir-T have similar surface roughness, $R_q$, but ASE is not observed in Pir-S. In addition, ASE is observed even in film treated samples with increased trap density as compared to non-film treated ones (Figure 4.8), indicating that ASE does not stem from slight modulations in trap densities or morphology. Earlier we noted that the increase in trap density in solvent engineered samples is largely surface related, suggesting that ASE is more affected by bulk traps rather than surface ones. Notably, film treatment would have improved quality of the perovskite grains somewhat such that ASE is observed in engineered films.

4.5 Conclusions

In conclusion, the effects of film and substrate treatments (sample engineering) on MAPI perovskite samples were investigated using photoluminescence and transient absorption optical spectroscopic techniques. Our findings reveal new insights into the convoluted relationship over the substrate and film treatments on the film morphology and the ensuing carrier recombination dynamics, defect densities, carrier diffusion lengths and light emission properties. Carrier lifetimes as long as 9.1 ns and as short as 4.1 ns were recorded on the samples, depending on the combination of treatments. The former sample comprised of film treated perovskite grown on plasma-cleaned quartz, whereas the latter was film treated perovskite grown on piranha-etched quartz.

The differences in lifetimes were explained by comparing the morphological differences and trap densities between the samples. We found that even though perovskite film treatment resulted in superior coverage and lower surface roughness on plasma-cleaned substrates, the same result was not observed in piranha-etched substrates. Also, we clearly demonstrated that not all treatments are suitable: e.g., the surface trap densities in toluene-dripped samples are much higher than standard samples; and for films fabricated on piranha-etched substrates, which leads to poor hole extraction. Across the board, only the toluene film treated samples exhibited ASE, highlighting morphological improvements as a result of film treatments. Nonetheless, piranha-etching of the substrates could possibly offer an approach to improve the balance between the electron and hole diffusion lengths in the perovskite film.

One must therefore exercise prudence in choosing appropriate treatments dur-
ing sample fabrication. Although new insights could be gained by studying the charge dynamics, it is important to note that a device with different charge transporting layers and interfaces are significantly more complex than the bare films studied here. It would be myopic to draw strict conclusions from the findings in thin films and extend them to real devices. We anticipate that with improvements in growth techniques, together with sedulous modulation of the perovskite morphology through a judicious choice in sample engineering is key to the scaling-up of high efficiency perovskite devices.

References


Chapter 5

Reducing Traps in Perovskite Solar Cells: The Role of Water Additives

Perovskite solar cells offer high performance devices at low-cost and ease of fabrication. Consequently, this leads to rapid advancement in fabrication processes and methods to further improve device performance. Specifically, water additives incorporated into the perovskite in small amounts has been shown to enhance light harvesting despite negligible morphological influence. By optimizing the additive concentration, we obtained an efficiency of 12.3% for the champion cell using the inverted architecture.

5.1 Introduction

Even though MAPI cells can achieve respectable efficiencies, its instability presents an obstacle for commercialisation. The biggest setback for MAPI is its inherent vulnerability to air and particularly, moisture, eventually degrading to PbI$_2$ and hydrated compounds and thus destroying the film and device [1, 2, 3]. Interestingly, further studies have also established that trace amounts of water in the perovskite solution can be beneficial for device performance. It has been shown that moisture induces grain boundary creep and recrystallisation to merge adjacent grains together and form high quality films [4, 5]. The grain healing properties could be exploited to alleviate the adverse increase of trap densities in MAPI films, presented in Chapter 4. In this chapter, we look at how adding H$_2$O additives into the perovskite solution prior to spincoating affects carrier recombination and device performance in perovskites.

Devices produced at ambient conditions under controlled humidity (up to 50%) were able to achieve high efficiencies [6, 7, 8]. However, when the humidity exceeds 50%, the cells began to show significant decomposition [9].
It has also been reported that water additives do not significantly impact film formation and device performance [10]. Eperon et al. postulated that moisture treatment of the perovskites in higher relative humidity reduction in trap density plays the role in improving photoluminescence properties [11]. An increase in efficiency is highly correlated to morphology. Wu et al. explained that, for their two-step deposition films, an optimal amount of water additive (2 vol% H$_2$O in their study) forms large grains with very dense films, concluding that morphology is key to photovoltaic performance [5]. This observation was also reported by Gong et al. where adding a small amount of water to one-step solution improved their film morphology and increased the carrier lifetime [12]. Further increase of the additive concentration causes the efficiencies to plummet, but the cause for this phenomenon has not been fully addressed. It is noteworthy to mention that in these reports, the solvent engineering technique was not applied. These reports highlight the importance of studying the effects of water on the carrier dynamics and transport in perovskites. Ultimately, apart from attributing the improvements to morphological improvements, there is no clear conclusion on what H$_2$O does in the perovskite films and how exactly it affects device performance.

We hypothesise that in the samples with small amounts of water additive would yield superior photophysical properties, which would it is beneficial and result in efficient devices. To test our hypothesis, the photophysical and recombination aspects in the perovskites with varying concentrations of water additive are considered. In order to distinguish the effects H$_2$O has on the morphology and the carrier dynamics, we subject all samples to solvent engineering to obtain uniform films for all samples.

5.2 Experimental Details

5.2.1 Samples

In this chapter, stoichiometric 40 wt% MAPI perovskite films were used and synthesised with minor modifications to the procedures detailed in Section 3.1. We used the well-established one-step method to fabricate the perovskite devices and films as previously reported [13, 14, 15]. This is crucial to avoid any possible interaction of the water additive with other solvents.
which may result drastically change the additive concentration. The stock perovskite solution was equally divided into four separate bottles for different additive concentration. To achieve the desired additive concentration (0, 1, 2 and 5 vol% $\text{H}_2\text{O}$) in the perovskite solutions, different volume ratios of de-ionized water were then added in the corresponding bottles. The final solutions were filtered again prior to spincoating.

For characterisation and optical spectroscopy, we used thin film samples that were prepared by spincoating perovskite solutions for each additive concentration on plasma-cleaned glass substrates. The perovskite films were individually prepared by spincoating the corresponding perovskite solutions (with and without $\text{H}_2\text{O}$ additive) on the substrates at a speed of 5000 RPM for 12 sec. Solvent engineering of the perovskite active layer was performed using 100 $\mu\text{l}$ toluene, dripped 3 sec into the start of the spin-coating and the samples were subsequently annealed at 100°C for 30 min. Samples used for diffusion length measurements are prepared in a bilayer architecture, with either PC$_{61}\text{BM}$ or poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) used as the electron and hole quencher, respectively.

The fabricated samples on plasma-cleaned glass are summarised below,

1. MAPI with 0 vol% $\text{H}_2\text{O}$ (control)
2. MAPI with 1 vol% $\text{H}_2\text{O}$
3. MAPI with 2 vol% $\text{H}_2\text{O}$
4. MAPI with 5 vol% $\text{H}_2\text{O}$
5. samples 1 to 4 with PC$_{61}\text{BM}$
6. samples 1 to 4 with PEDOT:PSS

### 5.2.2 Device Fabrication

To fabricate the inverted architecture perovskite solar cell devices, indium tin oxide (ITO)-coated glass substrates (Xin Yan Technology Company, 15 Ω/square) were first ultrasonicated with deionized water, then followed by equal parts of acetone, ethanol and isopropyl alcohol. A 30 ± 5 nm thick hole transporting layer of PEDOT:PSS (Clevios HTL Solar SCA388P VP Al 4083) was spin-coated onto the plasma-treated substrates.
PEDOT:PSS-coated substrates were then heated on a hotplate at 130 °C for 15 min and transferred into a N₂ glove box. The perovskite active layers were individually prepared by spincoating the corresponding perovskite solutions (with and without H₂O additive) on the PEDOT:PSS-coated substrates using the abovementioned procedure. Afterwards, PC₆₁BM (Sigma Aldrich), dissolved in chlorobenzene with a concentration of 20 µg ml⁻¹, was spin-coated at 1200 RPM for 45 sec. Finally, a 100 nm thick silver cathode was deposited on the active layers by thermal evaporation through a shadow mask. This produces a multi-device substrate with 10 small devices each with an active area of 0.07 cm².

5.2.3 Sample and Device Characterisation

XRD, SEM and other optical spectroscopic techniques are as described in Section 4.2.

The current density-voltage (J-V) characteristics of the perovskite devices were measured using a Keithley SMU 2400 under simulated AM 1.5G sunlight at 100 mW cm⁻² irradiance.

5.3 Sample Characterisation

5.3.1 Sample Morphology

Since H₂O is known to cause moisture-induced degradation of MAPI, it is helpful to determine if adding H₂O additives into the perovskite solution influences or impedes crystal formation, or in the worst case, causes degradation of the film during characterisation. The first step would be to image sample uniformity. Figure 5.1 shows the SEM images of the MAPI perovskite films prepared using solutions with 0 to 5 vol% H₂O. The films were observed to be highly uniform with no visible pinholes, a characteristic signature of solvent-engineered films grown on plasma-cleaned substrates (as demonstrated in Chapter 4).

