

Efficient Planar Formamidinium-Based Perovskite Solar Cells

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&

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Statement of Originality

I hereby declare that the work in this thesis is my own otherwise stated or referenced in text. The work presented here has been carried out in the Department of Materials and Centre for Doctoral Training in Plastic Electronics at Imperial College London (January 2019 – June 2022), under the supervision of Prof. Martyn McLachlan and Prof. Martin Heeney.

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Abstract

Organic-inorganic metal halide perovskites are receiving significant research attention as key materials for next-generation solar cells, owing to their excellent optoelectronic properties. Recent advancements in perovskite solar cells (PSCs) have resulted in unprecedented progress, with power conversion efficiencies (PCEs) approaching 26%. To further advance this cutting-edge technology, extensive strategies have been developed to improve the device performance. In addition to the pursuit of highly efficient PSCs through different approaches, this thesis also considers the long-term stability. In Chapter 1, an introduction to photovoltaic (PV) technology is presented. With traditional energy sources being limited and environmental concerns growing, renewable energy is urgently needed, and solar energy is a top alternative due to its abundant resources and cost-effectiveness. PSCs are considered as the next-generation solar cells because of their low cost, high efficiencies, and facile fabrication processes. Chapter 2 provides a literature review, including fundamentals from materials to devices, fabrication approaches, and foremost challenges. Chapter 3 demonstrates the experimental methods employed for materials characterization and device optimization, including thin film and device fabrication, structural, optical, energetic characterization, and stability analyses. Chapter 4 investigates the influence of the highest occupied molecular orbital (HOMO) of the hole transport layer (HTL) on the open-circuit voltage (V_{OC}). The energetic offset between the HTL HOMO and the perovskite valence band (VB) is critical in determining the non-radiative recombination losses, which in turn affects the V_{OC} losses. The stability studies show that FA-based perovskite is susceptible to degradation from light and moisture exposure, leading to the α -to- δ phase transition. In Chapter 5, a novel sequential dynamic deposition (SDD)

approach with methylammonium chloride (MACl) treatment is introduced to fabricate perovskite films with a wide processing window, resulting in highly efficient formamidinium (FA)-based PSCs. In Chapter 6, outstanding results from previous chapters are summarized, and future perspectives are discussed.

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Table of Contents

Statement of Originality	2
Copyright Declaration	2
Abstract	3
Acknowledgements	5
Table of Contents	7
List of Figures	12
List of Tables	22
Abbreviations	24
Publications	27
Declaration of Contributions	28
1. Introduction	29
1.1 Motivation	29
1.2 Project Objectives	31
2. Literature Review	32
2.1 Fundamentals of Organic Lead Halide Perovskite Materials	32

2.1.1 Optoelectronic Properties of Perovskite Materials	32
2.1.2 Recombination in Perovskite Materials	39
2.2 Perovskite Solar Cells.....	40
2.2.1 Solar Energy Evolution.....	40
2.2.2 Device Architecture	41
2.2.3 Working Principle	44
2.3 Approaches in Achieving High-Efficiency Devices	47
2.3.1 Processing Engineering	47
2.3.2 Interface Engineering	51
2.3.3 Additive Engineering	54
2.4 Challenges of Perovskite Solar Cells.....	57
2.4.1 Stability.....	57
2.4.2 Toxicity	59
2.4.3 Flexibility.....	60
2.4.4 Device Upscaling	62
3. Experimental Methods.....	65

3.1 Thin Film and Device Fabrication	65
3.2 Device Characterization.....	70
3.2.1 Current Density-Voltage Characteristics (J-V)	70
3.2.2 External Quantum Efficiency (EQE).....	71
3.3 Structural Characterization	72
3.3.1 Diffraction (XRD)	72
3.3.2 Scanning Electron Microscopy (SEM).....	75
3.4 Optical Characterization	75
3.4.1 Ultraviolet-visible Spectroscopy (UV-Vis).....	75
3.4.2 Steady-state Photoluminescence Spectroscopy (Stead-state PL).....	77
3.4.3 Time-resolved Photoluminescence Spectroscopy (TRPL).....	79
3.5 Energetic Characterization	80
3.6 Stability Analysis	81
4. Deciphering the Role of Hole Transport Layer HOMO Level on the Open Circuit Voltage of Perovskite Solar Cells	82
4.1 Introduction	82
4.2 Results and Discussion	84

4.2.1 Intrinsic Properties	84
4.2.2 Device Performance.....	87
4.2.3 Light-intensity Dependent PL and JV Measurements	95
4.2.4 Photoluminescence Studies of Charge Extraction and Recombination Dynamics.....	100
4.2.5 Stability of Mixed-Cation Perovskite.....	102
4.3 Conclusion	110
5. Methylammonium Chloride Treatment with Wide Processing Window for Highly Efficient Perovskite Solar Cells	112
5.1 Introduction	112
5.2 Results and Discussion	117
5.2.1 Modification of Perovskite Film Processing.....	117
5.2.2 Morphological Analyses	118
5.2.3 Optical Characterisations	125
5.2.4 Structural Characterisations	127
5.2.5 Device Performance.....	132
5.2.6 Versatility of SDD Approach.....	136

5.2.7 Stability of MACl-Treated Perovskite	148
5.3 Conclusions	157
6. Conclusions and Future Work	159
6.1 Conclusions	159
6.2 Future Work	162
7. References	164
8. Appendix	183
Supplementary Figures.....	183
Stability of Pure FAPbI ₃ Perovskite.....	185

List of Figures

Figure 1.1. NREL best research cell efficiencies chart. Reproduced from ref. ⁴	30
Figure 2.1. Crystal structure of organic lead halide perovskite.	33
Figure 2.2. Device structures of perovskite solar cells. (a) mesoporous structure, (b) planar n-i-p structure, (c) planar p-i-n structure, (d) HTL-free structure, (e) ETL-free structure.....	44
Figure 2.3. Energy level diagram of different materials in perovskite solar cells. Reproduced from Ref. ⁵	46
Figure 2.4. Charge transfer processes involved in perovskite solar cells.	46
Figure 2.5. Two-step spin-coating method. Firstly, a 1M PbI_2 solution is spin-coated onto the m- TiO_2 film. The PbI_2 -coated film is dried at 40 °C for 3 min and 100 °C for 5 min. Then a $\text{CH}_3\text{NH}_3\text{I}$ solution is loaded onto as-deposited PbI_2 film for 20s and spun. Finally, the film is heated at 100 °C for 5 min. Reproduced with permission. ⁷³	48
Figure 2.6. Solvent engineering process for preparing a uniform and dense perovskite film. Reproduced with permission. ⁵⁷	49
Figure 2.7. Dual-source thermal evaporation system for depositing perovskite using MAI and PbI_2 (or PbCl_2). Reproduced with permission. ⁵⁶	50
Figure 2.8. Sequential layer-by-layer vacuum deposition to fabricate perovskite solar cells. Reproduced with permission. ⁷⁴	51

Figure 2.9. a) Device structure with PCBM migrated into perovskite grain boundaries. b) Cross-section SEM image of perovskite device. Reproduced with permission.⁸⁴.53

Figure 2.10. The mechanism for the formation of perovskite grains in the a) absence and b) presence of PCBM. The perovskite grains are much larger with the presence of PCBM. Reproduced with permission.⁸⁵ 53

Figure 2.11. Summary on different strategies of additive engineering. Reproduced with permission.⁸⁶ 56

Figure 2.12. a) Photograph of a flexible solar cell. b) PCE, J_{sc} , V_{oc} , and FF as a function of bending cycles. Reproduced with permission.¹⁸⁶ 61

Figure 2.13. a) Schematic and photograph of a flexible artemisinin-doped perovskite solar cell, and the molecular structure of artemisinin. b) PCE of the PSC as a function of artemisinin concentration. Reproduced with permission.¹⁸⁷ 61

Figure 2.14. a) Image of 7m² fully printed PSC-based modules. b) Schematic of fabrication process for fully printed PSCs. Reproduced with permission.²⁰⁵ 63

Figure 2.15. a) Set up of roll-to-roll slot-die coating. b) resulting large-area perovskite film. Reproduced with permission.²⁰⁶ 64

Figure 3.1. Illustration of solvent engineering method for perovskite formation. 67

Figure 3.2. (a) Schematic of inverted perovskite device structure; (b) Cross-section SEM of a MAPbI₃ device. 67

Figure 3.3. Typical J-V scan of a perovskite solar cell with reverse and forward scans shown as indicated.	70
Figure 3.4. Typical EQE spectrum of a MAPbI ₃ perovskite film.	72
Figure 3.5. Typical XRD pattern of a MAPbI ₃ perovskite thin film. Major peaks of perovskite are indexed, and ITO substrate are labelled.	74
Figure 3.6. Typical XRD pattern of a FAPbI ₃ perovskite thin film. Major peaks of perovskite are indexed, and ITO substrate are labelled.	74
Figure 3.7. Typical SEM top image and cross-section image of a MAPbI ₃ perovskite film. Scale bar is the same for both images.	75
Figure 3.8. UV-Vis absorption spectrum of a MAPbI ₃ perovskite film.	76
Figure 3.9. The Tauc plot from the absorption data of a MAPbI ₃ film. Bandgap E_g is obtained from the x-intercept.	77
Figure 3.10. Photoluminescence (PL) emission spectrum of a MAPbI ₃ thin film. Excitation wavelength is set at 600 nm, the peak position of PL emission is determined to be 774 nm.	78
Figure 3.11. Photoluminescence (PL) emission spectrum of a FAPbI ₃ thin film. Excitation wavelength is set at 450 nm, the peak position of PL emission is determined to be 804 nm.	79
Figure 3.12. Schematic of a TCSPC setup.	80
Figure 3.13. Schematic of an environmental chamber.	81

Figure 4.1. (a) Schematic illustration showing the p-i-n device architecture. (b) Cross-section scanning electron microscopy (SEM) image of a typical PSC.	88
Figure 4.2. Surface topography SEM images of $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ films deposited on (a) PTAA and (b) PF8TAA respectively. Scale bar (200 nm) is the same for PTAA and PF8TAA sample. Grain size analysis obtained from SEM images for $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ films deposited on (c) PTAA and (d) PF8TAA.	89
Figure 4.3. XRD patterns for $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ films deposited on ITO, PTAA and PF8TAA layers.	90
Figure 4.4. Statistical distribution of measured device parameters for PTAA and PF8TAA PSCs.	91
Figure 4.5. (a) J–V curves obtained for devices with the highest V_{OC} values, (b) External quantum efficiency (EQE) spectra of PTAA and PF8TAA PSCs.	93
Figure 4.6. The reverse (from open circuit to short circuit) and forward (from short circuit to open circuit) J-V curves of devices employing (a) PTAA and (b) PF8TAA as HTLs.	93
Figure 4.7. J–V curves of champion PTAA and PF8TAA PSCs, employing MAPbI_3 as light absorber.	94
Figure 4.8. The molecular structures of PTAA and PF8TAA.	84
Figure 4.9. (a) Ambient pressure photoemission spectroscopy (APS) spectra of PTAA, PF8TAA and $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ films (three plots at different X, Y scales). (b) Tauc plots from the UV-vis spectra (Appendix) of PTAA, PF8TAA and $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ films.	85

Figure 4.10. Flat band energy diagram at the HTL/perovskite interfaces.	86
Figure 4.11. (a) Light intensity dependent photoluminescence measured on PTAA and PF8TAA PSCs (b) Light intensity dependent V_{OC} measured on PTAA and PF8TAA PSCs respectively, with extracted ideality factors.	96
Figure 4.12. Schematic representations of the band diagrams at open circuit, under (a) low light conditions and (b) high light conditions.	99
Figure 4.13. Time-resolved photoluminescence spectroscopy of neat, $FA_{0.95}Cs_{0.05}PbI_3$, PTAA/ $FA_{0.95}Cs_{0.05}PbI_3$, and PF8TAA/ $FA_{0.95}Cs_{0.05}PbI_3$ films over the time ranges (a) 0-100 ns and, (b) 0 – 400 ns.	100
Figure 4.14. Photographs of $FA_{0.95}Cs_{0.05}PbI_3$ films aged under different testing conditions: (1) light and humid (1 sun illumination, 75% RH), (2) dark and humid (75% RH), 3) light and dry (1 sun illumination, 13% RH), (4) dark and dry (13% RH). The size of each substrate is 1.2 cm × 1.2 cm.....	103
Figure 4.15. X-ray diffraction (XRD) patterns of perovskite films at 0 h (fresh). The diffraction peaks of α -FAPbI ₃ are labelled in the plots.....	104
Figure 4.16. XRD patterns of perovskite films aged under different testing conditions: (1) light and humid (1 sun illumination, 75% RH), (2) dark and humid (75% RH), 3) light and dry (1 sun illumination, 13% RH), (4) dark and dry (13% RH). The peaks assigned to α -phase and δ -phase are labelled on the plots, and * denotes PbI ₂ peak.	105

Figure 4.17. XRD analyses of fresh (0 h) and aged (32 h) films on the α -phase (001) peak: (a) perovskite peak position, (b) d-spacing, (c) integrated peak area, (d) corresponding crystallite size of perovskite on three different substrates, ITO, PTAA, and PF8TAA. 107

Figure 5.1. Schematic illustration of traditional deposition method and sequential dynamic deposition (SDD) method for preparing the perovskite film. 117

Figure 5.2. Schematic illustration of peel-off method to obtain the bottom-side of perovskite films. 118

Figure 5.3. (a-b) Photographs of perovskite films from the (a) top side and (b) bottom side. The size of the substrate is 1.2 cm $\times$ 1.2 cm. (c-d) Corresponding surface scanning electron microscopy (SEM) images from (c) top side and (d) bottom side. The scale bar (200 nm) is the same for both images. 119

Figure 5.4. Surface topography and grain size distribution of perovskite films from the top side. (a-f) Surface SEM images of $\text{FA}_{0.95}\text{MA}_{0.05}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$ films with different amount of MACl: (a) pristine (without addition), (b) 1 mg/ml MACl, (c) 3 mg/ml MACl, (d) 5 mg/ml MACl, (e) 7 mg/ml MACl, and (f) 9 mg/ml MACl. The scale bar (200 nm) is the same for all images. (g) Grain size distribution of the films as a function of MACl concentration (0, 1 mg/ml, 3 mg/ml, 5 mg/ml, 7 mg/ml, and 9 mg/ml). 121

Figure 5.5. Surface topography and grain size distribution of perovskite films from the bottom side. (a-f) Surface SEM images of $\text{FA}_{0.95}\text{MA}_{0.05}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$ films with different amount of MACl: (a) pristine (without addition), (b) 1 mg/ml MACl, (c) 3 mg/ml MACl, (d) 5 mg/ml MACl, (e) 7 mg/ml MACl, and (f) 9 mg/ml MACl. The scale bar (200

nm) is the same for all images. (g) Grain size distribution of the films as a function of MACl concentration (0, 1 mg/ml, 3 mg/ml, 5 mg/ml, 7 mg/ml, and 9 mg/ml)..... 123

Figure 5.6. Cross-section morphology of vertical crystallization and the schematic of perovskite formation. (a-f) Cross-section SEM images of $\text{FA}_{0.95}\text{MA}_{0.05}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$ films with different amount of MACl: (a) pristine (without addition), (b) 1 mg/ml MACl, (c) 3 mg/ml MACl, (d) 5 mg/ml MACl, (e) 7 mg/ml MACl, and (f) 9 mg/ml MACl. The scale bar is the same for all images. 124