The crystal grain sizes across the different samples appear to vary according to how much H₂O additive is present within the films. Upon inspecting both 0 vol% and 5 vol% H₂O films, there is a substantial number of grains that are about 300 nm, and a number of smaller grains about 100 nm. This
is in contrast to 1 vol% and 2 vol% H₂O films, where the former has crystal grains of roughly the same size, but the latter still has some large grains. This phenomenon seems to be strongly influenced by the amount of H₂O additive present in the films, and affects carrier recombination and transport properties. Nonetheless, there is no significant differences between the samples’ morphology and coverage, as expected when film treatment using toluene drip was applied.

![SEM images of neat MAPI perovskite films on glass with varying H₂O additive concentration](image)

**Figure 5.1:** SEM images of neat MAPI perovskite films on glass with (a) 0 vol% (control), (b) 1 vol%, (c) 2 vol% and (d) 5 vol% H₂O additives.

### 5.3.2 Sample Crystallinity

XRD spectra of the perovskite films on glass with varying H₂O additive concentration in Figure 5.2 shows the characteristic peaks of tetragonal MAPI. The spectra are in good agreement with Figure 5.2, with the main perovskite peaks resolved and having a strong intensity. Although H₂O is one of the major degradation agents of organic-inorganic halide perovskites, the XRD results indicate that the perovskite films in our study still crystallises well and form continuous films even up to 5 vol% H₂O additives. Although there
are residual PbI$_2$, as seen from the small peaks at about 12.5°, the contributions from any residual PbI$_2$ on the recombination kinetics and device performance are negligible compared to that of the H$_2$O additives (see later sections).

![XRD spectra of neat MAPI perovskite films on glass with 0 vol% H$_2$O control film (black), 1 vol% (red), 2 vol% (green) and, 5 vol% (blue) H$_2$O additives.](image)

**Figure 5.2:** XRD spectra of neat MAPI perovskite films on glass with 0 vol% H$_2$O control film (black), 1 vol% (red), 2 vol% (green) and, 5 vol% (blue) H$_2$O additives.

### 5.3.3 Optical Properties

The absorption spectra of the various MAPI films are shown in Figure 5.3. The absorption onset of the films are similar to Figure 4.4, around 790 nm for all samples, suggesting that modulating the additive concentration does not influence its optical bandgap.
5.4 Carrier Dynamics and Transport in Perovskite Samples with H$_2$O Additives

5.4.1 The Efficacy of H$_2$O Additives on Trap Density and Carrier Recombination

Although MAPI has been reported to possess an unusually high tolerance to defects, they are still undesirable in photovoltaic devices. We employ ultrafast optical spectroscopy to investigate the mechanisms that occur in the perovskite films with varying water additive concentration. In these experiments, the samples are excited by an optical pulse train with a wavelength of 600 nm and we directly measure the PL response as a function of wavelength and time.

We estimate the trap density of the samples, shown in Figure 5.4a, by measuring the power-dependent PL in the low-fluence regime. The excited carrier density is plotted against the integrated PL spectra of each sample, and fitted with the theoretical model described in Section 4.4.3. We note that the trap density value of the control sample (0 vol% H$_2$O) differs slightly from the control sample (Plas-S) in Chapter 4 even though they are both on plasma-cleaned substrates. However, it is important to consider...
that environmental and glovebox conditions can influence perovskite sample fabrication somewhat, and the discrepancy between the two control samples is small and still within the same order. This underscores the importance of preparing samples at one go in order to minimise variations of the ambient conditions. From the figure, there are striking differences between the various samples due to the differing additive concentration. As the concentration of water additive is increased from 0 vol% to 1 vol%, the estimated trap density decreases from \( n_0 \% \text{H}_2\text{O} = 4.8 \pm 0.3 \times 10^{17} \text{cm}^{-3} \) to \( n_{1\%} \text{H}_2\text{O} = 3.2 \pm 0.2 \times 10^{17} \text{cm}^{-3} \), suggesting that small amounts of H\(_2\)O acts as a passivating agent, and also induce recrystallization of the grain boundaries to repair defects [4, 5]. Furthermore, any excess CH\(_3\)NH\(_3\)I can be aided by the trace H\(_2\)O to react with remnant PbI\(_2\) to form MAPI grains that may further serve to passivate the grain boundaries [16]. However, increasing the water concentration to 5 vol% H\(_2\)O counteracted the beneficial properties of the additives, resulting in the trap densities gradually increasing and returning to the trap density values without additives.

As shown in Figure 5.4b, the differences in trap density has a pronounced impact on the carrier lifetime of the samples, revealed from low-fluence (0.5 \( \mu \)J cm\(^{-2} \)) TRPL kinetics traces. We observe that the kinetics of each sample is consistent with the trap density estimation, with the 0 vol% H\(_2\)O sample with the highest trap density and shortest TRPL lifetime, and the 1 vol% H\(_2\)O sample with the lowest trap density and consequently longest TRPL lifetime. Similarly, the TRPL lifetime of the 5 vol% H\(_2\)O sample approaches that of the 0 vol% H\(_2\)O sample with its increasing trap density. It is noteworthy that 1 vol% and 2 vol% H\(_2\)O samples have delayed onsets of non-radiative recombination. This is consistent with our observation of lower trap states in both 1 vol% and 2 vol% H\(_2\)O samples, and thus a smaller number of non-radiative recombination pathways. Figure 5.6a shows the fitted amplitudes of the TRPL lifetime components for the different samples. The amplitude of the long and short lifetime components are denoted by \( A_1 \) and \( A_2 \), respectively. From the graphs, we see that only the 1 and 2 vol% H\(_2\)O samples have no \( A_2 \) term even at 2.5 \( \mu \)J cm\(^{-2} \), one order higher than the preceding data point. This suggests that higher order carrier recombination is suppressed for these samples.

To gain a further understanding of H\(_2\)O’s role in the recombination mecha-
Figure 5.4: Ultrafast optical spectroscopy detailing the optical characteristics of MAPI perovskite thin films with H$_2$O additives. (a) Calculation of trap density by plotting measured integrated PL intensity against photoexcited carrier density. (b) TRPL kinetic traces of the samples in the low fluence regime, showing the superiority of 1 vol% additive.
organisms, we collected the power-dependent TRPL kinetics of neat perovskite thin films, with a fluence range of 0.5 to 50 µJ cm$^{-2}$ corresponding to excitation carrier densities $3.86 \times 10^{16}$ to $3.86 \times 10^{18}$ cm$^{-3}$. These kinetics are also fitted with a multi-exponential decay function (Equation 4.1). The data can be well fitted by using a mono-exponential decay at low fluences, and a bi-exponential decay at higher fluences. The slower transition ($A_1$) seen in biexponential traces is attributed to radiative bulk lifetime, whereas the faster transition ($A_2$) is due to non-radiative recombination, as detailed by deQuilettes et al [17]. Figure 5.5 reveals the striking differences between the different recombination rates of the different samples. While all samples exhibit fast initial decay components with increasing pump fluences, from the timescales of the plots, it is clear that both 0 vol% and 5 vol% H$_2$O samples recombine much faster than the others. This trend is clearly illustrated in Figure 5.6b.

![Figure 5.5](image_url)

**Figure 5.5:** Recombination kinetics of MAPI perovskite thin films with (a) 0 vol%, (b) 1 vol%, (c) 2 vol% and, (d) 5 vol% H$_2$O additives after excitation at 600 nm between 0.5 µJ cm$^{-2}$ and 50 µJ cm$^{-2}$. Solid lines are fits based on the differential equation as described in the text (Equation 5.1).
Charge carrier recombination rates were determined by global fitting the normalised power-dependent decay kinetics (solid lines in Figure 5.5 of each sample with with the recombination rate equation,

$$\frac{dn}{dt} = -k_3n^3 - k_2n^2 - k_1n,$$

(5.1)

where $n$ is the charge carrier density, $k_1$, $k_2$, and $k_3$ are the monomolecular, bimolecular and Auger recombination rate constants, respectively. Monomolecular recombination rate consists of either a bound electron hole-pair (exciton), a free single conduction-band electron or valence-band hole. A basic assumption of using this model is that the lifetime decay is based entirely on the rate of charge carrier recombination. Furthermore, since the exciton binding energy of the MAPI is low at room temperature, monomolecular recombination is most likely trap-assisted and is widely reported [18]. On the other hand, bimolecular recombination consists of two particles, namely a free hole and electron, which leads to radiative decay. Auger recombination involves multiple particles, and is thus strongly dependent on excitation fluence. An electron and hole recombines to release energy and/or momentum that is absorbed by another electron and hole, known as an Auger particle. Like most semiconductors, both excitons and free carriers can contribute to PL, however due to the low exciton binding energy [19], the observed PL in MAPI is predominantly recombination of free carriers.

Table 5.1: Recombination rate constants and diffusion lengths calculated from TRPL measurements on MAPI films containing H₂O additives.