Figure 5.7. (a) Perovskite PL peak position as a function of MACl concentration, (b) Perovskite PL peak intensity as a function of MACl concentration. 125

Figure 5.8. Ultraviolet-visible (UV-vis) absorption spectra of perovskite with different MACl concentrations 126

Figure 5.9. (a) X-ray diffraction (XRD) pattern of perovskite with different MACl concentrations, and (b) Zoom-in figure of the (001) peak. 128

Figure 5.10. X-ray diffraction (XRD) analyses on the α -phase (001) peak. (a) Perovskite peak position as a function of MACl concentration. (b) d spacing as a function of MACl concentration. (c) Integrated peak area of the (001) peak as a function of MACl concentration. (d) Corresponding crystallite size as a function of MACl concentration. 130

Figure 5.11. Representative J-V curves of PSCs with different MACl concentrations, measured with reverse scan (scan rate of 50 mV s^{-1}). 132

Figure 5.12. Statistical distribution of (a) short circuit current density (J_{sc}), (b) open circuit voltage (V_{oc}), (c) fill factor (FF), and (d) power conversion efficiency (PCE) on PSCs with different MACl concentrations..... 134

Figure 5.13. Cross-section SEM images of the 500nm (1.3M), 650nm (1.5 M) and 1 μ m (1.8 M) perovskite films (a-c) without MACl treatment, and (d-f) with MACl treatment respectively. Scale bar (200 nm) is the same for all images. 137

Figure 5.14. Power conversion efficiency (PCE) of PSCs as a function of perovskite layer thickness (500nm, 650nm, and 1 μ m), without and with MACl post treatment. Measured from 6 devices for each condition..... 139

Figure 5.15. Photovoltaic parameters of PSCs as a function of perovskite layer thickness (500nm, 650nm, and 1 μ m), without and with MACl post treatment. (a) short circuit current density (J_{sc}); (b) open circuit voltage (V_{oc}); (c) fill factor (FF). 139

Figure 5.16. Power conversion efficiency (PCE) of PSCs as a function of antisolvent dripping time (8 s, 10 s, 15 s, and 20 s), with respect to three different antisolvents: diethyl ether (DE), chlorobenzene (CB), and toluene; (a) without and (b) with MACl treatment. Measured from 6 devices for each condition. 141

Figure 5.17. Photovoltaic parameters of PSCs as a function of perovskite layer thickness (500nm, 650nm, and 1 μ m), without and with MACl post treatment. Top panel: short circuit current density (J_{sc}); Middle panel: open circuit voltage (V_{oc}); Bottom panel: fill factor (FF). 143

Figure 5.18. Photographs of perovskite films with different MACl concentrations (x mg/ml, x=1, 3, 5, 7) aging in ambient air (30% RH) for different times (0 – 666 h). The

corresponding perovskite films are termed as MACI-x for convenience. The substrate size is 1.2 cm × 1.2 cm for each film..... 148

Figure 5.19. XRD patterns of perovskite films with different MACI concentrations before (0 h) and after (666 h) aging. (a) Fresh films (0 h). (b) Zoom-in figure of the (001) peak of fresh films. (c) Aged films (666 h). (d) Zoom-in figure of the (001) peak of aged films. δ denotes δ -FAPbI₃, α denotes α -FAPbI₃ and * denotes PbI₂. The diffraction peaks of α -FAPbI₃ are labelled in the plots (a) and (c). 150

Figure 5.20. XRD analyses of fresh (0 h) and aged (666 h) films on the α -phase (001) peak: (a) Perovskite peak position as a function of MACI concentration. (b) d spacing as a function of MACI concentration. (c) Integrated peak area as a function of MACI concentration. (d) Corresponding crystallite size of perovskite as a function of MACI concentration..... 152

Figure 5.21. XRD patterns of perovskite films with different MACI concentrations for different times. 156

Figure 8.1. Ultraviolet-visible (UV-vis) absorbance spectra for PTAA, PF8TAA and FA_{0.95}Cs_{0.05}PbI₃ respectively. 183

Figure 8.2. Steady state photoluminescence (PL) spectra of perovskite with different MACI concentrations (Reference, 1 mg/ml, 3 mg/ml, 5 mg/ml, and 7 mg/ml). 184

Figure 8.3. Photographs of FAPbI₃ films at different environmental conditions (light, dark, and heating) with 75% RH. The size of each substrate is 1.2 cm × 1.2 cm... 185

Figure 8.4. XRD patterns of FAPbI₃ films aged at different environmental conditions (light, dark, and heating) with 75% RH. The peaks assigned to α -phase and δ -phase are labelled on the plots, and * denotes PbI₂ peak..... 186

Figure 8.5. Photographs of FAPbI₃ films aged under different testing conditions: (1) light and humid (1 sun illumination, 75% RH), (2) dark and humid (75% RH), 3) light and dry (1 sun illumination, 13% RH), (4) dark and dry (13% RH). The size of each substrate is 1.2 cm $\times$ 1.2 cm. 188

Figure 8.6. X-ray diffraction (XRD) patterns of perovskite films before aging at 0 h (fresh). The diffraction peaks of α -FAPbI₃ are labelled in the plots. 189

Figure 8.7. XRD patterns of fresh and aged perovskite films under different testing conditions: (1) light and humid (1 sun illumination, 75% RH), (2) dark and humid (75% RH), 3) light and dry (1 sun illumination, 13% RH), (4) dark and dry (13% RH). The peaks assigned to α -phase and δ -phase are labelled on the plots, and * denotes PbI₂ peak..... 192

List of Tables

Table 2.1. Ionic radii of commonly used ions in ABX_3 perovskite materials. (Adapted from ref ^{5, 12}).....	37
Table 4.1. Grain size analyses of perovskite film deposited on PTAA and PF8TAA.....	89
Table 4.2. Statistical distribution of PV parameters for $FA_{0.95}Cs_{0.05}PbI_3$ PSCs.....	92
Table 4.3. PV parameters for champion cells using $MAPbI_3$ PSCs.....	94
Table 4.4. Energetic properties of PTAA, PF8TAA and $FA_{0.95}Cs_{0.05}PbI_3$ obtained from ambient pressure photoemission spectroscopy (APS) and UV-vis spectra, all units given in eV.....	86
Table 4.5. Calculated XRD parameters of the α -phase (001) peak, for fresh (0 h) and aged (32 h) perovskite films on different testing conditions.	109
Table 5.1. Corresponding band gap energy obtained from Tauc method.....	127
Table 5.2. Calculated X-ray diffraction (XRD) parameters of the α -phase (001) peak.	131
Table 5.3. Photovoltaic parameters of PSCs with different MACl concentrations. Measured from 6 devices for each condition.....	135
Table 5.4. Photovoltaic parameters of PSCs with different perovskite thicknesses (500nm, 650nm, and 1 μ m), without and with MACl post treatment. Measured from 6 devices for each condition.....	140

Table 5.5. Photovoltaic parameters of PSCs using DE as antisolvent. Measured from 6 devices for each condition.	146
Table 5.6. Photovoltaic parameters of PSCs using CB as antisolvent. Measured from 6 devices for each condition.	146
Table 5.7. Photovoltaic parameters of PSCs using toluene as antisolvent. Measured from 6 devices for each condition.	147
Table 5.8. Calculated XRD parameters of the α -phase (001) peak, for fresh (0 h) and aged (666 h) perovskite films with different MACl concentrations.	154

Abbreviations

APS	Air photoemission spectroscopy
BCP	Bathocuproine
CB	Conduction band
CdTe	Cadmium telluride
CIGS	Copper indium gallium selenide
CTL	Charge transport layer
DE	Diethyl ether
DMF	N, N-Dimethyl methanamide
DMSO	Dimethyl sulfoxide
DSSC	Dye sensitized solar cell
EQE	External quantum efficiency
ETL	Electron transport layer
FA	Formamidinium
FAPbI ₃	Formamidinium lead iodide
FF	Fill factor
FTO	Fluorine-doped tin oxide
FWHM	Full width half maximum

HCVD	Hybrid chemical vapor deposition
HOMO	Highest occupied molecular orbital
HTL	Hole transport layer
ITO	Indium-doped tin oxide
J _{sc}	Short circuit current
KP	Kelvin probe
LUMO	Lowest unoccupied molecular orbital
MA	Methylammonium
MACl	Methylammonium chloride
MAI	Methylammonium iodide
MAPbI ₃	Methylammonium lead iodide
NMP	1-Methy-2-pyrrolidinone
OPV	Organic photovoltaic
PCBM	Phenyl-C61-butyric acid methyl ester
PCE	Power conversion efficiency
PEDOT: PSS	Poly (3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
PFN-Br	Poly (9,9-bis (3'-(N, N-dimethyl)-N-ethylammonium-propyl-2,7-uorene)-alt-2,7-(9,9-dioctyluorene)) dibromide
PL	Photoluminescence

PLD	Pulsed layer deposition
PSC	Perovskite solar cell
PTAA	Poly[bis(4-phenyl) (2,4,6-trimethylphenyl) amine]
PTPD	poly[N, N'-bis(4-butylphenyl)-N,N'-bisphenylbenzidine]
PV	Photovoltaic
PVD	Physical vapor deposition
SDD	Sequential dynamic deposition
SEM	Scanning electron microscopy
TCO	Transparent conductive oxide
TCSPC	Time correlated single photon counting
TRPL	Time-resolved photoluminescence spectroscopy
UV-vis	Ultraviolet-visible spectroscopy
VASP	Vapor-assisted solution process
VB	Valence band
V _{oc}	Open circuit voltage
XRD	X-ray diffraction

Publications

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Declaration of Contributions

Chieh-Ting Lin aided with solar cell optimization, developed the peel-off method, and aided with data discussion and analysis.

Tian Du aided with external quantum efficiency (EQE) measurement, data discussion and analysis.

Thomas J. Macdonald aided with solar cell optimization and data discussion.

Yi-Chun Chin carried out the air photoemission spectroscopy (APS) and Kelvin probe (KP) measurement.

Weidong Xu carried out the light-intensity dependent photoluminescence (PL) measurement.

1. Introduction

1.1 Motivation

With increasing global energy consumption and a diminishing supply of traditional fossil fuels, the development of renewable energy has been extensively investigated. Traditional sources also have negative effects on climate and environment. Furthermore, solar energy is one of the most abundant renewable energies which is clean and carbon-free, and solar energy can be easily converted into electricity via photovoltaic (PV) solar cell technologies.^{1, 2}

PV technologies have made notable progress with three generations of evolution. First generation solar cells are made of silicon wafers including monocrystalline and polycrystalline silicon. Second generation solar cells are based on thin film technologies and include amorphous silicon, cadmium telluride (CdTe) and copper indium gallium selenide (CIGS). Third generation solar cells utilize emerging PV technologies, such as organic solar cells, dye sensitized solar cells (DSSCs), nanocrystals, quantum dots and perovskite solar cells (PSCs).³

PSCs have emerged as a promising next-generation PV technology, offering high power conversion efficiency (PCE), easy processability, and low fabrication costs, owing to their excellent optoelectronic properties, such as high light absorption, long charge carrier diffusion lengths, and tunable bandgap *etc.* The unique optoelectronic properties of perovskite materials have driven intense research efforts in PSCs, with the PCE of PSCs improving from 3.8 % in 2009 to over 25.7 % recently (Figure 1.1).⁴ Additionally, PSCs have the potential to be fabricated using low-cost, scalable

solution-based processes, allowing for the production of large-area and flexible solar modules. As a result, further exploration and investigation into perovskite solar cells could potentially pave the way for the development of highly efficient and sustainable solar energy conversion systems.

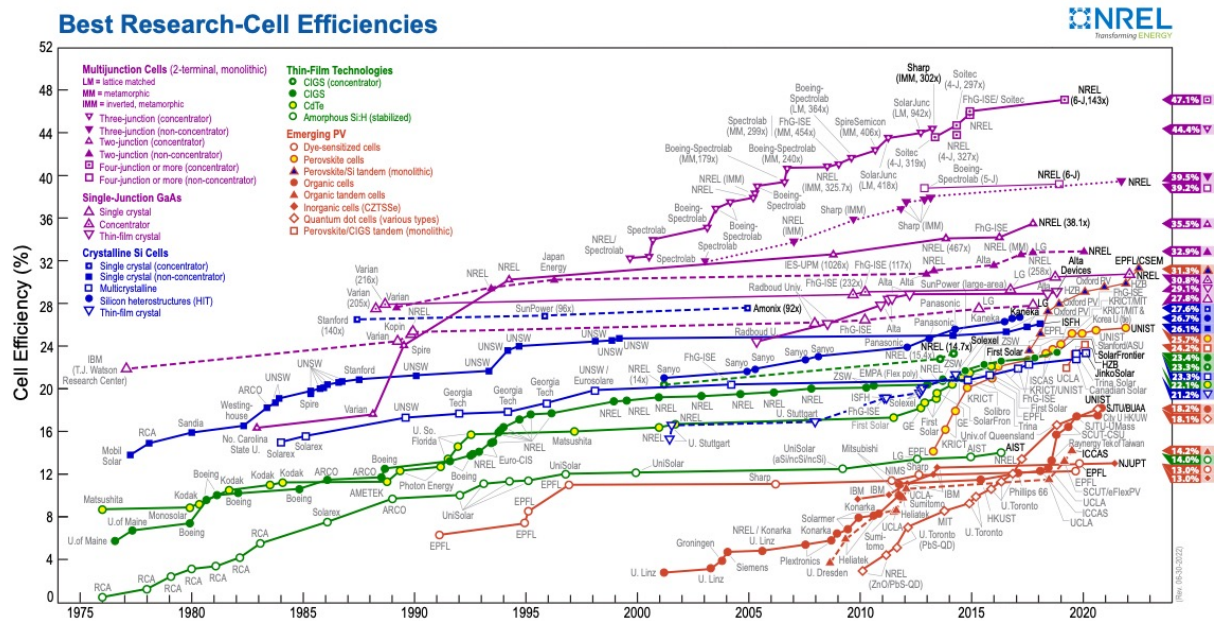


Figure 1.1. NREL best research cell efficiencies chart. Reproduced from ref.⁴

1.2 Project Objectives

The first results chapter investigates the role of the highest occupied molecular orbital (HOMO) level of the hole transport layer (HTL) on the open-circuit voltage (V_{OC}) of PSCs. The study aims to analyse and compare the HTL performance of two polymers, which have similar molecular structures, optical band gaps, and doping levels, but differ in their HOMO levels. This research employs light-intensity dependent steady-state photoluminescence (PL) and current density-voltage (J-V) measurements to investigate the relationship between the $HOMO_{HTL}$ and practical V_{OC} .

The second results chapter investigates the effectiveness and versatility of a novel sequential dynamic deposition (SDD) approach with methylammonium chloride (MACl) treatment in mitigating the imperfections and inhomogeneities of FA-based perovskite at the buried interfaces. The focus is on understanding the mechanism of MACl treatment in removing microstructural defects and enhancing the structural coherence of perovskite grains. The goal is to achieve continuous and uniform perovskite films on both top and bottom sides, increased grain sizes and crystallinity, reduced interfacial recombination, and enhanced device performance. This project also explores the reproducibility and scalability of the SDD approach with MACl treatment. Additionally, it aims to widen the processing window of narrow bandgap PSCs.

2. Literature Review

2.1 Fundamentals of Organic Lead Halide Perovskite Materials

2.1.1 Optoelectronic Properties of Perovskite Materials

Organic lead halide perovskites have the general formula of ABX_3 , where A is an monovalent cation, B is a divalent metal cation and X is a halogen anion. In an ideal cubic perovskite structure (Figure 2.1), the B cation (Pb^{2+} or Sn^{2+}) has a 6-fold coordination, surrounded by an octahedron of X anion (Cl^- , Br^- , I^-), and A has a 12-fold cuboctahedral coordination. In such a cubic unit cell, A cations are sitting at the corner of cubes, with B cations occupying the body-centered positions, and X anions occupying the face-centered positions.^{5, 6} The structural stability of perovskite materials can be predicted by the Goldschmidt tolerance factor (t). As an empirical index to predict perovskite crystal structure, the Goldschmidt tolerance factor can be described by the following equation:

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (1.)$$

Where r_A , r_B , and r_X are the ionic radii of A-site cations, B-site cations and X-site anions respectively. Ideally, when $t = 1$, a perfect cubic perovskite crystal structure can be formed. Generally, the perovskite materials preferentially form ideal cubic structure with t value ranging from 0.8 - 1. Whereas orthorhombic structure is formed when t value is smaller than 0.8, hexagonal structure is formed instead when t value is greater than 1.^{5, 7} Although the tolerance factor is mainly based on geometrical aspects of the

perovskite materials rather than physicochemical interactions between the ions, it provides valuable understanding about crystal structure transition and intrinsic stability of the perovskite materials.⁸

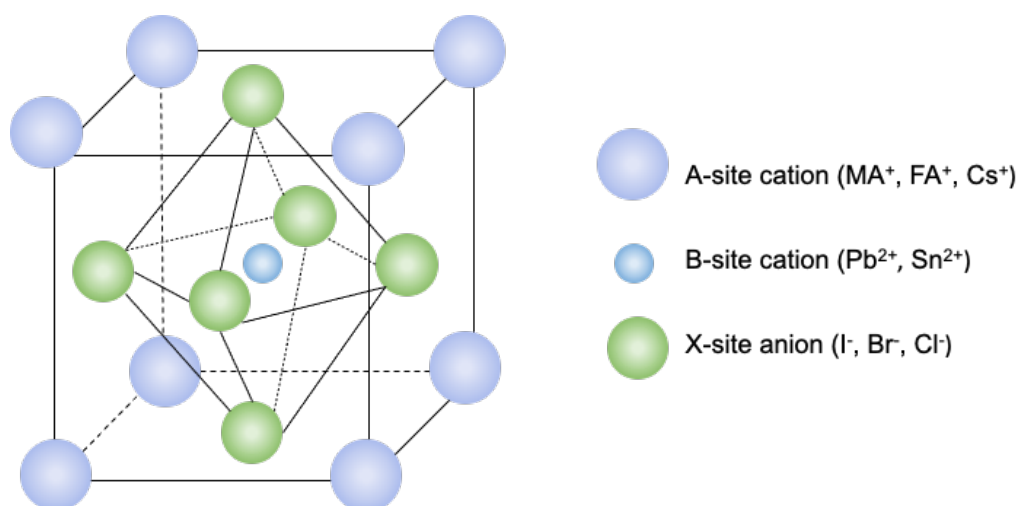


Figure 2.1. Crystal structure of organic lead halide perovskite.

Unlike conventional semiconductors, the ionic nature of perovskite materials makes these materials both more soluble in solutions with a range of polar aprotic solvents and easy to be processed through solution-based fabrication approaches. Nevertheless, the highly polar ionic chemical bonding of perovskite also tends to degrade readily with the presence of moisture, oxygen and polar solvent.⁸ Thus, it is necessary to find a feasible solution to address the environmental instability issue of perovskite materials. With the development of PSCs over recent decades, compositional engineering has been a valid way to tune the chemical bonding nature of perovskite materials, achieving not only enhanced efficiencies of PSCs, but also more thermodynamically stable devices in ambient environment.^{5, 7-11}

A-site cation-modified perovskites.

Cations in the A-site are not directly contribute to the band structure of perovskite materials, instead, they support the structural stability by charge compensation with the corner-sharing BX_6 octahedra.^{5, 8} Changes in size or symmetry of the A-site cations can alter the bond distance and angle, thus expand or contract the crystal lattice with resulting band gap variation. For the typical perovskite MAPbI_3 , the incorporation of a larger cation FA^+ ($r = 0.253 \text{ nm}$) can expand the lattice and reduce the band gap of the mixed cation perovskite system. Whereas adding smaller cation *i.e.* Cs^+ ($r = 0.188 \text{ nm}$) or Rb^+ ($r = 0.172 \text{ nm}$) into MA^+ ($r = 0.217 \text{ nm}$) perovskite can contract the crystal lattice thus increase the band gap (see Table 2.1).^{5, 12}

MAPbI₃. As the first widely developed perovskite absorber, MAPbI_3 has been extensively studied by a large number of researchers. At room temperature, MAPbI_3 forms a tetragonal structure and a Goldschmidt tolerance factor of 0.91.¹³ It is noted that MAPbI_3 undergoes a phase transition from tetragonal to cubic structure at elevated temperature around 54°C .^{8, 14, 15} The phase transition temperature sits within the solar cell operation window which has raised some concerns on the device performance as well as stability. Whereas some researchers reported the phase transition is slow and reversible, thus it should not be a problematic issue in practical application.^{14, 16-18}

FAPbI₃. Although pure MAPbI_3 has achieved remarkable PCEs over 22%, the relatively large band gap ($E_g = 1.5 \sim 1.61 \text{ eV}$)¹⁹⁻²¹ limits its potential to reach the

theoretical maximum performance according to Shockley-Queisser (S-Q) limit theory (ideally E_g between 1.1 ~1.4 eV).^{15, 22} As a popular alternative, FAPbI₃ has smaller band gap ($E_g = 1.47 \sim 1.55$ eV)²³⁻²⁶ which is ideal to reach the theoretical S-Q limit of single junction solar cells. Compared to MAPbI₃, the larger size of FA⁺ cation (253 pm)(tolerance factor $t = 0.99$) creates a higher activation energy barrier to intercalate with PbI₂ layers to form perovskite film, thus a higher annealing temperature is required for black cubic phase crystallization. For pure FAPbI₃, the black photoactive perovskite phase forms at 125~165 °C.^{7, 27-30} However, with its own issues, FAPbI₃ perovskite suffers from structure instability.⁸ The α (black) perovskite cubic phase can readily transform to δ (yellow) photoinactive hexagonal phase at room temperature due to the large ionic size of FA⁺.³¹

CsPbI₃. Similar to FAPbI₃, CsPbI₃ also possess two polymorphs, the α and δ phases, with a wide band gap. The black α -CsPbI₃ has a band gap of 1.73 eV, and typical band gap for yellow δ -CsPbI₃ is 2.82 eV.¹⁵ Compared to MA⁺ and FA⁺, the relatively smaller size of Cs⁺ cation (167 pm) and corresponding tolerance factor of 0.81 relate to its thermodynamic instability at room temperature.⁸ The black α -CsPbI₃ cubic phase can be preferentially formed at high temperature, typically above 300 °C, while it can easily transform to yellow δ -CsPbI₃ orthorhombic phase at room temperature which is a non-perovskite structure.³²

Mixed A-cation perovskites. The low environmental stability of pure FAPbI₃ can be modified by compositional engineering.^{6, 33, 34} The incorporation of the smaller cation MA⁺ into FA⁺ perovskite can stabilize the black cubic phase at room temperature and enhance device performance.^{10, 35} However, the photo and thermal stability of FA/MA

mixed perovskite are inferior to the pure FAPbI₃ counterpart, which correlates to a relatively higher activation energy barrier for FAPbI₃ ($115 \pm 3 \text{ kJ/mol}$) in contrast to MAPbI₃ ($93 \pm 8 \text{ kJ/mol}$).³⁶ An alternative choice is the addition of inorganic Cs⁺ cation, which does not weaken the stability of FAPbI₃. Instead, the partial replacement of Cs⁺ with FA⁺ can enhance the perovskite film stability in a humid environment.^{5, 8} The formation energy barrier of perovskite film is reduced because of the incorporation of Cs⁺, resulting in a relatively lower annealing temperature.^{37, 38} Lee *et al.* first introduced the FA/Cs mixed perovskite by adding 10% Cs *i.e.* FA_{0.9}Cs_{0.1}PbI₃, and it was found that a black perovskite is already formed at room temperature, upon successful tuning of the tolerance factor to form a cubic structure.³⁷ Compared to pure FAPbI₃, the crystallinity of FA/Cs mixed perovskite is improved and device performance is enhanced. The incorporation of Cs⁺ led to enhancement of the average PCE from 16.3% in FAPbI₃ to 17.1% in FA_{0.9}Cs_{0.1}PbI₃ devices, which is mainly contributed from the improved FF and V_{OC}. Apart from MA, FA and Cs cations, more diverse organic and inorganic cations (*e.g.*, GA, K, Rb) have been investigated as A-site dopants, as binary, ternary or other complex multi-cation systems. FA/Rb mixed perovskite (FA_{0.95}Rb_{0.05}PbI₃) was reported by Park *et al.* with enhanced moisture stability and device performance over pure FAPbI₃.³⁰ De Marco *et al.* firstly explored the use of large GA cation (278 pm) into MAPbI₃ perovskite as MA_xGA_{1-x}PbI₃.³⁹ It was found that MA/GA mixed perovskite films exhibit longer PL lifetime, resulting in enhanced charge carrier lifetime in devices thus improved PV performance. Peng *et al.* reported MA/FA/Cs mixed perovskite as Cs_{0.05}FA_{0.88}MA_{0.07}PbI_{2.56}Br_{0.44} with a remarkable PCE of 23.17% with high V_{OC} = 1.240 V and FF = 0.845.⁴⁰ More complex Rb/Cs/MA/FA mixed perovskite device was reported by Saliba *et al.* with a PCE of 21.6%, notably

achieving good thermal and light stability about retaining 95% of its initial PCE at 85°C over 500h of illumination.⁴¹

Table 2.1. Ionic radii of commonly used ions in ABX₃ perovskite materials. (Adapted from ref 5, 12)

A-site cation	Effective ionic radius (pm)	B-site cation	Effective ionic radius (pm)	X-site anion	Effective ionic radius (pm)
Ammonium, [NH ₄] ⁺	146	Lead, Pb ²⁺	119	Iodide, I ⁻	220
Methylammonium, [(CH ₃)NH ₃] ⁺ (MA ⁺)	217	Tin, Sn ²⁺	110	Bromide, Br ⁻	196
Formamidinium, [NH ₂ (CH)NH ₂] ⁺ (FA ⁺)	253	Germanium, Ge ²⁺	73	Chloride, Cl ⁻	181
Guanidinium, [C(NH ₂) ₃] ⁺ (GA ⁺)	278	Antimony, Sb ³⁺	76	Fluoride, F ⁻	129
Potassium, K ⁺	164	Bismuth, Bi ³⁺	103		
Rubidium, Rb ⁺	172				
Cesium, Cs ⁺	167				

X-site anion-modified perovskites.

Unlike A-site cations, anions in the X-site have direct influence on the band edge states of perovskite materials. Replacements of different halides in the X-site can dramatically alter the optoelectronic properties, such as band gap, charge carrier lifetime and diffusion length *etc.*^{5, 8}

I/Br mixed perovskites. Incorporating Br⁻ into a pure I⁻ perovskite generally increases the band gap because the smaller ionic radius of Br ion (196pm) compared to I ion (220pm) reduce the bond length between halide anion and the Pb, enhancing the coupling of atomic orbitals. Within relatively small portion of Br ions (0 - 20 %) as MAPb(I_{1-x}Br_x)₃ can enhance the device performance because of the improved V_{OC} and FF . Further increase of Br ions will decrease the PCEs due to the reduced J_{SC} , which is caused by relatively high band gap. Despite reduced PCEs at relatively high Br ion ratios over 20%, it is worth mentioning the superior ambient stability of perovskite devices observed at elevated Br ratios (>20 %), which is also true in ambient air conditions with RH > 50%.⁸ However, there is one major issue with I/Br mixed perovskite as photo-induced phase segregation, which is observed both in MAPb(I_{1-x}Br_x)₃ and FAPb(I_{1-x}Br_x)₃ systems.⁴²⁻⁴⁴

Cl-incorporated perovskites. It is widely reported that evolution of gaseous Cl occurs during film formation and thermal processing, thus there is some ambiguity regarding the Cl incorporation. Cl⁻ plays an indirect and positive role in perovskite devices.⁵ Cl-containing additives such as HCl,^{45, 46} NH₄Cl,⁴⁷ MACl⁴⁸⁻⁵⁰ etc. have been reported to improve crystallinity and morphology of perovskite, as a result of slowing the crystallization process, resulting in pin-hole free and uniform films - therefore enhancing the device performance. With addition of MACl in the MAPbI₃ system, the Cl ions facilitate the formation of intermediate MAPbI_{3-x}Cl_x phase during the crystallization process, which eventually transformed into MAPbI₃ films through the sublimation of MACl. The intermediate phase increases the grain sizes and crystallinity of perovskite films, therefore enhances the overall performance of PSCs.^{5, 8}

2.1.2 Recombination in Perovskite Materials

The charge-carrier recombination mechanism can be explained by the following recombination rate equation:

$$\frac{dn}{dt} = G - k_1 n - k_2 n^2 - k_3 n^3 \quad (2.)$$

where G is the charge-density generation rate, n is the charge-carrier density, k_1 is the first-order Shockley-Read-Hall (SRH) trapping rate constant, also termed as ‘monomolecular charge-carrier recombination’ to be nonradiative; k_2 is the second-order band-to-band electron-hole recombination rate constant, also called ‘bimolecular recombination’ to be radiative; k_3 is the third-order Auger recombination rate constant, to be nonradiative.^{8, 51} The recombination rate constants are estimated to be $k_1 = \sim 10^7 \text{ s}^{-1}$ for SRH trap-assisted recombination, $k_2 = \sim 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for radiative recombination, $k_3 = \sim 10^{-28} \text{ cm}^6 \text{ s}^{-1}$ for Auger recombination,³¹ for typical perovskite materials as MAPbI₃ and FAPbI₃.^{8, 51}

2.2 Perovskite Solar Cells

2.2.1 Solar Energy Evolution

Organic-inorganic metal halide perovskites were first introduced as a visible-light sensitizer in solar cells in 2009, when the Miyasaka group deposited nanocrystals of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ on TiO_2 surfaces of DSSCs. This work established the development of organic-inorganic perovskite technology with devices achieving a modest PCE of 3.8%.⁵² In 2011, the Park group applied $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanocrystals (2-3 nm in size) in quantum-dot-sensitized solar cells achieving a PCE of 6.5%.⁵³ However, these devices degraded rapidly due to perovskite dissolution in the corrosive liquid electrolyte. The metal halide perovskite instability issues were addressed by replacing the liquid electrolyte with a solid hole conductor spiro-OMeTAD in 2012.⁵⁴ The Park group reported this perovskite all-solid-state mesoscopic solar cells using $\text{CH}_3\text{NH}_3\text{PbI}_3$ as light harvesters with a PCE of 9.7%.⁵⁴ This report was a breakthrough as the first solid-state PSC. In the same year, the Snaith group introduced a meso-super structured PSC with a PCE of 10.9%, by replacing mesoporous n-type semiconductor TiO_2 with insulator Al_2O_3 .⁵⁵ These devices showed much faster electron transport through perovskite itself than mesoporous TiO_2 , indicating the outstanding ambipolar charge transfer ability of metal halide perovskites. In 2013, the Snaith group achieved 15% PCE in planar PSCs, showing the unnecessary of mesoporous structure.⁵⁶ In 2014, solvent engineering was introduced in solution process PSCs by the Seok group, yielding a remarkable PCE of 16.2%.⁵⁷ This fabrication method deposited dense and uniform film with well-controlled perovskite morphology by forming a $\text{CH}_3\text{NH}_3\text{I}-\text{PbI}_2$ -DMSO intermediate phase. Tremendous

efforts have been made on PSCs with recent years with the PCE record up to 25.7% in 2022.⁴

2.2.2 Device Architecture

Mesoporous structure As described above, perovskite solar cells developed from DSSCs, which consist of mesoporous structure with liquid electrolyte.^{58, 59} In 2012, Kim *et al.* reported the first solid-state perovskite solar cells using $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) as light absorber, mesoporous TiO_2 as scaffold and 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) as hole transport material.⁶⁰ The solid hole transport material spiro-OMeTAD was found to have better stability than the liquid electrolyte. The all-solid-state perovskite device achieved a PCE of 9.7%, with better device stability than the counterpart made with liquid electrolyte.⁵⁴ A typical mesoporous perovskite solar cell generally consists of a transparent conductive oxide (TCO), electron transport layer (ETL), mesoporous scaffold, photoactive perovskite layer, hole transport layer (HTL) and top metal electrode (Figure 2.2a).