<table>
<thead>
<tr>
<th>vol% H₂O</th>
<th>Recombination rate constants</th>
<th>Diffusion lengths (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ ($\times 10^8$ s⁻¹)</td>
<td>$k_2$ ($\times 10^{-9}$ cm³ s⁻¹)</td>
</tr>
<tr>
<td>0</td>
<td>4.7 ± 0.3</td>
<td>2.6 ± 0.2</td>
</tr>
<tr>
<td>1</td>
<td>0.502 ± 0.006</td>
<td>0.234 ± 0.006</td>
</tr>
<tr>
<td>2</td>
<td>1.10 ± 0.02</td>
<td>0.26 ± 0.01</td>
</tr>
<tr>
<td>5</td>
<td>3.08 ± 0.07</td>
<td>2.23 ± 0.06</td>
</tr>
</tbody>
</table>

The curves can be well-fitted even if the Auger term is not considered and just fitting the monomolecular and bimolecular rate constants. The fitted rate constants are summarised in Table 5.1. The monomolecular rate obtained for the 0 vol% sample is $k_{1:0\%\text{ H}_2\text{O}} = 4.7 ± 0.3 \times 10^8$ s⁻¹, which is
Role of Water Additives in Perovskites

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consistent with previously reported values [18, 20]. Since the monomolecular recombination in MAPI is dominated by trapping, as previously mentioned, passivating these trap states would decrease the monomolecular rate constant. When the H$_2$O concentration is increased to the optimal concentration of 1 vol\%, the monomolecular rate plummet by one order of magnitude.

Large crystal grains were reported to slow recombination [21], but the invariance of our XRD spectra and SEM images across different samples suggests that it is highly likely that the crystal grains in our films did not contribute to lifetime or photovoltaic improvements. Therefore, this decrease in very likely due to the trap passivation offered by trace H$_2$O instead of morphological improvements. However, as the additive content is increased to 2 vol\% and further on to 5 vol\%, the monomolecular rate increases monotonically and approaches that of the 0 vol\% H$_2$O control sample. Such low trap-mediated monomolecular recombination over nanosecond timescales is ideal for MAPI in solar cells, and it is not surprising, considering its stellar growth and having record efficiencies that approach that of silicon. As observed earlier, this trend is also seen in the calculated trap states of the samples. The preferential dissolution of CH$_3$NH$_3$I in water relative to PbI$_2$ in higher H$_2$O concentrations could potentially have resulted in MA vacancies and/or Pb dangling bonds along the grain boundaries. This results in an increase in the trap density, and thus the trap-dominated monomolecular recombination rate.

The bimolecular recombination rate constants also follow the same trend as the monomolecular rate constant, which initially decreases to $k_{2.1\%\ H_2O} = 2.34 \pm 0.06 \times 10^8$ cm$^3$ s$^{-1}$ in the 1 vol\% H$_2$O sample. Similarly, the bimolecular recombination rate also increases when higher concentrations of H$_2$O was added. The extraordinarily low recombination rates of the 1 vol\% H$_2$O sample is reflected in higher values of the fill factor and other photovoltaic parameters.

5.4.2 Charge Carrier Diffusion Lengths

Now having knowledge on the recombination kinetics of the perovskites, it is also useful to determine the charge carrier diffusion lengths within these samples. This can help us determine the type of device architecture suitable for our MAPI with H$_2$O additives. By using a similar approach as detailed
Figure 5.6: Ultrafast optical spectroscopy detailing the recombination photophysics of MAPI perovskite thin films with H$_2$O additives. (a) Amplitude of lifetime components obtained from fitting of power-dependent TRPL kinetics, the fitting function is described in Equation 4.1 and can be simplified to $y \propto A_1 \exp\left(-\frac{t-t_0}{\tau_1}\right) + A_2 \exp\left(-\frac{t-t_0}{\tau_2}\right)$, where the indices 1 and 2 correspond to the long and short lifetime components, respectively. (b) Recombination rates obtained by fitting the recombination rate equation (Equation 5.1).
in Chapter 4, the carrier diffusion lengths were extracted using TRPL measurements on neat MAPI films, films with PC\textsubscript{61}BM electron extraction layer, and films with PEDOT:PSS hole extraction layer. PEDOT:PSS was used in this scenario to emulate charge extraction in the inverted architecture.

Such low bimolecular recombination rates yield long carrier diffusion lengths, making MAPI suitable for solar cells utilising the planar heterojunction geometry. The low monomolecular and bimolecular recombination rates are evidently reflected in longer carrier diffusion lengths (Figure 5.7a). In particular, the greatly reduced bimolecular recombination rate, the 1 vol\% H\textsubscript{2}O sample exhibits carrier diffusion lengths that is a factor of four longer as compared to the 5 vol\% H\textsubscript{2}O sample.

From the charge carrier diffusion length, $L$, we can calculate its associated diffusion coefficient, $D$, using the expression

$$L = \sqrt{D\tau_{PL}}$$  \hspace{1cm} (5.2)

where $\tau$ is the PL decay lifetime in the absence of quenching layers. By adopting the approach used by Wehrenfennig et al. to model the diffusion lengths as a function of experimentally determined charge carrier density, $n$, the diffusion lengths can be modelled and compared at solar cell operating conditions ($n = 1 \times 10^{15} \text{cm}^{-3}$) [22]. The total decay rate of each sample can be calculated from the recombination rate constants according to the expression,

$$k_{\text{total}}(n) = -\frac{1}{n} \frac{dn_0}{dt} = \phi^2 k_3 \left( \frac{n_0}{\phi} \right)^2 + \phi k_2 \left( \frac{n_0}{\phi} \right) + k_1 \hspace{1cm} (5.3)$$

$$= \phi^2 k_3 n^2 + \phi k_2 n + k_1 \hspace{1cm} (5.4)$$

where $n = \frac{n_0}{\phi}$, and $\phi$ is the branching ratio of photogenerated charge carriers to the absorbed photon density, and it is assumed that $\phi = 1$ for simplicity.

From the diffusion coefficient and total recombination rate, the diffusion lengths can be modelled as a function of $n$,

$$L(n) = \sqrt{\frac{D}{k_{\text{total}}(n)}} \hspace{1cm} (5.5)$$

The computed results of the electron and hole diffusion lengths using
Figure 5.7: (a) Electron (square) and hole (cross) diffusion length of the various samples with the respective quencher. PC$_{61}$BM is used as the electron quencher in a bilayer architecture to estimate the electron diffusion length, and PEDOT:PSS is used as the hole quencher. (b) Modelling the diffusion lengths as a function of carrier density using Equation 5.5. Solid lines denote the results assuming $k_3 = 0$, since this term was not required when fitting the power-dependent transients. Dashed lines denote the results assuming $k_3 = 10^{-28} \text{cm}^6 \text{s}^{-1}$, a value typical of OIHPs.
the model are shown in Figure 5.7b and c, respectively. From the graphs, it can be seen that the diffusion lengths sufficiently exceed perovskite layer thickness (about 275 nm) at low charge carrier densities that corresponds to solar cell operating conditions. We note that with values of $\phi < 1$, the calculated diffusion lengths will get longer. In the low carrier concentration regime, the Auger $k_3$ term (solid line in Figure 5.7) plays an insignificant role because of its multi-particle nature that requires high carrier concentrations to have an effect. When we remodel the diffusion lengths and assuming $k_3 = 10^{-28} \text{cm}^6 \text{s}^{-1}$ (dashed line in Figure 5.7, a value typical of OIHPs, the diffusion lengths get understandably much shorter. Nonetheless, these trends in H$_2$O additive diffusion lengths is similarly observed in device performances, where the 1 vol% H$_2$O device exhibits slightly higher performance in power conversion efficiency (PCE) and other parameters, notably the fill factor and $J_{sc}$.

5.4.3 Device Performance

<table>
<thead>
<tr>
<th>vol% H$_2$O</th>
<th>PCE (%)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.9 ± 0.5</td>
<td>17.8 ± 0.5</td>
<td>0.82 ± 0.01</td>
<td>0.69 ± 0.02</td>
</tr>
<tr>
<td>1</td>
<td>11.4 ± 0.9</td>
<td>19.5 ± 0.9</td>
<td>0.81 ± 0.02</td>
<td>0.72 ± 0.02</td>
</tr>
<tr>
<td>2</td>
<td>10.1 ± 0.7</td>
<td>18.1 ± 0.7</td>
<td>0.82 ± 0.02</td>
<td>0.68 ± 0.02</td>
</tr>
<tr>
<td>5</td>
<td>8.8 ± 0.5</td>
<td>17.7 ± 0.8</td>
<td>0.78 ± 0.02</td>
<td>0.64 ± 0.02</td>
</tr>
</tbody>
</table>

The solar cells were fabricated with the inverted planar heterojunction geometry ITO/PEDOT:PSS/MAPI/PC$_{61}$BM/Ag (inset of Figure 5.8). A total of fifteen MAPI cells with H$_2$O additives were fabricated for each additive concentration. The $J$-$V$ curves of the best performing cell for each corresponding additive concentration is shown in Figure 5.8a. The 0 vol% H$_2$O control device has an average PCE of 9.9 ± 0.5%, which increases to 11.4 ± 0.9% when 1 vol% H$_2$O is present, with the champion cell exhibiting a PCE of 12.3% with its $J$-$V$ curve shown in Figure 5.8b.

Notably, the short-circuit current density of the 1 vol% H$_2$O device is higher compared to 0 vol% H$_2$O. However, morphology may not be a dom-
inant factor in our films, since there is hardly any morphological difference between the samples. Therefore, we attribute this improvement in $J_{SC}$ directly to increase in charge extraction because of reduced recombination which may stem from reduced trap density and recombination centres in the 1 vol% H$_2$O device.

On the contrary, at increasing H$_2$O concentrations, the PCE decreases to 10.1 ± 0.7% and subsequently to 8.8 ± 0.5% at 2 vol% and 5 vol% H$_2$O, respectively. This decrease in PCE was also previously documented in literature [5, 12, 21]. This has also been attributed to morphological changes, because H$_2$O is able to readily dissolve CH$_3$NH$_3$I but not PbI$_2$. By preferentially dissolving one of two precursors, large voids can form in the perovskite crystal grains or film which results in poor PCE [12]. While the abovementioned literature cites improvements in PCE associated with morphology, in our study, since the morphology of the films are rather similar due to film treatment, it is very likely that there are other underlying causes to the variation in PCE. The improvements in the observed trap state densities, TRPL lifetimes and $J_{SC}$ support our conclusion of the beneficial trap passivation properties of trace H$_2$O additives.

5.5 Conclusions

In conclusion, we have investigated the carrier dynamics in H$_2$O additives perovskite films and correlated our photophysical results with photovoltaic...
device data. We have shown that trace amounts of H$_2$O effectively recrystallises MAPI grain boundaries and passivates the trap states leading to reduced recombination rates and higher $J_{SC}$. At the optimal additive concentration of 1 vol% H$_2$O, the greatly reduced monomolecular and bimolecular recombination rates was correlated with an increase in power conversion efficiencies, as observed in the 1 vol% H$_2$O device.

As the H$_2$O additive concentration is increased past the optimal additive concentration, a competition of factors affect the outcome of the photo-physics and carrier recombination in the perovskite films. In high H$_2$O concentrations, the preferential dissolution of CH$_3$NH$_3$I compared to PbI$_2$ can increase the trap density. Thus, a corresponding increase in monomolecular and bimolecular recombination rates were observed in the 2 to 5 vol% H$_2$O samples. This shows that the concentration of H$_2$O additives play a crucial role in carrier dynamics in the perovskites, and correspondingly, photovoltaic performance. Higher concentrations of H$_2$O would instead counteract the beneficial effects, and lead to degradation of the films and devices.

References


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Role of Water Additives in Perovskites


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Chapter 6

Higher Excited States in Lead Halide Perovskites

The slowing growth in perovskite solar cell efficiency prompted researchers to explore other methods in improving performance. Hot carrier solar cells are one such possibility, and this makes the studying of excited states in perovskites relevant. A portion of this work is focused on building and testing the three-pulse experimental configurations. We revisit the broad photoinduced absorption band in the visible region and attribute it to promotion of photoexcited carriers to higher energy states. Using an electron acceptor whose levels lie far above the perovskite’s conduction band minimum and pushing photogenerated charge carriers via a secondary perturbation, charge transfer of hot carriers were observed at the sub-picosecond timescale.

6.1 Introduction

The performance of perovskite solar cells have seen tremendous growth over the past years, primarily driven by optimisation of growth techniques, careful interfacial engineering and process controls. Additionally, the perovskite’s intrinsic optical properties, such as high optical absorption coefficients, long carrier diffusion lengths, low trap state densities and coupled with its defect tolerance makes it exceptionally good photoactive materials in solar cells. However, progress has but slowed as device efficiencies creep towards the Shockley-Queisser limit of about 31\% for a bandgap of 1.6 eV [1]. As it becomes increasingly difficult to improve PCE in homojunction cells, complex concepts in photovoltaic devices have to be exploited.

One well-studied option is multi-junction solar cells whereby two or more semiconductors with bandgaps, that matches the region of sunlight they are intended to capture, work in tandem to maximise the solar energy conver-
It was found that the detailed balance limit of a two-cell structure can convert 42%, a three-cell one can convert 49%, and an infinite-cell structure can convert up to 68% of unconcentrated solar energy [2]. These values can be further increased by concentrating incident sunlight via concentrators, which is another approach that is widely explored. Here, it is important to note that an inherent advantage in tandem systems is through their electroluminescence and re-emission of lower energy photons. While the beneficial effect is miniscule in low-cell tandem structures, they become increasingly important as the number of tandem cells increase [2]. Recapture, or recycling of these photons can also prove useful in exceeding the fundamental limit. Recently, photon recycling was demonstrated in lead halide perovskites, where they demonstrated charge extraction even at 50µm away from the photoexcitation centre due to multiple absorption, diffusion and re-emission events [3]. However, other groups have found that the photon recycling effect in perovskites is small and already exhibited in today’s cells [4]. In order to really maximise gains, device geometry, reflectivity optics and transport layers must be greatly optimised [5].

In homojunction cells, the extraction of hot carriers is arguably the most favourable to exceed the fundamental limit and achieve higher efficiencies [6]. In unconcentrated sunlight, a hot carrier solar cell using a semiconductor with a bandgap of 1.6 eV, which the archetypical MAPI has, can theoretically achieve PCE that slightly exceeds 40% if Auger recombination is dominant. On the contrary, where there is negligible Auger losses, the cells can reach an efficiency of 66% [7]. The extraction of hot carriers from photoactive materials has always been sought after to improve power conversion efficiencies in solar cells. However, extracting these hot carriers are not trivial because thermalisation from the hot excited state to the conduction band minimum/valence band maximum is energetically more favourable and occurs at very short timescales. This makes studying the higher excited states important, and one method of directly measuring these ultrafast transient states is using ultrafast pump-push-probe (PPP) spectroscopy [8]. While this technique is most commonly applied in the highly excitonic organic photoactive systems, where evidence of charge generation from the higher excited states were uncovered [9, 10, 11], this has never been used to probe perovskites. This is of utmost importance, especially since excitons were
discovered to coexist with free carriers in MAPI, which could impose a limit on device efficiency [12].

This chapter will present my work on the fundamental higher excited states in MAPI. We revisit the broad PIA band whose origins remain debatable. A clear understanding of the intrinsic photophysics in perovskites allow for better design of optoelectronic devices. Through in-depth interpretation and analysis of the TA transients, it was found that excited state absorption (ESA) of the excited carrier population forms the dominant contribution to the PIA signal. Using a non-injecting charge acceptor, we were able to phenomenologically demonstrate hot charge extraction in MAPI, by means of supplying excess energy via a push pulse. However, due to an interfacial barrier than forms between the perovskite and acceptor layer, using lower push photon energies were not favourable for injecting the hot carriers. Nonetheless, the PPP technique can be extended to more excitonic systems, such as MAPbBr$_3$, the more stable 2D, and even Ruddlesden-Popper perovskites, to study their fundamental photophysics and how best to exploit them for efficient charge generation.

6.2 Experimental Details

6.2.1 Samples

In this chapter, stoichiometric 12.5 wt% MAPI perovskite films were used and synthesised with minor modifications to the procedures detailed in Section 3.1. The film was placed in a thermal evaporator with a chamber pressure of about $1 \times 10^{-6}$ m bar. A 100 nm thick bathophenanthroline (bphen) (Sigma Aldrich, 97%) was then evaporated at a rate of 0.2 to 0.3 A s$^{-1}$ for the first 20 nm and 0.3 to 0.5 A s$^{-1}$ for the remaining 80 nm. By placing a quenching layer whose acceptor energy level lies above the conduction band minimum (CBM) and valence band maximum (VBM) of MAPI [13], it allows us to investigate the relaxation of hot carriers and to determine if they can be extracted.
6.2.2 Considerations Involving the Optical Setup

PPP is an elaborate spectroscopic technique which is based on conventional two-beam pump-probe spectroscopy ($\Delta T$), with an additional pulse. This additional so-called push pulse allows for secondary perturbation ($\Delta \Delta T$) of the semiconducting material, and was commonly used to study excited states and excitons in conjugated polymers [14]. Significant advances in the stability aspects of femtosecond laser technology has made it possible to obtain signals originating from secondary perturbations. But the fact is that these signals are inherently noisier, and thus significantly harder to measure accurately. In this section, we detail the considerations involved to ensure accuracy of the collected data.

In pump-probe TA experiments, the $\Delta T$ is measured by the lock-in amplifier referenced to the modulated pump beam. This is how the pump-induced change in the probe transmittance is obtained as an output of the lock-in amplifier. The results presented here, as in the rest of the thesis, are in terms of differential transmission, Hence GSB is positive, and PIA is negative (further discussed in Section 6.3.1). Similarly, in order to solely obtain the push-induced change in the probe transmittance ($\Delta \Delta T$), the lock-in amplifier can be referenced to the modulated push beam. However, we lose the $\Delta T$ signal as a result of chopping the push beam. Alternatively, to preserve both the pump-probe and push-induced signals, the push-induced signal can be extracted via LabVIEW by the data acquisition computer taking the difference between the pump-probe and PPP signals, without and with the push pulse, respectively.

$$\Delta \Delta T(\lambda, t) = \Delta T(\lambda, t)_{\text{push-off}} - \Delta T(\lambda, t)_{\text{push-on}}$$  \hspace{1cm} (6.1)

This signal is experimentally obtained by modulating the push pulse while leaving the pump pulse on the sample at all time delays. Listed below are a number of possible data acquisition schemes, with Scheme 2 being more effective than others. Unfortunately, while Scheme 3 works great in theory, it falls short in practical laboratory conditions. The pump-probe and pump-push-probe signals can be measured

1. separately across different scans (delay stage scans twice)
2. consecutively during the same scan (delay stage scans once)

3. simultaneously during the same scan (delay stage scans once)

Scheme 1: Acquiring the pump-probe and PPP signals across two delay stage passes

The most practical and straightforward approach to obtain the \( \Delta \Delta T \) signal is to first block the push beam and collect the \( \Delta T_{\text{push-off}} \) dataset, which is just a normal pump-probe scan. Then, unblock the push beam to collect the \( \Delta T_{\text{push-on}} \) dataset in a separate scan, and finally subtract the datasets according to Equation 6.1. The requisite for this approach is for the laser power to remain stable across a long period of time because of the mandatory averaging of the inherently weak \( \Delta \Delta T \) signal.