Planar n-i-p structure Lee *et al.* reported the replacement of mesoporous TiO_2 scaffold by mesoporous insulator Al_2O_3 scaffold, with device achieving PCE of 10.9%.⁶¹ A significant finding is that the mesoporous TiO_2 is not necessary for the whole device structure, either as electron transport material or hole blocking material. The planar architecture is based on the Al_2O_3 -related study, which is a perovskite solar cell without the mesoporous structure. Ball *et al.* reported the first planar perovskite solar cell as FTO/c- TiO_2 /Perovskite/Spiro-OMeTAD/Au.⁶² Liu *et al.* from

the same group (Snaith) successfully fabricated planar n-i-p PSCs with an enhanced PCE of 15.4% via dual-source vapor deposition method in 2013.⁵⁶ A planar n-i-p perovskite solar cell, essentially a n-type ETL is deposited on TCO substrate, then a perovskite layer is spin-coated on top of it, followed by a p-type HTL and completed by a top metal electrode (Figure 2.2b).

Planar p-i-n structure. Here the relative position of respective charge transport layers is opposite that seen in planar p-i-n structures, namely, inverted planar structure. In other words, the perovskite active layer is sandwiched between the HTL on the bottom and ETL on top of it (Figure 2.2c). Guo *et al.* fabricated the first p-i-n PSC as ITO/PEDOT:PSS/CH₃NH₃PbI₃/PCBM/BCP/Al, with a PCE of 3.9%.⁶³ HTL is the poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT: PSS) and ETL is a fullerene derivative, [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM). Inverted planar p-i-n structure is preferred in many studies because of its low temperature processing, negligible hysteresis, compatibility with materials from OPVs and comparable efficiencies with conventional counterpart.

HTL-free structure. HTLs are usually p-type semiconductors that can effectively extract holes and block electrons from the perovskite layers, then transport to the electrode.⁶⁴ Commonly used HTLs are polymers (*e.g.* PTAA, PEDOT: PSS, PTPD), small molecules (*e.g.* Spiro-OMeTAD) and inorganic materials (*e.g.* NiO_x, CuSCN).^{5, 59, 64} Nevertheless, all these HTLs either need complicated synthesis routes or require high costs, as which PSCs made from them are difficult to achieve low-cost manufacture. HTL-free PSCs are needed for this reason and perovskite materials act as both light absorber and hole conductor owing to their ambipolar charge transport ability. The working mechanism of HTL-free PSCs is the formation of depletion region

between perovskite and ETLs, where the built-in field drives the charge separation process.^{58, 64} A typical conventional architecture is FTO/TiO₂/perovskite/Au (Figure 2.2d). Etgar *et al.* reported the first HTL-free PSC with a PCE of 5.5% in 2012.⁶⁵ In contrast, another type is the inverted architecture as ITO/perovskite/ETL/Ag. Inverted HTL-free PSCs was reported by Tsai *et al.* as ITO/CH₃NH₃PbI₃/PC₆₁BM/Bis-C₆₀/Ag with a PCE of 11.0%.⁶⁶ Li *et al.* also reported an enhanced PCE of 16.0% as ITO/CH₃NH₃PbI₃/C₆₀/BCP/Ag.⁶⁷

ETL-free structure. ETLs are typically n-type semiconductors which can effectively extract electrons and block holes from the active layer, and then transport to the counter electrode.^{64, 68} Some common ETLs are fullerene derivatives (e.g. PC₆₁BM, C₆₀), others are inorganics (e.g. TiO₂, SnO₂, ZnO).^{5, 64} Conventionally, the fabrication of ETLs requires high-temperature processing which is energy-consuming and high-cost. As mentioned before, the ambipolar ability of perovskite materials make it possible to remove the ETLs without affect the integrity of the device structure, whereas it still has the potential to achieve comparable performance as the full device stack. The working mechanism for ETL-free PSCs is not very clear yet, as some researchers believe the built-in field in the TCO and perovskite interface facilitate the charge transfer, while others speculate the charge accumulation in the perovskite bulk provide the driving force instead.^{58, 64} Typical ETL-free architecture is ITO/perovskite/HTL/metal (Figure 2.2e). In 2014, Liu *et al.* reported the first ETL-free PSC as ITO/CH₃NH₃PbI₃/P3HT/Ag with a PCE of 13.5%.⁶⁹

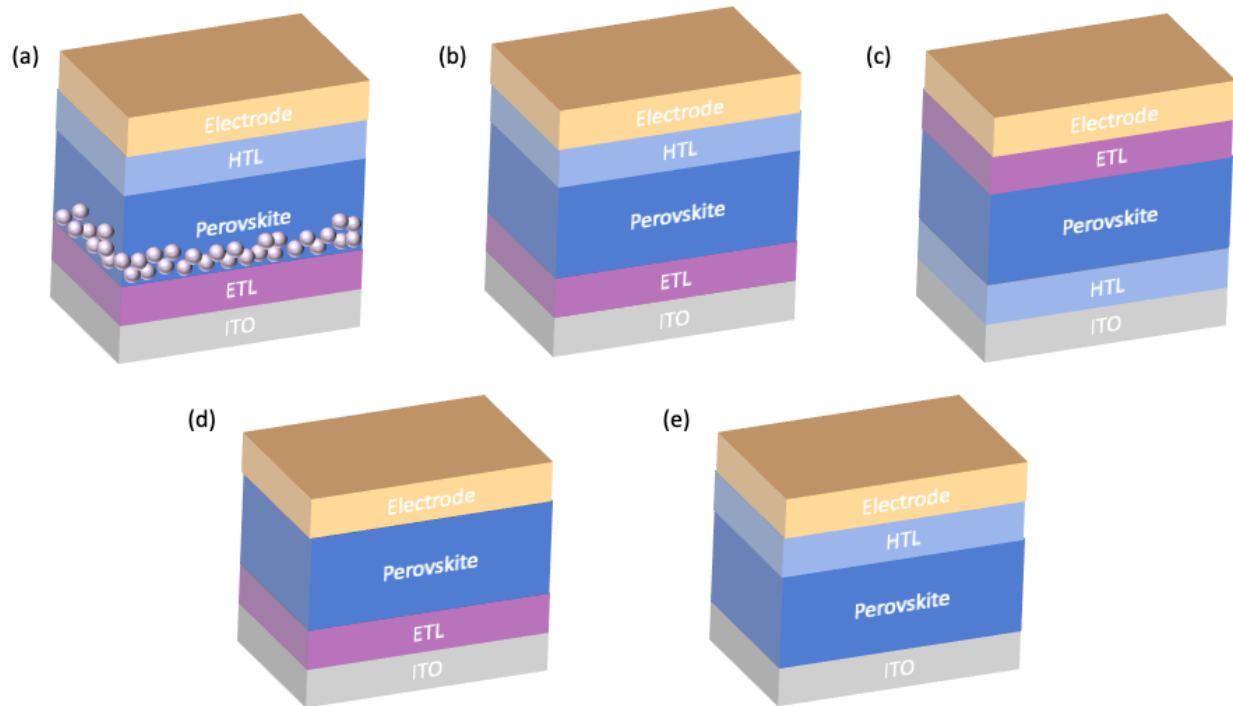


Figure 2.2. Device structures of perovskite solar cells. (a) mesoporous structure, (b) planar n-i-p structure, (c) planar p-i-n structure, (d) HTL-free structure, (e) ETL-free structure.

2.2.3 Working Principle

The working principle of PSCs is universally acknowledged as one in which the perovskite layer operates sandwiched between a p- and n-type layer (n-i-p or p-i-n), where the perovskite acts as an intrinsic light absorber between two charge transport layers (ETL/HTL).⁵ Light is absorbed by the perovskite and electron-hole pairs are subsequently generated. The electrons and holes are separated which are then extracted by the ETL and HTL respectively, followed by charge transport to the electrodes. Several optoelectronic processes happen during PSCs operation, including charge generation, separation, extraction, transport and collection. Charge

transport layers (*i.e.*, ETLs and HTLs) are expected to have suitable energy alignment with the light absorber as they play a vital role in solar cell operation (

Figure 2.3).⁵ The ETLs and HTLs are simultaneously required to selectively extract charge carriers and effectively block the opposing charge carrier in order to prevent charge recombination. Specifically, HTLs require a slightly shallower HOMO (highest occupied molecular orbit) or VB (valence band) to smoothly extract holes from VB of perovskite layer, along with a shallower LUMO (lowest unoccupied molecular orbit) or CB (conduction band) to effectively prevent electrons transport. As for ETLs, they need a slightly deeper LUMO or CB to productively extract electrons from the CB of perovskite layer. Also, ETLs need a deeper HOMO or VB to prevent holes transport from perovskite layer.

The dynamics of charge transfer processes consist of both desirable and undesirable routes (Figure 2.4). The desirable processes include photoexcitation of electron-hole pairs in the photoactive layer (1), electrons transfer from photoactive layer to ETL (2), hole transfer from active layer to HTL (3) and collection of electrons and holes respectively at two electrodes. While undesirable processes involve non-radiative recombination of electrons and holes within the active layer (4), electron transfer back from ETL to active layer (5), electron-hole recombination between the ETL and HTL (6), and hole transfer back from HTL to active layer (7).^{68, 70}

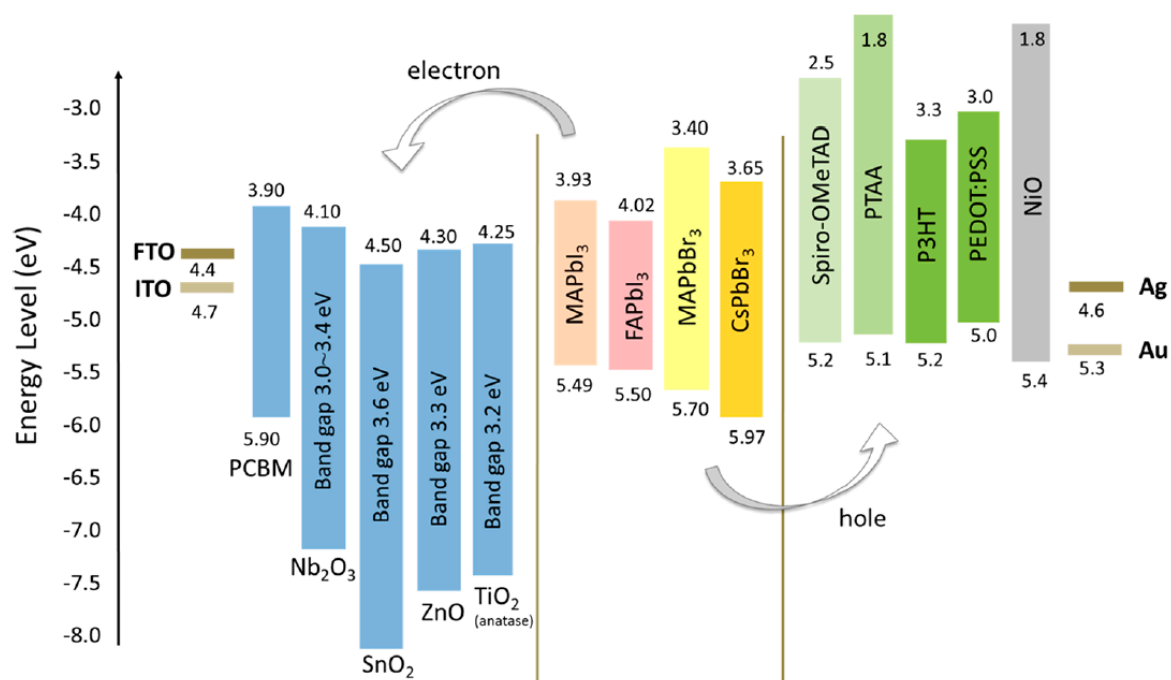


Figure 2.3. Energy level diagram of different materials in perovskite solar cells. Reproduced from Ref.⁵

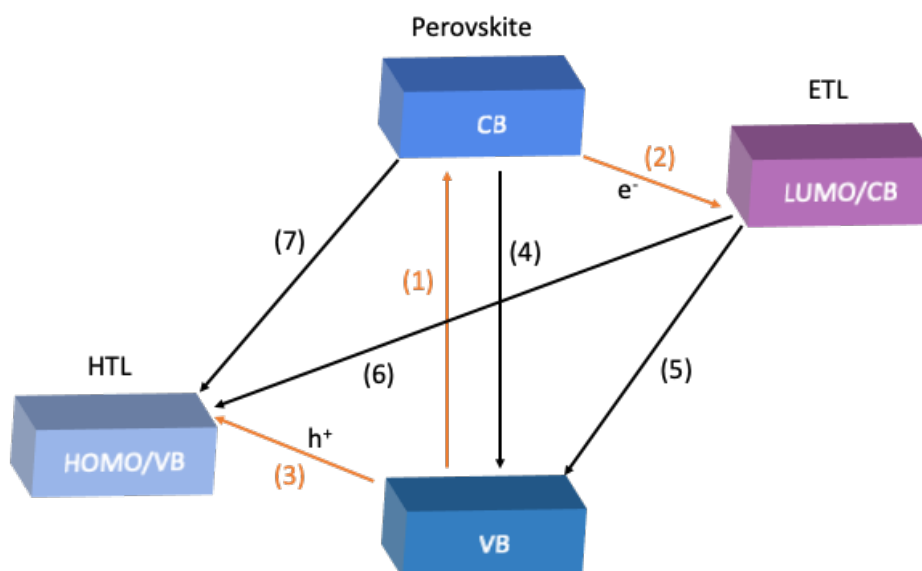


Figure 2.4. Charge transfer processes involved in perovskite solar cells.