Regardless of the pump-probe signal’s SNR, the fact that the \( \Delta \Delta T \) signal is embedded within puts stringent requirements on obtaining SNR that far exceeds that of conventional pump-probe datasets. A common strategy to alleviate power drops in optical system is to employ a reference beam and dividing the measured signal from the lock-in amplifier by this reference beam, analogous to commercial UV/vis spectrometers (Section 3.6.1). However, we found that this approach did not yield much improved SNR, and still had a time cost of the delay stage traversing twice.

Laser power fluctuations are commonplace but they generally can be resolved by averaging across multiple datasets. In two-beam pump-probe experiments, albeit undesirable, these averaging could also smooth out small power dips or spikes. However, because the datasets are only subtracted after all the scans are complete, any significant fluctuation in laser output power would directly translate to jarring changes in the already small \( \Delta \Delta T \) signal. Artifacts in the derived \( \Delta \Delta T \) signal will arise, such as a non-zero signal before the arrival of the push pulse, and inconsistent traces, to name a couple. This interferes with the analysis of the carrier dynamics and would make any comparative investigation impossible. As such, it was crucial to devise a scheme that actively resolve this problem.
Scheme 2: Consecutively acquiring the the pump-probe and PPP signals in one delay stage pass

One surefire way to account for any significant power fluctuations and still get a smooth $\Delta \Delta T$ kinetic trace is to consecutively measure the pump-probe and PPP signal at each time delay. Doing so then requires the laser power to be stable for only a brief period of time, usually in seconds, as it is time-limited by how fast the electronics can acquire each data point. Nonetheless, it is considerably a lot less as compared to the time required for multiple scans to finish.

This is realised by means of a computerised mechanical shutter (Thorlabs SC10). By incorporating the shutter controls into the LabVIEW VI, the mechanical shutter can be so-called triggered to block and pass the push beam, essentially modulating it. The modifications can be broken down very simply. Firstly, at the very start of each scan, the shutter is closed thus blocking the push beam. The lock-in signal is then measured which yields the pump-probe signal. Secondly, the shutter is opened and in turn passes the push beam. Measuring the lock-in signal at this point yields the PPP signal. Finally, subtracting the two signals in accordance to Equation 6.1 yields $\Delta \Delta T$, the push-induced signal.

Addition of the shutter would mean software timing has to be optimised to avoid unnecessarily long wait times to allow the lock-in to complete its time constant cycle. Setting a shutter toggle time that is too short causes LabVIEW to obtain an output from the lock-in amplifier which contains signals from the previous measurement. For example, if the shutter was initially open, to measure the PPP signal and then closed to measure the pump-probe signal at the next time delay, a short shutter wait time coupled with a long lock-in amplifier time constant can result in erroneous data whereby the signals are mixed. Through optimisation, we found that a wait time of 1 s and a lock-in time constant of 100 ms works best.

Scheme 3: Simultaneously acquiring the the pump-probe and PPP signals in one delay stage pass

It is theoretically possible to measure all possible combinations of pump, push, probe pulses and their respective contributions simultaneously. This
is accomplished by means of double modulation as illustrated in Figure 6.1: modulating both probe and push beams with optical choppers triggered at $\frac{f}{2}$ and $\frac{f}{4}$, respectively and $f$ is the laser repetition rate (1000 Hz), and using two lock-in amplifiers to measure the signals. A suitable probe modulation frequency is at a half harmonic of the laser repetition rate, i.e. $\frac{f}{2} = 500$ Hz $\Rightarrow \frac{f}{4} = 250$ Hz. This allows to shave 1 s off each data point, which can be quite substantial during long scans. Processing these signals in the LabVIEW VI should allow the extraction of the $\Delta T$ and $\Delta \Delta T$ signals.

\[
\Delta T = C - D \quad (6.2)
\]

\[
\frac{\Delta T}{T} = \frac{C - D}{D} \quad (6.3)
\]

\[
\Delta \Delta T = A - C \quad (6.4)
\]

\[
\frac{\Delta \Delta T}{T} = \frac{A - C}{D} \quad (6.5)
\]

But we found that this was not the case as the lock-in amplifier does not distinguish between the different states (A through D). Due the nature of its operation, the lock-in performs the subtraction internally before it outputs a signal. Which was why solely chopping either the pump or push pulse trains yields the $\Delta T$ and $\Delta \Delta T$ signals, respectively. However, when modulating both the pump and push, states C and D periodically exists but do not supplement the signal in anyway. On the contrary it makes data interpretation arduous because the chopper phase and the resultant signal amplitudes output by the lock-ins are inconsistent, as shown in Figure 6.2. In order to use this scheme, it is likely that the each probe signal must be collected via a digitiser card that is triggered by the laser. As such, we will use Scheme 2 because of the lack of appropriate equipment.

### 6.3 Insights Into the Higher Excited States of MAPI

The choice of wavelength is crucial so as to avoid direct photogeneration of charges into the higher conduction or valence bands. To investigate these states, we used a pump wavelength of 600 nm (2.07 eV) which allows us to monitor the relaxation of hot carriers as well as any effects that arises due to secondary perturbations. In this work, although we are unable to
Figure 6.1: Illustration of the pulse trains, showing how the pump, and push are modulated by the optical choppers. Pulses that are being blocked by the choppers are translucent and inverted for clarity. The optical chopper for the pump is triggered at a half harmonic of the laser repetition rate, $f$, which results in alternately blocked pump pulses. For the push, it is triggered at a quarter harmonic, which results in a pair of alternately blocked push pulses.

Figure 6.2: Using double modulation technique, the PPP signals differ when chopper phases used are different, making accurate interpretation of the data arduous. The chopper phase is relative to the laser TTL trigger signal, and varying it changes which part of the pulse train is initially blocked by the chopper.
distinguish and determine whether an electron or hole is the primary charge carrier, the discussions herein will primarily be focused on the perspective of the electron. We note that it can also be extended to that of holes. In principle, however, this distinction can be made simply by including an electron or hole selective quenching layer to eliminate the respective signal and perform the same analysis done in Section 6.3.3.

6.3.1 Interpreting the Secondary Perturbations

Since we are interested in the excited states and how the material reacts to a secondary perturbation, we use TA to investigate the GSB transition. A WLC probe is used but with the acquisition optics set to detect 760 nm (1.63 eV). Figure 6.3 shows the pump-(push)-probe transients of MAPI. The pump-probe transient is obtained by mechanically delaying the probe, as illustrated in the black curve of Figure 6.3a. The radii of each beam is carefully adjusted such that $r_{\text{pump}} > r_{\text{push}} > r_{\text{probe}}$ to ensure uniform (secondary) excitation of the probed sample volume. A 600 nm push pulse, arrives $t_{\text{push}} = 3$ ps after initial photoexcitation, and changes the transmittance of the probe pulse. Delaying the push pulse 3 ps allows the initial photogenerated to sufficiently thermalise to the CBM. An ultrafast process occurs immediately after the push pulse arrives that causes a depletion in the $\Delta T$ signal (blue curve) of about 30 % followed by a gradual relaxation of the signal on the same timescale as the pump-probe signal. For simplicity, we term the 600 nm secondary perturbation as a ‘push’ instead of ‘dump’, with the latter being used if the secondary pulse overlaps the PL spectrum. We will distinguish between the two later in the chapter, and show that the secondary perturbation is actually a ‘push’ pulse.