2.3 Approaches in Achieving High-Efficiency Devices

2.3.1 Processing Engineering

Solution-based methods:

Two-step sequential deposition was initially proposed by Liang et al.,⁷¹ in which PbI_2 was deposited on the substrate as the first step, followed by dipping the deposited PbI_2 film into MAI solution to form MAPbI_3 during the second conversion step.⁶⁰ This two-step method was first applied to PSCs by Burschka et al. in 2013, yielding a PCE of 15%.⁷² In this method, it is crucial to control the solution concentration and dipping time for achieving uniform perovskite film with high crystallinity.^{34, 60} Two-step spin-coating method was then proposed to address these issues caused by dipping process (*Figure 2.5*).⁷³ The MAI was spin-coated onto as-deposited PbI_2 film, instead of immersing PbI_2 film into MAI solution previously. Im et al. fabricated PSCs yielding a PCE of 17% in 2014, with well-controlled grain growth of MAPbI_3 crystals.⁷³ Apart from these two-step strategies, perovskite films can also be fabricated through one-step spin-coating approach, in which perovskite was deposited and formed via spin-coating the precursor solution.⁶⁰ During the process, two key steps influence the perovskite formation: evaporation of excess solvents and crystallization of perovskite film. The main challenge for one-step method is the film shrinkage during the perovskite crystallization process induced by solvent evaporation. Though one-step spin-coating has less steps than two-step methods, generally it demonstrates inferior film morphology thus device performance to the two-step counterpart.³⁴ Approaches to improve this situation consist of two aspects: to retard the crystallization and to facilitate fast crystallization. By retarding the crystallization process, a smooth and

uniform precursor film can be formed initially, followed by slow crystallization of high-quality perovskite film.⁶⁰ This is usually achieved by manipulating solvent composition and applying additives.

Another effective approach to control crystal growth kinetics for high-performance PSCs is to facilitate fast crystallization of the perovskite.³⁴ Solvent engineering technology was proposed by Jeon et al. in 2014, resulting in extremely uniform perovskite film yielding a PCE of 16.5% without hysteresis (*Figure 2.6*).⁵⁷ Upon perovskite spin-coating process, an anti-solvent was drop-cast onto the film to facilitate the formation of an intermediate MAI-PbI₂-DMSO adduct phase. Normally, the anti-solvent (e.g. toluene, chlorobenzene, diethyl ether) cannot dissolve the perovskite film but is miscible with the precursor solvent.⁶⁰

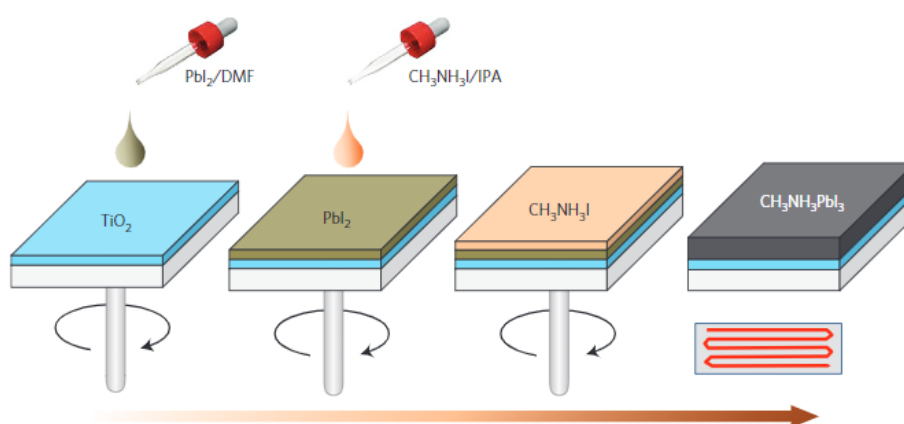


Figure 2.5. Two-step spin-coating method. Firstly, a 1M PbI₂ solution is spin-coated onto the m-TiO₂ film. The PbI₂-coated film is dried at 40 ° C for 3 min and 100 ° C for 5 min. Then a CH₃NH₃I solution is loaded onto as-deposited PbI₂ film for 20s and spun. Finally, the film is heated at 100 ° C for 5 min. Reproduced with permission.⁷³

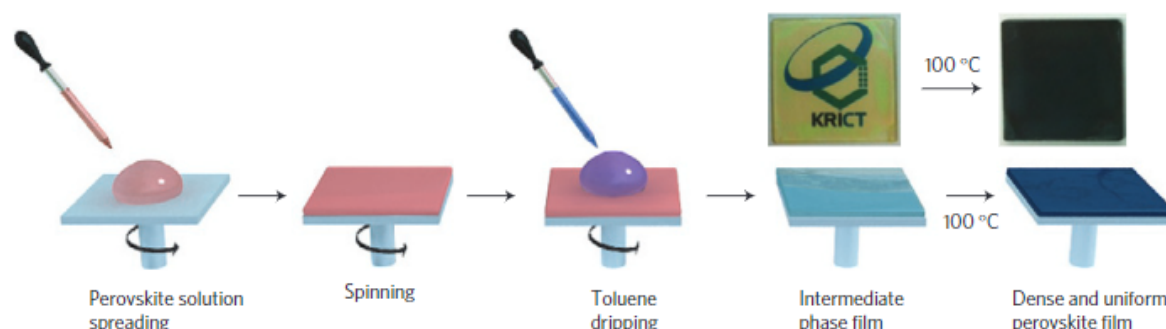


Figure 2.6. Solvent engineering process for preparing a uniform and dense perovskite film. Reproduced with permission.⁵⁷

Vacuum based methods:

Perovskite films can also be obtained using vacuum deposition techniques. In 2013, Liu et al. demonstrated co-evaporation of organic (MAI) and inorganic (PbI_2) source to fabricate flat and smooth perovskite absorber layers, comparing to the solution-processed counterpart with an undulating nature (*Figure 2.7*).⁵⁶ Another way to achieve thermal evaporation of perovskite is a sequential layer-by-layer vacuum sublimation method, introduced by Chen et al. in 2014 (*Figure 2.8*).⁷⁴ Firstly, PbCl_2 was deposited on substrate via thermal evaporation. Then, MAI was thermally sublimed onto the as-deposited PbCl_2 film, during which perovskite absorber will form as the transparent film gradually changing to dark brown color.^{34, 74} The resulting perovskite thin films are highly uniform and homogeneous with high coverage, which are promising to large-scale manufacture industry. Other vacuum based methods include vapor-assisted solution process (VASP), physical vapor deposition (PVD), hybrid chemical vapor deposition (HCVD) etc.³⁴ In VASP, a spin-coated PbI_2 film was treated with MAI vapor to form MAPbI_3 , this can also reduce the high vacuum input and

cost issue caused by the co-evaporation.⁷⁵ Chen et al. developed this VASP in 2014, fabricating perovskite films with full surface coverage and small surface roughness, and their grain sizes were up to microscale for high-performance PSCs. In PVD method, the perovskite film is produced via a single-source thermal evaporation of the prepared single-crystalline MAPbI_3 , reported by Fan et al. in 2016.⁷⁶ As a combination of vapor-based scalable deposition methods (PVD, CVD, spray coating etc.), HCVD was first introduced by Leyden et al. in 2014, with the advantages of scalable perovskite films, well-controlled gas flow rate, and high reproducibility.⁷⁷ For large-scale manufacture, there are other fabrication methods such as blade coating, spray coating, slot-die coating, inject printing, screen printing etc.^{34, 78}

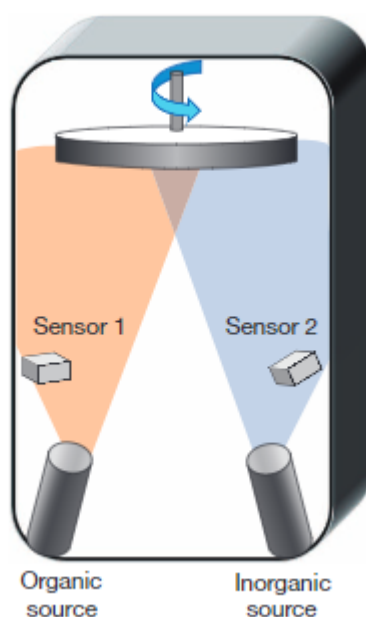


Figure 2.7. Dual-source thermal evaporation system for depositing perovskite using MAI and PbI_2 (or PbCl_2). Reproduced with permission.⁵⁶

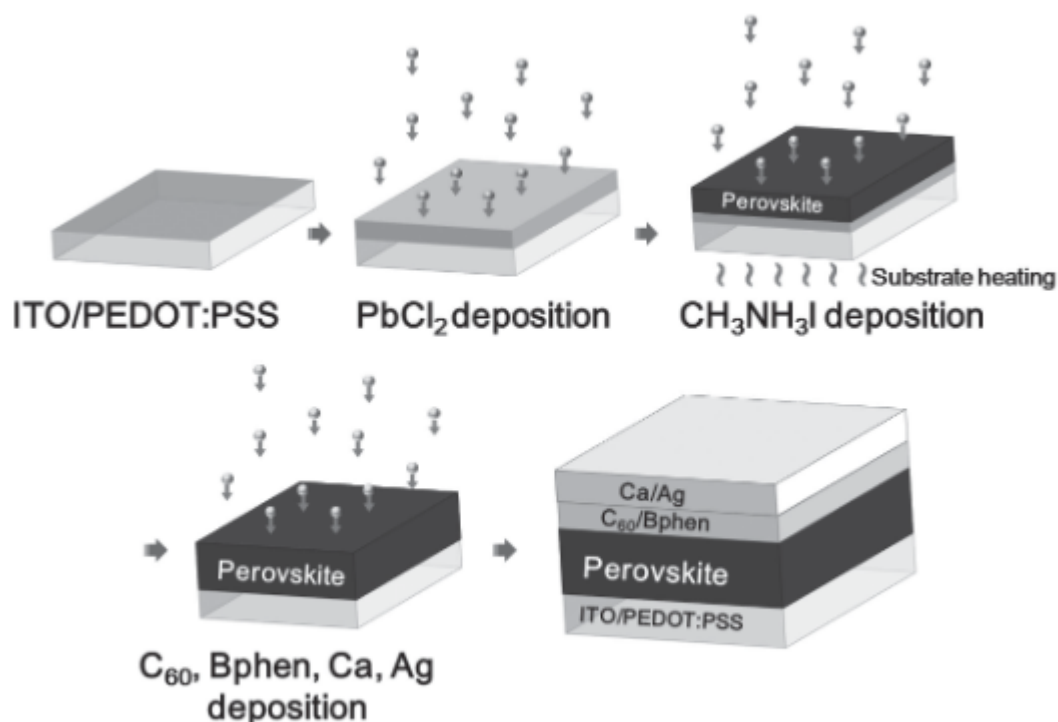


Figure 2.8. Sequential layer-by-layer vacuum deposition to fabricate perovskite solar cells. Reproduced with permission.⁷⁴

2.3.2 Interface Engineering

Interface engineering has been crucial to perovskite device optimization since the interfaces have great influence on PV parameters and operation lifetime.⁷⁹ These PV parameters (J_{sc} , V_{oc} , FF, PCE) are highly related to the charge extraction and transport between the charge transport layers (CTLs) and perovskite absorber. To optimize device parameters, it is of paramount importance to improve the interface quality to minimize non-radiative recombination at interfaces.⁷⁹ The main roles of different interface engineering approaches include but are not limit to: (a) passivation of defects at the interfaces through filling vacancies and fixing interstitial atoms; (b)

enhanced charge extraction through energy level alignment; (c) perovskite grain growth optimization to facilitate homogenous, uniform and smooth perovskite films.⁷⁹⁻

⁸¹ In typical PSCs, the most critical interfaces are ETL/perovskite, perovskite/HTL and CTLs/electrodes, which play a significant and immeasurable role on device performance and long-term stability. Besides, grain boundaries in the perovskite active layer which are the interfaces between polycrystalline domains, should also be carefully considered during device optimization.⁸⁰ Malinkiewicz *et al.* introduced poly-TPD as an electron blocking layer between PEDOT: PSS and perovskite to suppress charge recombination at HTL/perovskite interface.⁸² Zhou *et al.* used Yttrium-doped TiO₂ (Y-TiO₂) as ETL to modify the adjacent interfaces. Compared to the reference devices, the modified Y-TiO₂ devices showed reduced charge recombination and faster charge injection.⁸³ Shao *et al.* illustrated the photocurrent hysteresis in perovskite materials originates from the trap states present on their surface and grain boundaries. They found that depositing a PCBM layer on the perovskite can effectively passivate these charge trap states, resulting in the elimination of photocurrent hysteresis (Figure 2.9). Additionally, optimizing the thermal annealing process of the PCBM layer reduces interfacial charge recombination and increases charge carrier mobility.⁸⁴ Later, Chiang and Wu developed a bulk-heterojunction p-i-n device by incorporating PCBM molecules directly into the perovskite film, specifically at or near the grain boundaries (Figure 2.10). This led to a significant improvement in electronic properties by balancing electron and hole mobility and extending the charge carriers diffusion lengths, resulting in a highly enhanced fill factor, J_{SC}, and reduced hysteresis in the device.⁸⁵

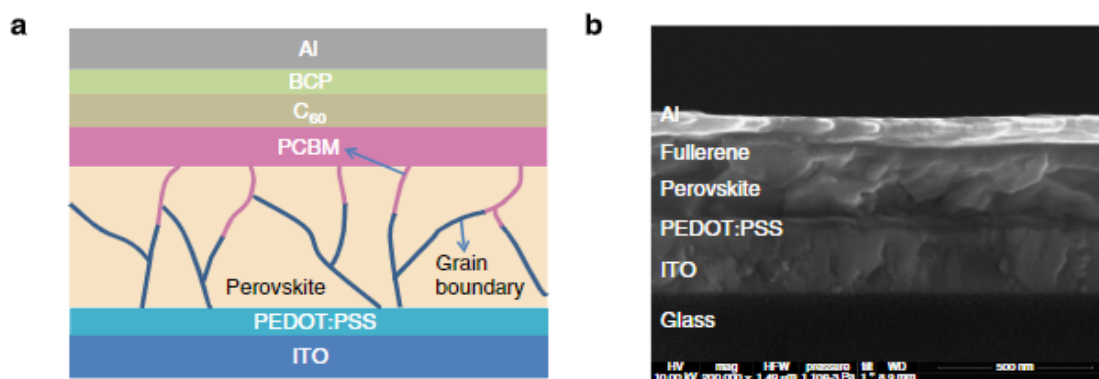


Figure 2.9. a) Device structure with PCBM migrated into perovskite grain boundaries. b) Cross-section SEM image of perovskite device. Reproduced with permission.⁸⁴

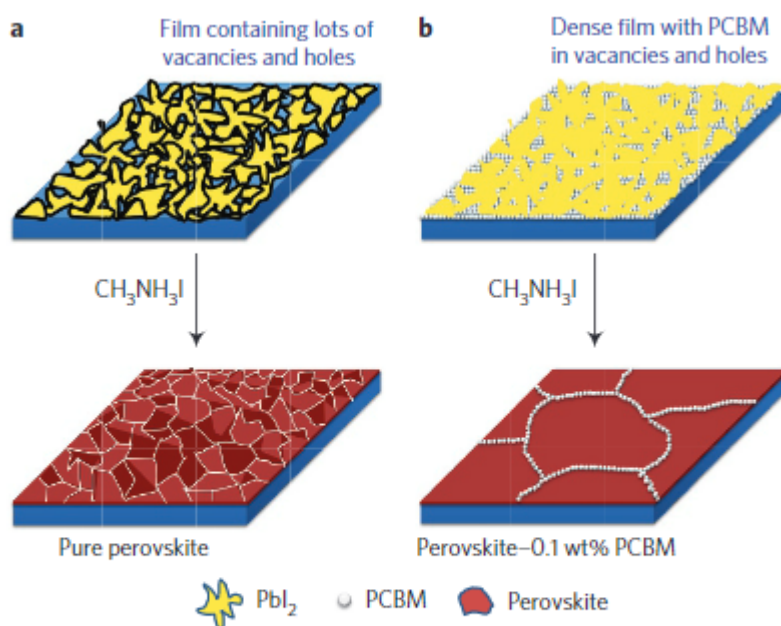


Figure 2.10. The mechanism for the formation of perovskite grains in the a) absence and b) presence of PCBM. The perovskite grains are much larger with the presence of PCBM. Reproduced with permission.⁸⁵

2.3.3 Additive Engineering

The introduction of additives can assist perovskite crystallization processes and film formation, passivation of defects in the perovskite bulk or at the interfaces. Additionally, additives may also influence the tuning the interface structure and energy level alignment.⁸⁶ Common additives include: Lewis bases, Lewis acids, ammonium salts, low-dimensional perovskites and ionic liquids (Figure 2.11).⁸⁶

Lewis bases are generally electron donors, which have the ability to passivate defects by forming a Lewis adduct with positive charged ions Pb^{2+} . Common Lewis bases additives include O-donors (e.g. *N,N*-Dimethylformamide (DMF)^{57, 87}, dimethyl sulfoxide (DMSO)^{57, 88-91}, 1-Methy-2-pyrrolidinone (NMP)⁹²), S-donors (e.g. thiophene⁹³, thiourea⁹⁴ and their derivatives⁹⁵⁻⁹⁸) and N-donors (e.g. $-\text{NH}_2$ derivatives⁹⁹, pyridine^{100, 101}, and pyridine derivatives¹⁰²).

Lewis acids can passivate defects and reduce undesirable non-radiative recombination by forming a Lewis adduct with electron rich defects such as halide anions and PbI_3^- . Typical examples are metal cations (e.g. PbI_2 ¹⁰³⁻¹⁰⁶, $\text{Pb}(\text{SCN})_2$ ¹⁰⁷, sodium ions (Na^+) in NaCl ¹⁰⁸, NaF ¹⁰⁹, potassium ions (K^+) in KI ¹¹⁰⁻¹¹⁴) and fullerene derivatives (e.g. C_{60} derivatives¹¹⁵⁻¹¹⁸, phenyl- C_{61} -butyric acid methyl ester (PC_{61}BM)^{84, 85, 119}).

Ammonium salts derivatives has the capability of facilitating perovskite crystal growth and enhancing film morphology, examples are organic halides (e.g. methylammonium iodide (MAI)^{120, 121}, methylammonium bromide (MABr)¹²², methylammonium chloride (MACl)¹²³⁻¹³²), ammonium chloride (NH_4Cl)¹³³⁻¹³⁶, ammonium thiocyanate (NH_4SCN)¹³⁷⁻¹³⁹ and ammonium acetate($\text{CH}_3\text{CO}_2\text{NH}_4$)¹⁴⁰ etc.

Low-dimensional 2D perovskite are attractive additives because of their higher moisture and phase stability compared to their conventional 3D perovskite counterparts. Previously reports on low-dimensional perovskite components include EDAPbI₄ (ethylenediamine, EDA)¹⁴¹, PEA₂PbI₄¹⁴²⁻¹⁴⁵, phenylethylammonium iodide (PEAI)¹⁴⁶, and FEAPbI₃¹⁴⁷ *etc.*

Ionic liquids are salts in the liquid state which usually consist of large organic cations, organic and inorganic anions. Ionic liquids possess high ionic conductivity and high electrochemical stability and thermal stability. Ionic liquid additives have the beneficial effects on suppressed ion migration,¹⁴⁸ defect passivation and controlling perovskite crystallization with enlarged grains.⁸⁶ Examples of reported additives are methylammonium formate (MAF)¹⁴⁹, 1-hexyl-3-methylimidazolium chloride (HmImCl)^{150, 151}, 1-butyl-3-methylimidazoliumtetrafluoroborate (BMIMBF₄)¹⁵², and 1-(4-ethenylbenzyl)-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctylimidazolium iodide (ETI)¹⁵³ *etc.*

Overall, additive engineering has been shown to have positive effects on controlling perovskite morphology, influencing grain boundary modification, grain size enhancement, charge recombination minimization, and optimization of defect density.¹⁵⁴ Further development on the additive engineering will facilitate the achievement of higher performance PSCs with better operation stability in the long run.¹⁵⁵

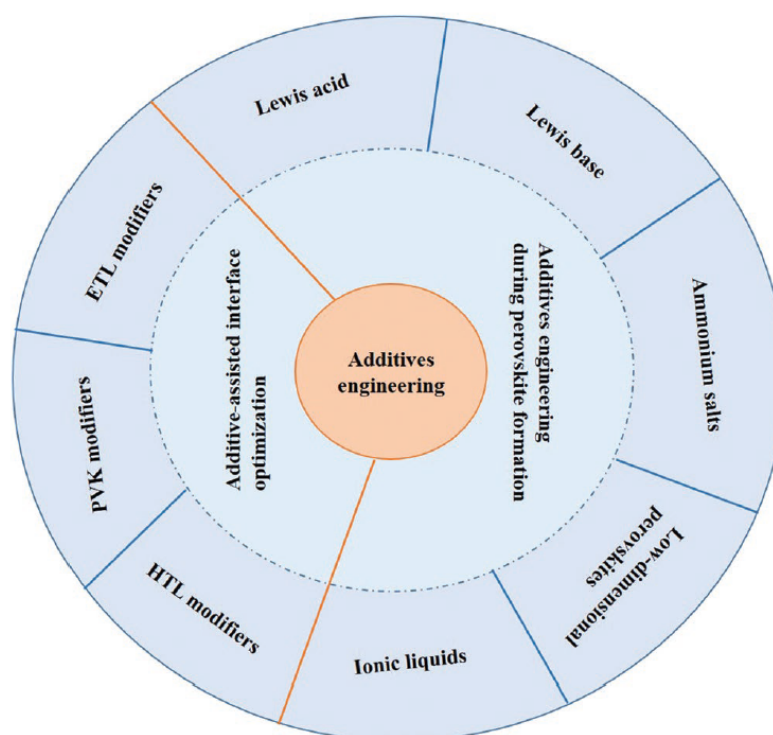


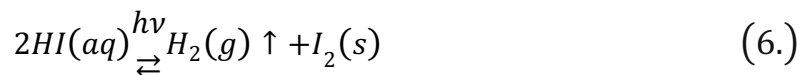
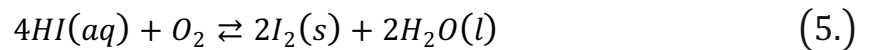
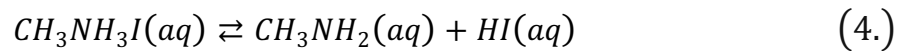
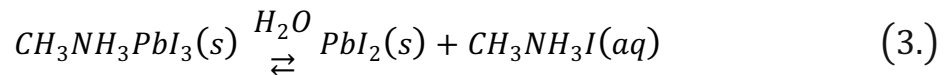
Figure 2.11. Summary on different strategies of additive engineering. Reproduced with permission.⁸⁶

2.4 Challenges of Perovskite Solar Cells

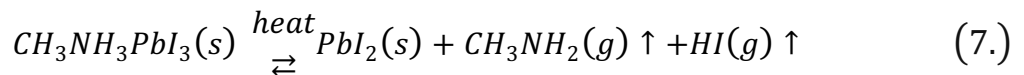
2.4.1 Stability

The long-term stability and robustness of perovskite devices are of great importance to be considered for device operation, which is particularly critical for commercialization of PSCs.^{156, 157} The degradation of PSCs usually derive from two aspects, extrinsic factors (e.g. moisture, oxygen, heat and UV light) and intrinsic factors (e.g. structure, phase, ion migration, interfacial reactions).^{78, 156}

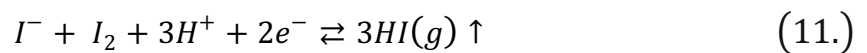
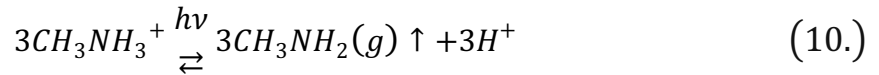
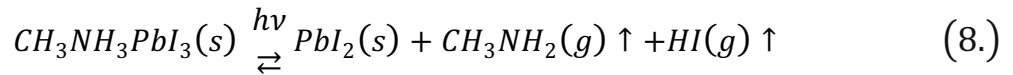
The possible perovskite degradation reaction under moisture and oxygen is as follows (Eqn 3-6):^{158, 159}



The possible perovskite degradation reaction under heat is as follows (Eqn 7):¹⁶⁰⁻¹⁶³



The possible perovskite degradation reaction under UV light is as follows (Eqn 8-11):^{158, 164-167}



The moisture and oxygen sensitivity of perovskite materials can be improved by encapsulation; however, it is still required to enhance the intrinsic stability to withstand light and heat under illumination. Besides, the intrinsic issues of perovskite stability need to be taken into consideration. For instance, as FAPbI₃ perovskite, it suffers from phase instability since the α black perovskite phase could be easily transfer to δ yellow photoinactive phase at room temperature.¹⁵⁶ Compositional engineering is a feasible solution to stabilize the photoactive black phase by incorporating cations such as Cs⁺ or MA⁺ to tuning the tolerance factor of pure FAPbI₃ (>1) to ideal region (0.8 -1).¹⁶⁸⁻¹⁷⁰ Additive engineering is one of the most common strategies to control perovskite crystallization and surface morphology. Effective additives can interact with perovskite precursor to form an intermediate phase and accelerate the formation of black phase, or passivate the defects on the surface and grain boundaries.^{171, 172} Interfacial engineering employs organic components to passivate and mitigate the undesirable defects on the FAPbI₃ perovskite film surface or at the interface.¹⁷² Apart from strategies that focusing on the process of crystallization and post-treatment of the perovskite films, there are other approaches for achieving stable α -phase FAPbI₃ perovskite such as substrate and surface conditioning,^{173, 174} vapor-assisted film

deposition.^{171, 175, 176} However, more in-depth investigations are still needed on the phase stability of pure FAPbI₃ perovskite.

2.4.2 Toxicity

Current high-efficiency PSCs generally contain Pb, however, perovskite devices may undergo degradation and damage upon operation in certain conditions such as high humidity or light. The perovskite degrades through different approaches and eventually decomposes into elemental lead or lead iodide PbI₂, both of which are toxic to the earth environment and living creatures. It is critical to control the Pb leakage to the external environment to prevent further contamination and harmful impacts.¹⁷⁷ Various strategies have been put forward to prevent Pb leakage, such as encapsulation with a physical barrier¹⁷⁸⁻¹⁸⁰, chemisorption layer via absorbing Pb to form chelates¹⁸¹⁻¹⁸³, recycling and reuse of Pb¹⁸⁴⁻¹⁸⁶. Moreover, development on Pb-free PSCs has been extensively studied recently to resolve the toxic issue from the root. Pb substitutes from IVA and VA in the periodic table, such as tin Sn, germanium Ge, antimony Sb, and bismuth Bi, have been investigated and fabricated into PSCs to address the toxicity issues.^{27, 187, 188} At the same time, however, proper optoelectronic properties such as high absorption coefficient, long carrier lifetime, narrow bandgap, high mobility as well as good stability should be taken into consideration.

2.4.3 Flexibility

Flexible devices are made from photovoltaic materials deposited on flexible substrates. The most widely used flexible substrate is polyethylene terephthalate (PET).⁵⁸ Flexible PSCs offer advantages over traditional rigid devices owing to their compatibility with roll-to-roll mass production technology, as well as ultrathin lightweight electronics, which are highly promising for future application. Initially, Snaith's group introduced a flexible inverted p-i-n device, based on the PET/ITO substrate as ITO/PEDOT:PSS/MAPbI_{3-x}Cl_x/PCBM/TiO_x/Al, reaching 6.4% PCE.¹⁸⁹ After that, You *et al.* reported an enhanced PCE of 9.2% on similar structure as ITO/PEDOT:PSS/MAPbI_{3-x}Cl_x/PCBM/Al.¹⁹⁰ In the meantime, a flexible regular n-i-p structure was reported by Liu and Kelly with a PCE of 10.2%, using the same flexible substrate with a device structure of ITO/ZnO/ MAPbI₃/spiro-OMeTAD/Ag.¹⁹¹ However, the devices tended to lose original efficiency quickly after cycles of bending tests, which was owing to the brittle nature of ITO. The replacement of PET/ITO by PET/AZO/Ag/AZO (aluminium-doped zinc oxide) was reported with more durable devices under cyclic loading (Figure 2.12).¹⁹² Recently Miyasaka's group achieved a PCE of 21.1% on flexible PSCs (Figure 2.13), with excellent stabilities.¹⁹³ However, the flexible substrates cannot withstand high temperature processing due to the polymer nature. Overall, current flexible PSCs are still not comparable as rigid counterparts, more efforts need to be put on to enhance the performance and durability of flexible devices.¹⁹⁴

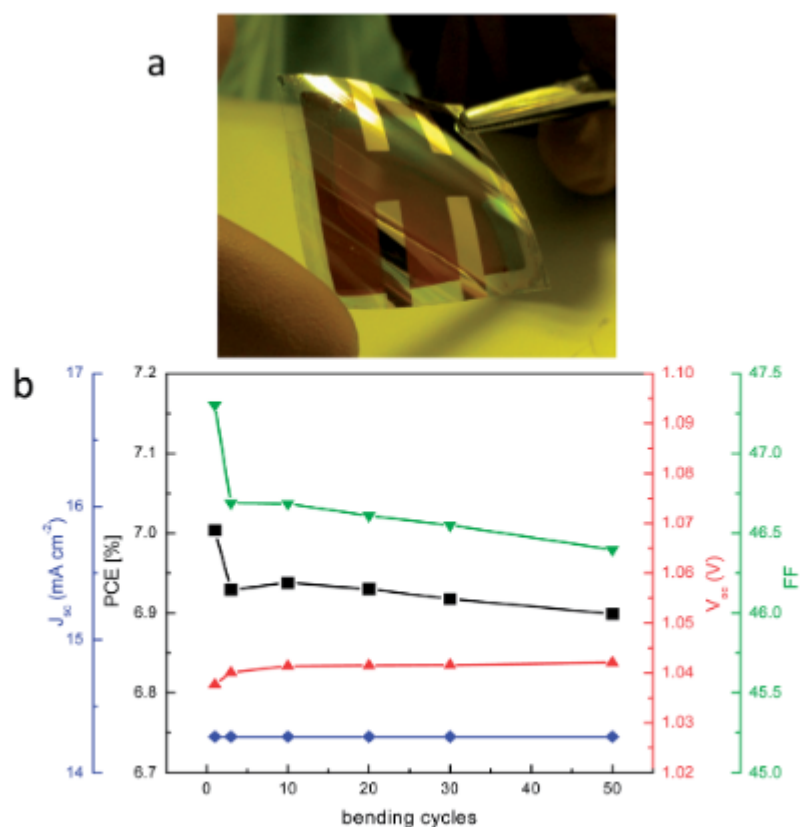


Figure 2.12. a) Photograph of a flexible solar cell. b) PCE, J_{sc} , V_{oc} , and FF as a function of bending cycles. Reproduced with permission.¹⁹²