We note that the PPP transients do not fully recover back to the pump-probe transient without push influence (black curve). If we consider the case where the 600 nm push pulse arrives immediately after the pump which corresponds to an energy of $2 \times 2.07 \text{ eV} = 4.14 \text{ eV}$. Comparatively, the energy difference between the vacuum level and VBM in MAPI is about 5.4 eV. It is likely that these carriers affected by the push pulse relaxes back to the ground state via other relaxation channels. The blue to green transients in Figure 6.3a shows that with increasing push fluence, the PPP signals are increasingly suppressed. At the highest fluence, we observe an almost...
Figure 6.3: Push-induced transient transmission dynamics of MAPI: (a) Pump-probe transients without any reexcitation (black) and PPP transients when reexcited 3 ps after time zero by a 600 nm pulse at as a function of push fluence (4.8 to 127 µJ cm$^{-2}$, blue to green curves). The decreasing probe transmission observed is due to increasing excitation of the carrier population to higher excited states with increasing push fluence. (b) The data points are obtained by taking the maximum difference between the pump-probe and PPP transients, revealing an increasing ‘lost’ carriers due to reexcitation observed in (a). (c) PPP transients as a function of pump-push delay shows the persistence of the push effect even until 100 ps after initial photoexcitation.
complete suppression of the PPP signal. Taking the maximum difference between the PPP and pump-probe signal in the time range of a few ps after the push arrives, averaged across 6 to 10 ps reveals a saturation-like behaviour as illustrated in Figure 6.3b. Measuring the PPP kinetics as a function of push delay shows that this behaviour persists even until 100 ps, as shown in Figure 6.3c.

Having observed how the push pulse influences the free carriers, it sets the stage to discuss what the secondary perturbation does in the time window investigated. Figure 6.4 illustrates the various photophysical processes that can occur following initial excitation by the pump pulse.

![Energy level diagram showing the photophysical processes involved: initial photoexcitation by a pump and the subsequent optical transitions, namely, thermalisation (T<sub>m</sub>), PIA, and PL. The pump, GSB probe, PIA probe wavelengths are, 600 nm, 760 nm, and 560 nm which corresponds to 2.07 eV, 1.63 eV, and 2.20 eV, respectively. The push wavelengths used are 600 nm, 800 nm, and 1200 nm which corresponds to 2.07 eV, 1.55 eV, and 1.03 eV.](image)

**Figure 6.4:** Energy level diagram showing the photophysical processes involved: initial photoexcitation by a pump and the subsequent optical transitions, namely, thermalisation (T<sub>m</sub>), PIA, and PL. The pump, GSB probe, PIA probe wavelengths are, 600 nm, 760 nm, and 560 nm which corresponds to 2.07 eV, 1.63 eV, and 2.20 eV, respectively. The push wavelengths used are 600 nm, 800 nm, and 1200 nm which corresponds to 2.07 eV, 1.55 eV, and 1.03 eV.

In addition, as illustrated in Figure 6.5, secondary perturbations can result in various processes that calls for careful interpretation:

1. The secondary perturbation functions as a push pulse, re-exciting the carriers from an excited state (including states which is populated by thermalised carriers) to higher excited states.
2. The secondary perturbation functions as a secondary excitation from the ground state to the initial excited state. This is possible if the push pulse has sufficient photon energy (The push pulse is able to do this in our scenario because \( \lambda_{\text{pump}} = \lambda_{\text{push}} = 600 \text{ nm} \))

3. The secondary perturbation functions as a dump pulse, depleting of the carriers in excited state to the ground state. This is in accordance to Einstein’s A and B coefficients, which states that the probability of absorption and stimulated emission are equal.

**Figure 6.5:** Schematic of the three photophysical processes that can arise due to secondary perturbations following initial 600 nm photoexcitation. In this example, it is a 600 nm pulse that arrives 3 ps after initial photoexcitation. Based on the arguments presented in the main text, we conclude that process 1 is dominant in our experiments involving a push pulse. For simplicity and consistency, the energy levels are drawn with respect to the electron. AES: arbitrary excited state; IES: initial excited state.

Since the discussion involving the PIA band and excited states will get more complex, it is crucial we distinguish between PIA and ESA. In this thesis, PIA simply refers to a negative \( \Delta T \) signal without any form of interpretation, similar to how a positive \( \Delta T \) signal refers to a photobleaching signal. On the other hand, ESA specifically refers to absorption of photons by the photogenerated carriers in the excited state, thereby promoting it to higher excited states. Process 1 is ESA, a typical transient response of any photoexcited semiconductor (Refer to Section 3.4.1 for further discussion). As such, we approach this by means of elimination to determine which is
the probable process that gives rise to the push-induced response observed in our plots.

We next discuss Processes 2 and 3 as they can be easily eliminated based on our results. For Process 2, if a secondary excitation from the ground state occurred, probing the GSB transition at 760 nm would have revealed an increase in the PPP $\Delta T$ signal. The reason for this is because it would result in another GSB-like signal, since more carriers from the ground state are promoted to the excited state. However, this is not seen in our transients, which rules out Process 2 as the dominant factor when a 600 nm push is used.

Finally, we discuss Process 3. A depletion of the initial excited state is highly unlikely to be dominant due to a few reasons. Firstly, it requires the secondary excitation wavelength to fall within the PL spectrum. This in turns causes a deactivation, or dumping, of the excited state carrier population back to the (non-equilibrium) ground state [14]. Since MAPI does not have any PL response at, or around 600 nm, which suggests that radiative recombination is unlikely (black plots in Figure 4.10). Secondly, due to $t_{\text{push}} = 3 \text{ ps}$, the hot carriers would have thermalised, which means that the probability of dumping the hot carriers is very low. Thirdly, the pump-probe spectrum around 600 nm is a broad PIA band rather than a photobleaching event. This means that carrier recombination is unlikely at this push wavelength, as state-filling processes (of which charge carrier recombination is one) will result in a photobleach. Lastly, a depletion of the initial excited state would require that the hot carriers be sufficiently long-lived, which is not the case in MAPI. Subsequently in the chapter, we show that this is indeed improbable, as the thermalisation lifetime is sub-picosecond, consistent with literature [15, 16]. Furthermore, the persistent effects of the push is observed even up to 100 ps pump-push delay (Figure 6.3c) lends further support to this conclusion.

The elimination of Processes 2 and 3 implies that Process 1 is dominant regardless of the push fluence used. Nonetheless, evidence of ESA can be interpreted from the depletion of the GSB signal, which directly reflects the depletion of the thermalised carriers in the CBM. Since the thermalised carriers are promoted to higher excited states, the CBM population decreases. If the push fluence is sufficiently high, it can almost fully deplete the CBM, as observed in Figure 6.3a. A depletion of the CBM population results in
an increased absorption (i.e. decreased transmission, or *negative* $\Delta T$) of the probe pulse, which is reflected as a decrease in the GSB signal. Furthermore, the persistence of this depletion (as shown up to 100 ps in Figure 6.3c) means that this signal must originate from a long-lived state, something the CBM is; with a fitted lifetime of a few nanoseconds in our MAPI films (see Table 6.1).

### 6.3.2 Origins of the PIA Band

Table 6.1: Fitted lifetime components of MAPI thin film in Figure 6.6a when probed at the 560 nm PIA and 770 nm GSB transitions. The $\tau_1$ and $\tau_3$ lifetimes are of interest, as they correspond to the ultrafast thermalisation and lifetime of the carriers in the CBM.

<table>
<thead>
<tr>
<th>$\lambda_{\text{probe}}$ (nm)</th>
<th>$A_1$</th>
<th>$\tau_1$ ps</th>
<th>$A_2$</th>
<th>$\tau_2$ ps</th>
<th>$A_3$</th>
<th>$\tau_3$ ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>560 (PIA)</td>
<td>-0.49</td>
<td>0.3 ± 0.2</td>
<td>-0.21</td>
<td>700 ± 500</td>
<td>-0.31</td>
<td>4500 ± 2900</td>
</tr>
<tr>
<td>770 (GSB)</td>
<td>-0.52</td>
<td>0.36 ± 0.02</td>
<td>0.14</td>
<td>470 ± 60</td>
<td>0.34</td>
<td>4200 ± 200</td>
</tr>
</tbody>
</table>

To illustrate the state filling of the CBM due to carrier thermalisation, we probe the broad PIA band which spans from 500 to 725 nm, as shown in Figure 4.5 previously and in Figure 6.6b (black). Since it is extremely difficult and tricky to probe at 600 nm due to excessive pump scattering, we used a representative probe wavelength of 560 nm (PIA probe, 2.20 eV), which lies in the same PIA band. In Figure 6.6a, the negative $\Delta T$ signal was negated (multiplied by $-1$) for clarity and to aid in comparison. From the plot and fitted lifetimes in Table 6.1, the immediate rise of the 560 nm signal stems from ESA of the initial excited carrier population to higher excited states. The subsequent sharp decrease in the $\tau_1$ component of the 560 nm PIA signal suggests that the initial excited carrier population undergoes thermalisation to the CBM. An ensuant rise in the $\tau_1$ component of the 770 nm (GSB probe, 1.61 eV) signal is observed indicates a state filling of the CBM by the thermalised carriers. Although 760 nm could be used, again, it is just a representative wavelength within the relatively broad bleaching band. Since the carriers that are promoted to higher excited states reside in the CBM, it is expected that the long lifetime component ($\tau_3$) of the 560 nm signal decays in the same order as that of the 770 nm signal – and indeed, this behaviour was observed. It is worth noting that the PIA band has been
largely neglected because of the difficulties in pin-pointing its origins, save for one report by Price that attributed it to photo-induced change in the refractive index [16]. However as shown in Figure 6.6b, Using the Kramers-Kronig relation to obtain the change in refractive index, Giovanni modelled the TA signal and found that the PIA signal due to a change in the refractive index is small when compared to the measured signal [17].