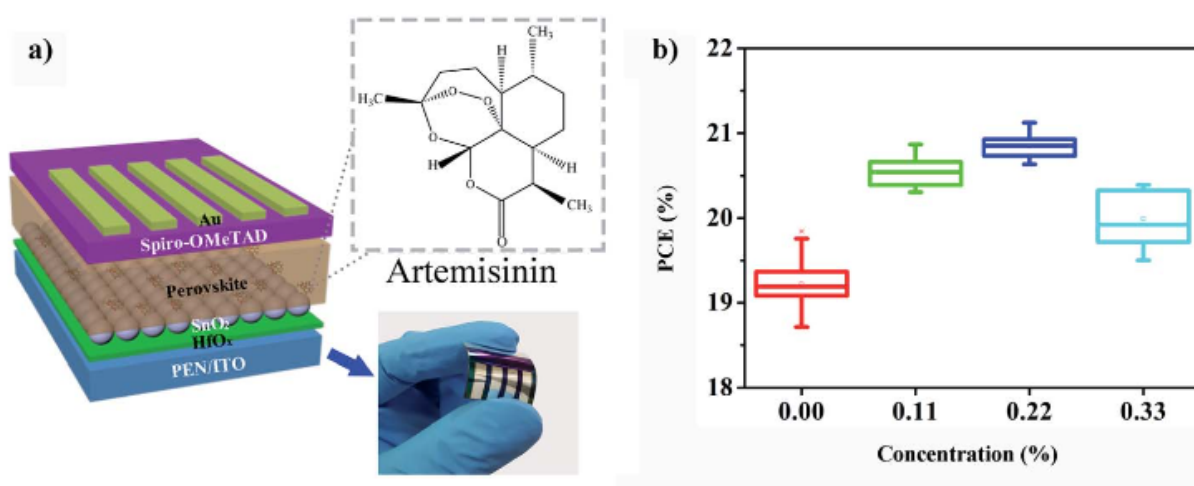


Figure 2.13. a) Schematic and photograph of a flexible artemisinin-doped perovskite solar cell, and the molecular structure of artemisinin. b) PCE of the PSC as a function of artemisinin concentration. Reproduced with permission.¹⁹³

2.4.4 Device Upscaling

Uniform and pinhole-free perovskite films can be achieved by appropriate deposition methods such as solution based or vacuum based processes.¹⁵⁷ In the laboratories, spin-coating has been applied widely and considered to be the most efficient approach to implement device fabrication, because not only the ionic nature of perovskite materials which is suitable for low-temperature solution process, but also the facile operation of spin-coating.¹⁹⁵ However, upscaling of PSCs from lab-scale to large-area need suitable adjustment on deposition approaches. Several limitations from spin-coating inhibit the further utilization on large-area manufacturing, including: the wastage of precursor solutions (>90 %), cost consideration, and the limited small scale (<10 cm).¹⁹⁵ Various approaches can achieve large-area perovskite films, such as screen printing¹⁹⁶⁻¹⁹⁸, blade coating^{199, 200}, slot-die coating^{201, 202}, spray deposition^{203, 204}, thermal evaporation^{56, 205, 206}, pulsed laser deposition (PLD)^{207, 208}, and hybrid chemical vapor deposition (HCVD)^{209, 210} *etc.* Hu *et al.* demonstrated the feasibility of a fully printable process by fabricating a 49 cm² perovskite module with a PCE of 10.4 %. Additionally, they successfully produced a 7 m² fully printed PSC-based module, indicating its potential for practical photovoltaic applications (Figure 2.14).²¹¹ Cost-effective processes based on coating and printing techniques should be primarily considered for efficient large-scale PSCs. Applying these approaches to be compatible with roll-to-roll (R2R) mass production process is considerably preferable owing to the low cost and fast processing properties (Figure 2.15).^{195, 212}

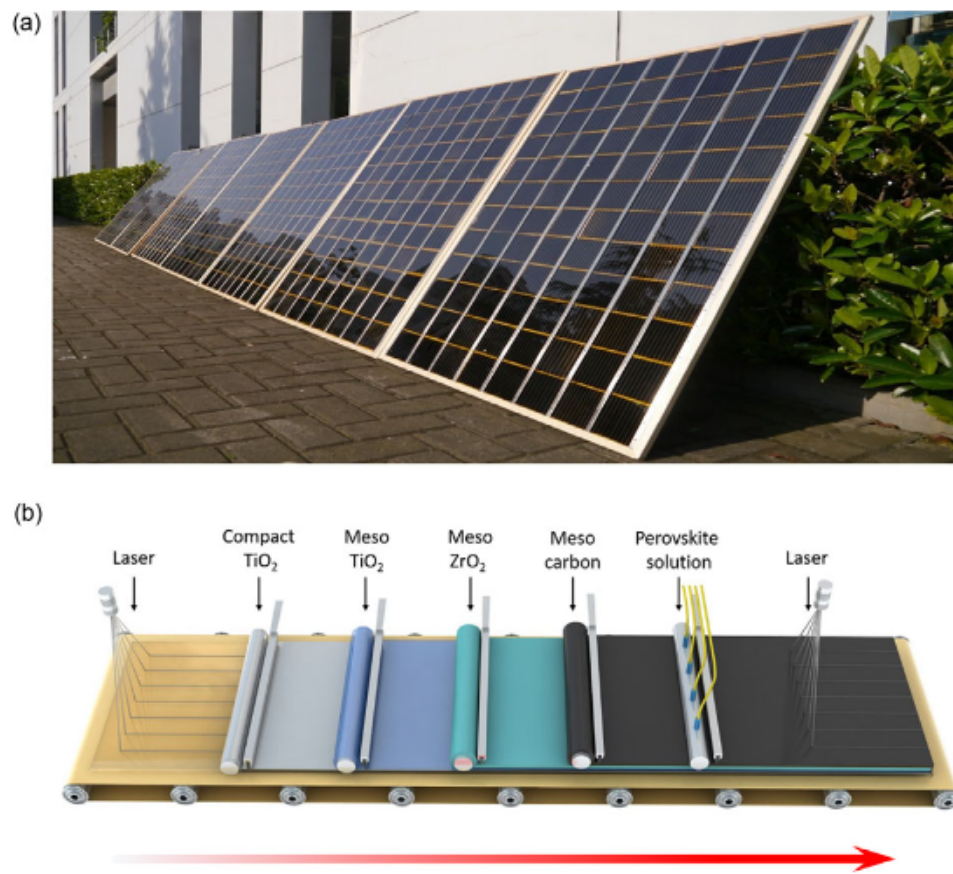


Figure 2.14. a) Image of 7m² fully printed PSC-based modules. b) Schematic of fabrication process for fully printed PSCs. Reproduced with permission.²¹¹

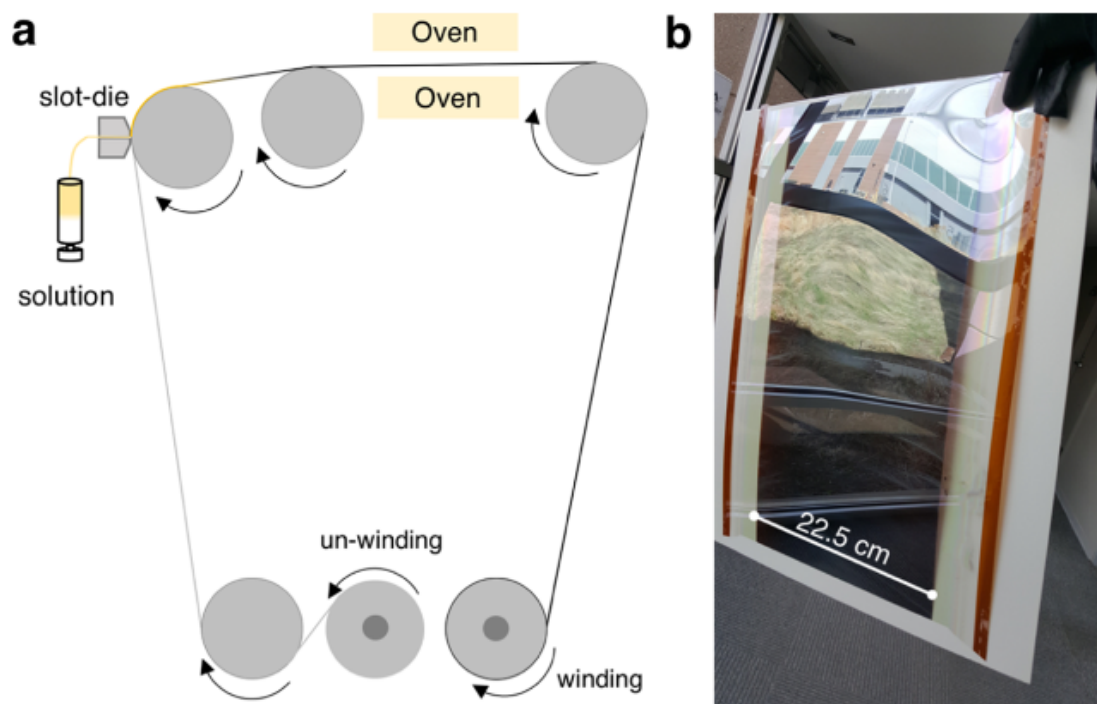


Figure 2.15. a) Set up of roll-to-roll slot-die coating. b) resulting large-area perovskite film. Reproduced with permission.²¹²

3. Experimental Methods

3.1 Thin Film and Device Fabrication

Subtle variations in methodology and specific recipes have been occasionally used, where appropriate specific details are given within the experimental chapters – here a general overview is presented.

Materials Preparation & Device Fabrication (Chapter 4)

All device processing was carried out in a nitrogen filled glovebox. 1.5M (i.e., 1.5 mol/l) $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPI) precursor solutions were prepared by dissolving equimolar ratios methylammonium iodide (MAI, >99.99%, Great Cell Solar) and lead iodide (PbI_2 , 99.99 %, TCI) into a mixed solvent of N, N-Dimethyl methanamide (DMF) and Dimethyl sulfoxide (DMSO) (9:1.1 volume ratio). The solution was stirred at 60 °C for 1 hour to fully dissolve the precursor materials before use.

$\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ was prepared in 1.25 M by co-dissolving formamidinium iodide (FAI, >99.99%, Great Cell Solar), caesium iodide (CsI, 99.9%, Alfa Aesar) and PbI_2 in a mixture solvent of DMF and N-Methyl-2-pyrrolidone (NMP) (8:2 in volume ratio). The solution was stirred at 60 °C for 1 hour to fully dissolve the precursor materials before use.

ITO coated glass (PsiOTec) was sequentially cleaned with soap, deionized water, acetone, iso-propanol in an ultrasonic bath, followed by drying under a nitrogen stream and finally treatment with oxygen plasma. The HTLs were subsequently deposited directly onto the clean substrates. Poly[bis(4-phenyl) (2,4,6-trimethylphenyl) amine

(PTAA, Ossila) 2.5 mg/ml in toluene was spin-coated at 5000rpm for 20 seconds, and PF8TAA (synthesized in-house) 2mg/ml in toluene was spin-coated at 4000 rpm for 20 seconds. Poly(9,9-bis(3'-(N,N-dimethyl)-N-ethylammonium-propyl-2,7-uorene)-alt-2,7-(9,9-dioctyluorene))dibromide (PFN-Br, 1-Material) 0.00625 wt.% in methanol (anhydrous, 99.8%, Merck) was filtered with 0.45 μm PTFE then spin-coated at 3000 rpm for 20 seconds. PFN-Br was introduced as interfacial compatibilizer to improve the wettability between the hydrophobic HTL and hydrophilic perovskite layers.²¹³

The perovskite layers were deposited using an anti-solvent dripping method⁵⁷ with post-treatment. Specifically, the precursor solutions were heated to 60 °C and deposited by spin-coating at 4000 rpm for 20 seconds, while dripping 0.5 ml diethyl ether²¹⁴ at 8th second for MAPI and 10th second for $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ (Figure 3.1). Subsequently the films were annealed at 100 °C for 60 minutes (MAPI) and 150°C for 15 minutes ($\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$). Fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM, >99%, Ossila) 30 mg/ml was dissolved in chlorobenzene and heated to 60°C then filtered through a 0.45 μm filter before being spin-coated at 2000rpm for 20 seconds. Bathocuproine (BCP, Lumitec) 0.5 mg/ml in methanol was deposited by spin-coating at 5000rpm for 20 seconds. Finally, the devices were completed by thermal evaporation of 100 nm Cu (Figure 3.2).

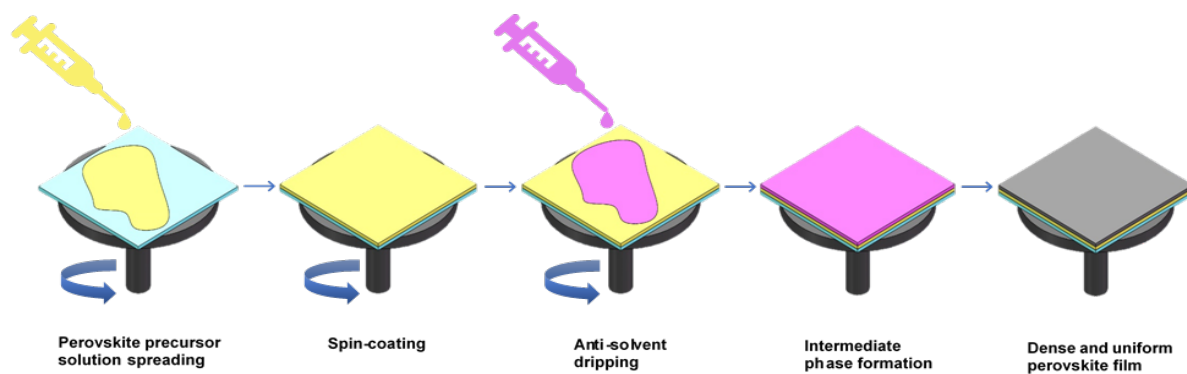


Figure 3.1. Illustration of solvent engineering method for perovskite formation.