![Figure 6.6:](image)

From our results, we therefore conclude that the 600 nm secondary perturbation is a push pulse. In addition, we conclude that the PIA band has dominant contributions from ESA of carriers in any excited state to higher excited states, which is further corroborated by the fact that the 600 nm push overlaps the PIA band. The persistence, near-complete depletion and lack of recovery in the PPP $\Delta T$ signal suggests that excited carriers are promoted to higher excited states and relax via another decay channel. It is also worthy to note that the $\Delta T$ transient is zero at negative pump-push delay, i.e., when the push arrives before the pump (dark red curves in Figure 6.3c). In this scenario, the push pulse excites the carriers from the ground state; or in other words, the push is acting as the pump pulse. Therefore, when we subtract the ‘push on’ and ‘push off’ signals, they yield a flat zero line, since we are essentially collecting the pump-probe data in both instances. As the pump-push delay increases ($t_{\text{push}} > 0$), the push-induced signal becomes obvious.
6.3.3 Evidential Hot Carrier Extraction in MAPI

Having established that the push can promote photoexcited carriers to higher excited states, we can then probe the relaxation mechanisms and extraction of these hot carriers and excited states. The energy alignment of MAPI and bphen is illustrated in Figure 6.7 [13, 18]. The large energy difference between the acceptor levels of bphen and the CBM and VBM of MAPI makes it undesirable as a charge extraction layer. However, using a push pulse allows us to promote carriers sufficiently high enough to inject into bphen. Figure 6.8 shows the pump-probe and PPP $\Delta T$ transients of MAPI, and how a bphen quencher layer influences said signals. The samples were excited with a 600 nm pump and probed at the 760 nm GSB band. Different push wavelengths are used to promote carriers to various excited states above bphen. Since the push pulse arrives 3 ps following initial photoexcitation, we assume that the push pulse promotes carriers from the same excited state to differing excited states depending on the push wavelength (and by extension, different push photon energies).

![Figure 6.7](image)

**Figure 6.7:** Energy level diagram showing the energy band alignment of MAPI with an evaporated bphen layer. The large energy difference (1 eV) between the acceptor levels of bphen and the CBM and VBM of MAPI makes it undesirable as a charge extraction layer. However, using a 600 nm (1.73 eV) push pulse allows us to promote the photoexcited carriers sufficiently high enough to inject into bphen.
The solid lines shown in Figure 6.8 are best-fit curves of the $\Delta T$ pump-probe data using a multi-exponential function (Equation 4.1). The TA measurements were all done on the same MAPI and MAPI with bphen (henceforth referred to as MAPI/bphen sample. As such, the pump-probe signals for each push wavelength should be similar and any discrepancy might be from deviation of the sample position and laser power fluctuations. In all cases, the carrier lifetimes of MAPI/bphen are longer than neat MAPI. This suggests that a capping layer, whose energy level is higher than MAPI and does not allow direct extraction of carriers, can passivate surface states and lead to a lengthening of the carrier lifetimes. A similar behaviour was observed when poly(methyl methacrylate) was spincoated on a MAPI film [19]. Expectedly, the 600 nm push pulse causes a depletion of the $\Delta T$ signal due to ESA. We postulate that both 800 nm and 1200 nm also function as a push effect due to the ultrafast thermalisation upon pushing. This is corroborated by past reports of PIA being observed at these wavelengths [16, 20].

Figure 6.9 shows the $\Delta \Delta T$ push-induced signals, focused around 3 ps, revealing the interesting ultrafast behaviours of the pushed carriers. It was obtained by taking the difference between the ‘push off’ and ‘push on’ $\Delta T$ signal. Hot carrier extraction is demonstrated when a 600 nm push pulse is used. As shown in Figure 6.9a, on the neat MAPI film in the absence of bphen (black), there is a fast decay on the sub-picosecond timescale which can be directly attributed to thermalisation of the pushed excited carrier population to the CBM. In MAPI/bphen, the hot carriers that were promoted to higher excited states by the 600 nm push would have acquired sufficient energy and to be injected into bphen. Thus, explaining why the fast decay disappears; these hot carriers, now in bphen, will not be able to thermalise back to the MAPI conduction band.

Although data obtained from the 600 nm push comparative measurements on MAPI/bphen is adequate proof of hot carrier extraction, a significant photon energy is required to realise this. We set out to determine if lower push photon energies but still in excess of the bphen acceptor level, i.e. 800 nm and 1200 nm (1.03 eV and 1.55 eV), will suffice. Figure 6.9b and c shows the presence of the fast decay associated with ultrafast thermalisation from higher excited states in both MAPI and MAPI/bphen films. The
Figure 6.8: PPP $\Delta T$ transients of MAPI without (neat film, black solid symbols) and with bphen (green open symbols) quenching layer probed at the 760 nm GSB. The push pulse arrives 3 ps after the 600 nm pump (5 $\mu$J cm$^{-2}$), with varying wavelengths to probe different excited states: (a) 600 nm (15 $\mu$J cm$^{-2}$), (b) 800 nm (105 $\mu$J cm$^{-2}$), and (c) 1200 nm (1.4 mJ cm$^{-2}$). Solid lines are fits of the pump-probe $\Delta T$ signals and the raw data is depicted by symbols. The pump-probe data (push off) is denoted by squares, and the PPP data (push on) is denoted by circles.
Figure 6.9: PPP $\Delta \Delta T$ transients of MAPI without (neat film, black solid squares) and with bphen (green open squares) quenching layer probed at the 760 nm GSB. The push pulse arrives 3 ps after the pump, with varying wavelengths to probe different excited states. (a) When pushed with 600 nm pulses, a fast decay component can be seen in the neat film, which is interestingly disappears in the presence of bphen. (b,c) When pushed with (b) 800 nm, and (c) 1200 nm, the fast decay component is present even with bphen. Solid lines are fits of the PPP $\Delta \Delta T$ signals and the raw data is depicted by symbols.
results confirm that even a 800 nm push pulse is not sufficiently energetic to allow hot charge carrier transfer from MAPI to bphen. We ascribe this phenomena to an interfacial barrier that forms when the two materials come into contact with each other. This height of this barrier is between 0.6 eV and 1.17 eV above the acceptor level of bulk bphen, since a 600 nm push photon will suffice but not an 800 nm push photon. This is seen in Figure 6.10, when a direct generation of a photoexcited carrier using a 400 nm (3.1 eV) pump is unable to be extracted by bphen, since no quenching was observed at all.

![Image of Figure 6.10](image_url)

**Figure 6.10:** Transient transmission dynamics of MAPI pumped at 400 nm and probed at 760 nm reveals no quenching of the lifetime. This indicates that the photoexcited carriers are not able to be extracted by bphen.

### 6.4 Conclusions

In conclusion, our results reveal the intrinsic photophysics of the higher excited states in MAPI as measured by ultrafast all-optical PPP spectroscopy. Earlier in the chapter, the design considerations of the setup was explained. When pushed with a 600 nm pulse increasing depletion and persistence of the GSB signal was observed, leading us to suspect this behaviour arises due to ESA. Further analysis of the push-induced signals confirmed that the broad PIA, previously attributed to photoinduced refractive index change, is actually dominated by ESA of photoexcited carriers. In fact, the same recombination timescale of the PIA and GSB band indicates that ESA can occur anywhere in the conduction band, from the initial excited state to the CBM.
Hot charge carrier extraction was demonstrated using a bphen layer, whose acceptor level lies far from that of MAPI. This arises because the ultrafast sub-picosecond thermalisation of these hot carriers were notably absent in the presence of bphen. Utilising the same push wavelength of 600 nm, sufficient energy can be imparted to the photoexcited carriers such that they are in excess of the bphen energy level, thus facilitating hot carrier extraction. Due to an interfacial barrier that formed between MAPI and bphen, lower energy push photons, such as 800 nm and 1200 nm, were unable to inject hot carriers into bphen. This was subsequently verified when direct photogeneration of hot charges using a 400 nm pump were not quenched by bphen. However, the barrier which has a height between 0.6 eV and 1.17 eV above the acceptor energy level of bphen may prove difficult for practical hot carrier extraction. Nonetheless, this study, the first of its kind for perovskites, paves the way for designing functional devices with appropriate hot carrier quenchers to surpass the fundamental detailed balance limit of perovskite solar cells.

References


Chapter 7

Conclusion and Future Work

This chapter serves to draw the thesis to closure, by summarising the results, and discussing the implications and my scientific study. Outstanding questions left unanswered will also be presented, and forms the basis of possible future works to extend on my thesis.

7.1 Thesis Summary and Implications

Organic-inorganic halide perovskite (OIHP) film morphology is key to high performance functional devices. The serendipitous effectiveness of solvent engineering and H$_2$O additives on improving methylammonium lead iodide (MAPI) film morphology and charge transport was the main rationale of this study. These approaches involve the solvent directly interacting with the perovskite crystal grains, thus impacting its carrier dynamics and resultant charge transport. To help in designing and choosing appropriate acceptor materials for charge transport, an understanding of the fundamental photophysics of MAPI is necessary.

In my thesis, we investigated the charge dynamics and extraction to improve MAPI devices through two main tasks: how fabrication process controls influence the morphology, and hence the resultant photophysics and solar cell power conversion efficiency (PCE); and studying the fundamental excited states in the archetypal MAPI OIHP for improved charge transport. A deeper understanding of the fundamental photophysics is required in order to improve device performance beyond trial and error approaches.

We studied solution-processed 3D MAPI thin films and correlated the film morphology with data obtained from ultrafast optical techniques, e.g. steady-state and time-resolved photoluminescence (TRPL), and two/three pulse transient absorption (TA) spectroscopy. Through these techniques, we monitored the temporal evolution of excited state carriers and determined
how the carrier dynamics can be engineered.

By systematic sample engineering of MAPI thin films through treat-
ments of the film and substrate, we discovered that solvent engineering using
toluene drip increases trap densities that can quench carrier lifetimes, but it
can be alleviated with improvements in morphology. The films with the best
morphology still comes from plasma-cleaned, solvent engineered treatments.
Further investigation into the charge extraction of the engineered films re-
vealed that it is possible to shift the Fermi level sufficiently to prevent the
injection of hole through the MAPI/hole transport layer interface [1].

Focusing on the combination that consistently gives us the best mor-
phology, we introduced H$_2$O additives into the MAPI solution. We found
that, apart from morphology as previously reported [2, 3], the underlying
photophysics are modulated as well. At the optimal additive concentration
of 1 vol% H$_2$O, we observed passivation of trap states and an associated 1-
order decrease in recombination rates and an increase in $J_{sc}$. The effects are
attributed to recrystallisation of MAPI grain boundaries because of the pref-
erential dissolution of CH$_3$NH$_3$I compared to PbI$_2$. However, increasingly
high H$_2$O concentrations serve to counteract its beneficial effects, leading
to increased trap densities, recombination rates, and degradation of samples
and devices. These results collectively underscores that judicious consider-
ations of process controls are crucial for functional devices, and opens up
the possibility to study other existing or emerging solvents and additives in
order to minimise their adverse effects on charge transport.

This prompted the study of higher excited states in MAPI to facilitate
the design and choice of appropriate acceptor materials for efficient charge
extraction and transport. By using an elaborate three pulse technique, we
were able to directly investigate these higher excited states. We determined
that the photoinduced absorption (PIA) band, previously attributed to pho-
toinduced refractive index change, is actually dominated by excited state
absorption (ESA) of photoexcited carriers. Further analysis reveals that
ESA can occur anywhere in the conduction band, from the initial excited
state to the conduction band minimum (CBM). We also demonstrated hot
carrier extraction using a bathophenanthroline (bphen) acceptor, whose en-
ergy level lies far from that of MAPI. Using a push wavelength of 600 nm,
we noted the lack of carrier thermalisation, indicating charge injection into
Conclusion and Future Work

Chapter 7

bphen. However, the presence of an interfacial barrier prevents lower energy photons from inducing injection. Nonetheless, it forms the foundation to study and explore other appropriate acceptors. Furthermore, the broad ESA band spanning across the visible spectrum opens up a wealth of opportunities to manipulate these hot carriers, such as efficient hot carrier extraction, and induced charge generation from exciton dissociation [4, 5, 6]. Ultimately, these new insights and knowledge serve to chip away at the obstacles limiting theoretical maximum efficiencies in OIHP devices.

7.2 Outstanding Questions

The results presented in my thesis has provided a deeper insights of the use of process controls in perovskites and the behaviour of higher excited states. However, there remains questions unanswered which may help to further understanding of the material system.

7.2.1 Will other solvents and additives used in process controls bring about the same effects?

In Chapters 4 and 5, we presented that toluene, a solvent commonly used in solvent engineering, inadvertently increased the trap densities in perovskites. This is due to methylammonium (CH$_3$NH$_3^+$) and halide ions forms complexes with toluene [7] that may not necessarily recrystallise at grain boundaries. A similar phenomenon is observed in H$_2$O additives where preferential dissolution is responsible for the beneficial recrystallisation of perovskite grain boundaries [8, 2]. While we are able to directly observe the effects of these process controls, it might not be trivial to extend our conclusions to other solvents and additives without study. For example, apart from toluene, other solvents like hydroiodic acid and isopropanol are used. Luo et al. used these to fabricate air stable $\alpha$-CsPbI$_3$ thin films, that are notorious for being extremely unstable [9], and proposed a series of possible chemical reactions. This suggests that the reactions does more than just improving morphology as it is able to stabilise the $\alpha$-CsPbI$_3$ thin films in ambient conditions. Studying the origins of these effect might help in choosing appropriate solvents to produce 3D perovskites that are trap-free and air-stable for efficient devices.
7.2.2 How does the push pulse affect excitonic populations in OIHPs?

In Chapter 6, we presented the fundamental photophysics of the higher excited states in MAPI, and proved that the broad PIA band is due to ESA of carriers. Recently, a small exciton population was discovered to coexist with the large free carrier population in MAPI [10, 11]. But given our ensemble measurement, we were not able to distinguish if there are excitonic contributions in the PIA band. It would be interesting and useful to study the possibility of inducing free carrier generation in these exciton populations, as the latter imposes limits on theoretical maximum efficiencies. An extension of the study can involve excitonic OIHPs, such as MAPbBr$_3$, 2D and Ruddlesden-Popper perovskites.

7.2.3 Is it possible to directly extract hot carriers from OIHPs without push?

In Chapter 6, we also demonstrated that it was possible to extract these hot carriers into bphen with a very energetic 600 nm push photon following photoexcitation at the same wavelength (a huge total photon energy of 4.14 eV). The extraction of thermalised carriers is not an issue for most systems as long as the energy level alignments are favourable. However, ultrafast thermalisation timescales makes the extraction of hot carriers extremely difficult, but at the same time rewarding because of a lower $V_{oc}$ deficit. The sub-picosecond thermalisation inMAPI cells implies that charge extraction must occur at a shorter timescale. However, another obstacle is the presence of an interfacial barrier we discovered that prevents lower energy push photons from inject these hot carriers into bphen. Direct excitation (without push) using a 400 nm (3.1 eV) pump pulse also failed to inject these hot carriers, as it falls short by 1.04 eV. However, generation and usage of deep-ultraviolet (UV) 300 nm pulses is challenging, and is not readily available in the solar spectrum. That being said, it will be interesting to explore lower bandgap OIHPs such as FAPbI$_3$ with different acceptors for hot carrier extraction, barring any large interfacial barriers that might be present.
7.3 Proposed Future Works

In this section, we propose additional future works that can answer our outstanding questions, or to further expand the scope and capabilities of OIHPs for more efficient charge transport and devices.

7.3.1 Impact of Additives in Multiple Cation Perovskites

OIHPs containing multiple cations continue the push towards higher efficiencies. The current 22.1% record is obtained by adding triiodide (I$_3^-$) and using MAPbBr$_3$ and FAPbI$_3$ precursors to form perovskite films [12]. It would then make sense to attempt inclusion of H$_2$O or other additives into these films and study the ensuing carrier dynamics and device performance. One potential challenge can arise from the competing healing effects of I$_3^-$ and H$_2$O, leading to adverse dissolution of the perovskite grains. However, since the reported growth technique uses the two-step deposition method to first deposit a thick Pb-halide layer, the H$_2$O additives present can help the cation-halide dipping solution penetrate deeper [13]. This effectively maximises perovskite film formation and by optimising H$_2$O additive concentration it may reduce defects even further. The low defect, long carrier lifetimes in this high performance perovskite will also be an effective test bed to study the higher excited states for hot carrier extraction.

7.3.2 Broadband Push-induced TA Microscopy to Interrogate Charge Transfer States and Exciton Dissociation in OIHP

The higher exciton binding energy of MAPI at low sample temperatures [14] indicates that a substantial exciton population can exist without dissociating. This allow us to study the higher excited states of the exciton population easier, as compared to room temperature measurements. Wang et al. found that MAPI is excitonic in the orthorhombic phase. On the contrary, Phuong et al. showed that fast charge transfer from the orthorhombic to the room temperature tetragonal phase likely suppresses exciton formation, giving rise to free carrier behaviour even at low temperatures. These conflicting reports of exciton and free carrier behaviour in the low temperature orthorhombic phase suggests that the population at low temperatures remain debatable.
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This makes the direct investigation of exciton populations using ensemble TA measurements difficult. As such, a viable approach is to combine low temperature and large MAPI grains to promote the formation of spatially isolated excitons. Large grains can be fabricated using hot-casting processes with high boiling point solvents [15] and hydriodic acid [11] and investigating these films using TA microscopy. Introducing a push pulse would allow us to interrogate the exciton population for push-induced charge generation.

7.4 Conclusion and Outlook

Wrapping up, my thesis focused on studying the carrier dynamics in morphologically engineered MAPI films for improved charge transport and device performance. The versatility of various process controls in the growth of perovskites to improve morphology were studied and demonstrated that photophysical factors play a large role in guiding device performance. Having revealed the fundamental excited states in MAPI, this sets the stage for further advancements in hot carrier extraction in OIHPs for highly efficient charge transport. As the perovskites approach the detailed balance limit, it becomes even more imperative to further broaden the fundamental research of OIHPs, such as intrinsic photophysics and interfacial dynamics.

References