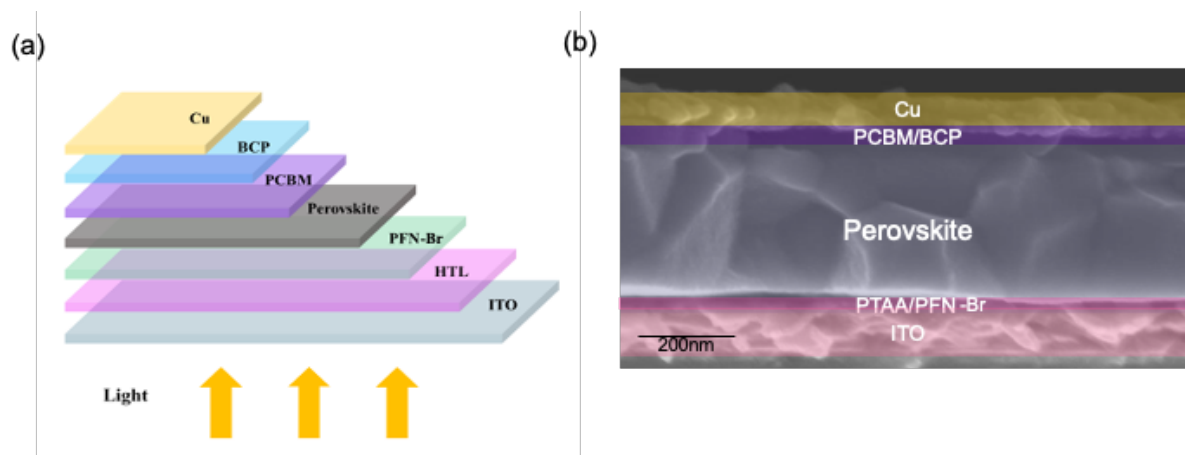


Figure 3.2. (a) Schematic of inverted perovskite device structure; (b) Cross-section SEM of a MAPbI_3 device.

Materials Preparation & Device Fabrication (Chapter 5)

The FA-based perovskite $\text{FA}_{0.95}\text{MA}_{0.05}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$ precursor solution was prepared by mixing FAPbI_3 and MAPbBr_3 in a volume ratio of 9.5:0.5. FAPbI_3 precursor solution was prepared by dissolving equal molar ratio of x M ($x=1.3, 1.5, 1.8$) formamidinium iodide (FAI, Great Cell Solar) and lead iodide (PbI_2 , 99.99 %, TCI) in a mixture solvent

of N, N-Dimethyl methanamide (DMF) and N-Methyl-2-pyrrolidone (NMP) (7.5:2.5 in volume ratio). MAPbBr₃ precursor solution was prepared by dissolving equal molar ratio of y M (y=1.3, 1.5, 1.8) methylammonium bromide (MABr, Great Cell Solar) and lead bromide (PbBr₂, 99.99 %, TCI) in a mixture solvent of DMF and NMP (7.5:2.5 in volume ratio). The FAPbI₃ solution was stirring at 60°C whereas MAPbBr₃ solution at room temperature for 1 hour to fully dissolve the precursor materials before use. The resulting FA_{0.95}MA_{0.05}Pb(I_{0.95}Br_{0.05})₃ thin films show a range of thicknesses from approximately 500 nm to 1 µm (1.3 M - 1.8 M).

Inverted planar structure ITO/PTAA/PFN/perovskite/PCBM/BCP/Cu devices were fabricated. ITO coated glass (PsiOTec) was sequentially cleaned with soap, deionized water, acetone, iso-propanol in ultrasonic bath, followed by blow drying with nitrogen gun and treated with oxygen plasma for 8 minutes. The HTL was deposited on the ITO substrate by spin-coating PTAA (Ossila) 2.5 mg/ml in toluene at 5000rpm for 20 seconds. PFN-Br (1-Material) 0.00625 wt.% in methanol (anhydrous, 99.8%, Merck) was filtered with 0.45 µm PTFE then spin-coated at 3000rpm for 20 seconds.

The perovskite layer was deposited by a sequential dynamic deposition (SDD) approach. The precursor solution was heated up to 60°C and deposited by spin-coating at 4000 rpm for 20 seconds, while dripping 0.5 ml diethyl ether at 9th second, forming a semi-transparent orange film. Methylammonium chloride (MACl, >98.0%, TCI) in isopropyl alcohol (IPA, ≥99.7%, Merck) was prepared in varied concentrations (1 mg/ml, 3 mg/ml, 5 mg/ml, and 7 mg/ml). 16 µl of MACl was dynamic spin-coated onto the as-deposited perovskite film by dripping the solution at two times (8 µl at each drop) at 4000rpm for 30 seconds. The first 8 µl of MACl solution was dripped at 5th second and second 8 µl at 15th second, after which the film became brown. Then the

film was annealed on hotplate at 100°C for 60 minutes to turn black, indicating the successful phase transition to photoactive phase. PCBM (>99%, Ossila) 30 mg/ml was dissolved in chlorobenzene and heated up to 60°C before use. PCBM was spin-coated by a 1ml syringe with 0.45 µm filter at 2000rpm for 20 seconds. BCP (Lumitec) 0.5 mg/ml in methanol was deposited by spin-coating at 5000rpm for 20 seconds. Finally, a Cu electrode (100 nm) was deposited on top of the BCP layer by thermal evaporation.

3.2 Device Characterization

3.2.1 Current Density-Voltage Characteristics (J-V)

Current density-voltage (J-V) characteristics were obtained to assess device performance, which were measured with a Keithley 2400 meter by applying external potential bias to the device and recording the current. Air Mass 1.5G global (AM 1.5G) Xenon lamp solar simulator (Oriel Instruments) was used as the source of illumination. The light intensity was calibrated to 1 sun (100 mW/cm^2) with a silicon reference photodiode, certificated by National Renewable Energy Laboratory (NREL). Prior to measurement, all devices were stored in dark. All devices were measured in a nitrogen-filled chamber, with both reverse and forward scans obtained, see typical example in (Figure 3.3).

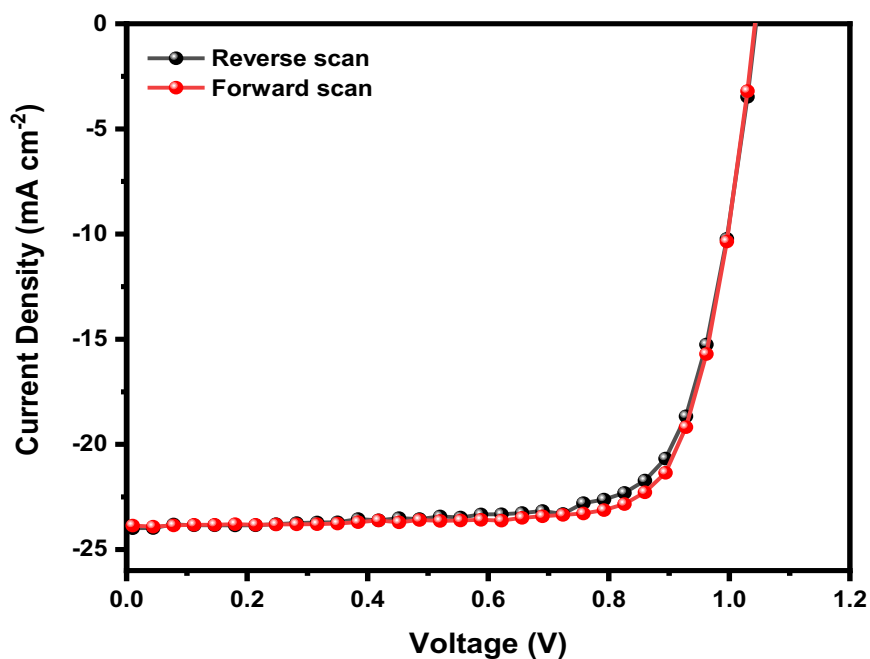


Figure 3.3. Typical J-V scan of a perovskite solar cell with reverse and forward scans shown as indicated.

3.2.2 External Quantum Efficiency (EQE)

External quantum efficiency (EQE) spectra were obtained to measure the number of charge carriers provided to the external circuit per incident photon on the solar cell device in a specific range of wavelength (see an example on Figure 3.4). A Bentham PVE300 photovoltaic QE system was used to obtain the EQE spectra between 300 and 850 nm. The system was calibrated with a silicon reference photodiode.

The short circuit current density J_{sc} can be determined by EQE measurement, which is the spectral response of a solar cell under illumination.²¹⁵

$$J_{sc} = \int qEQE(\lambda)S(\lambda)d\lambda \quad (12.)$$

Where q is the elementary charge, $S(\lambda)$ is the photons per second. J_{sc} is calculated by integrating the EQE data across all the relevant wavelengths. Optimally, the J_{sc} measured via a J-V measurement should match the J_{sc} determined by EQE measurement.²¹⁵

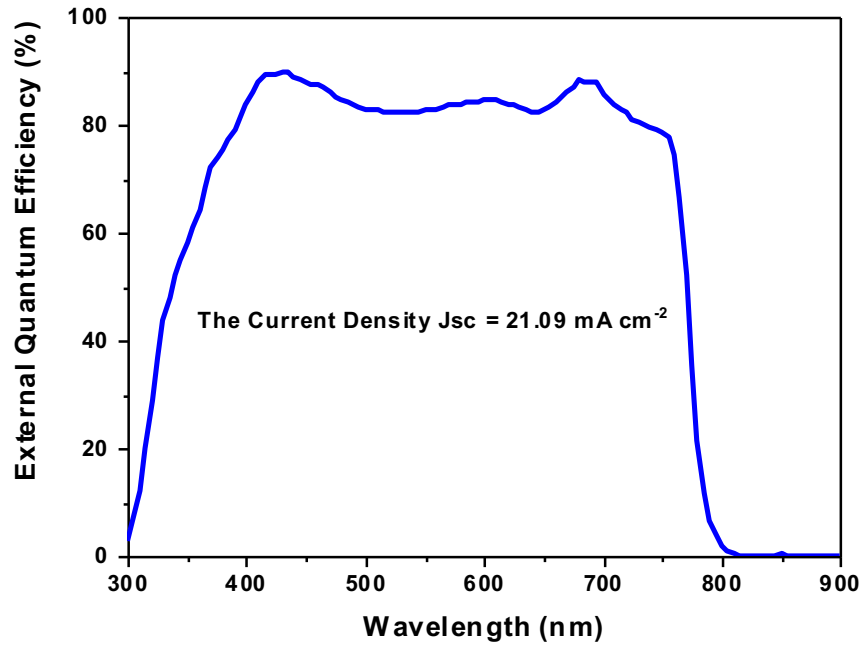


Figure 3.4. Typical EQE spectrum of a MAPbI₃ perovskite film.

3.3 Structural Characterization

3.3.1 Diffraction (XRD)

X-ray diffraction (XRD) data were obtained using a Bruker D2 PHASER instrument operating at 40 kV and 40 mA.

W. H. Bragg developed an equation to explain the diffraction of X-rays from atomic planes of crystals, which is known as the Bragg's Law. X-rays scattered from successive planes of a crystal lattice can interact constructively when the Bragg's Law is satisfied:²¹⁶

$$n\lambda = 2d \sin \theta \quad (13.)$$

Where λ is the wavelength of incident X-ray beam (0.154 nm in this study), d is the interplanar spacing, θ is the angle of incident beam, n is an integer, referred to as the order of diffraction.²¹⁶

The crystallite size can be obtained through Scherrer equation,^{217, 218} which relates the crystallite size (D) to the broadening of a peak in the diffraction pattern:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (14.)$$

Where K is the Scherrer constant, which depends on the shape of the crystallite, and is usually taken as 0.9. β is the full width at half maximum (FWHM) of the diffraction peak, which represents the peak broadening.^{217, 218}

Figure 3.5 shows a XRD pattern example of MAPbI₃ thin film deposited on ITO substrate, with major diffraction peaks indexed in the plot.²¹⁹ Another typical XRD pattern of FAPbI₃ thin film on ITO is shown on Figure 3.6, in which the major peaks are indexed.²²⁰

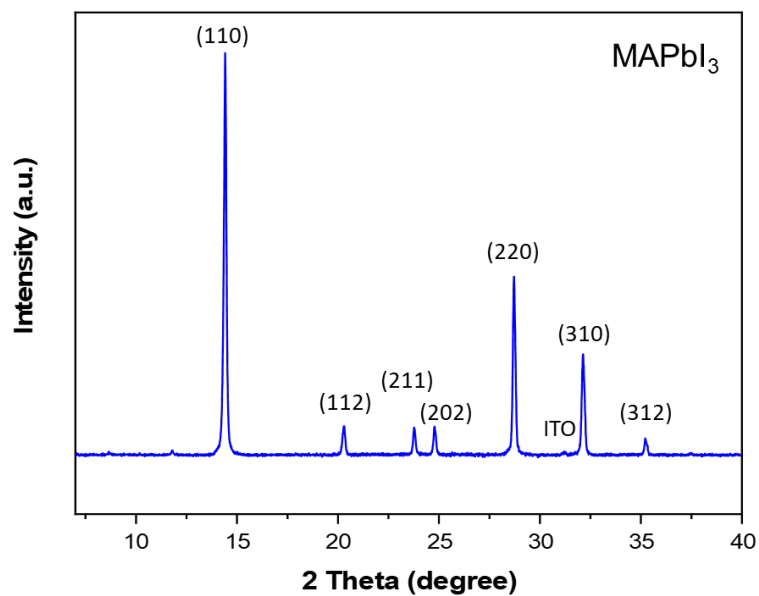


Figure 3.5. Typical XRD pattern of a MAPbI₃ perovskite thin film. Major peaks of perovskite are indexed, and ITO substrate are labelled.

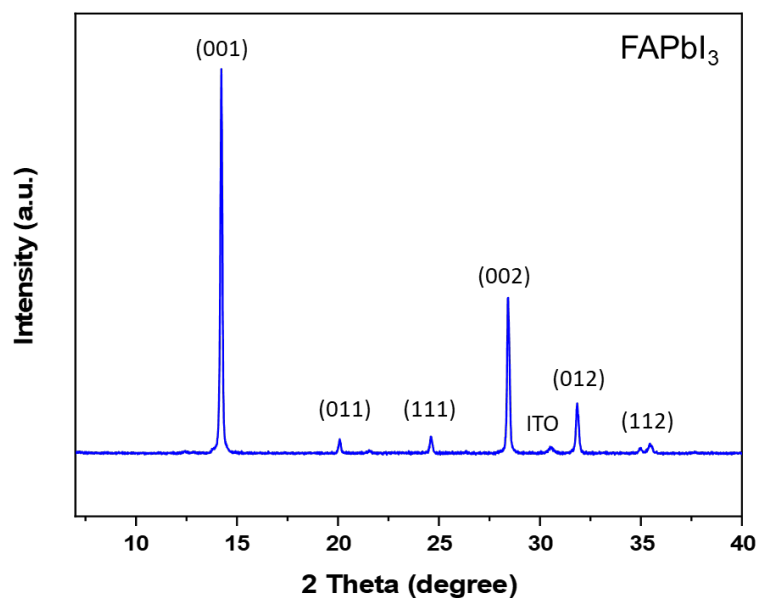


Figure 3.6. Typical XRD pattern of a FAPbI₃ perovskite thin film. Major peaks of perovskite are indexed, and ITO substrate are labelled.

3.3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is used in this thesis to observe the morphology of perovskite thin films and devices. Top-view and cross-section SEM images, Figure 3.7, were obtained by LEO Gemini 1525 field emission gun scanning electron microscope (FEG SEM). The accelerating voltages range from 3 – 5 kV and working distances are in the range of 3-5 mm. Films were coated with a thin (< 10 nm) chromium (Cr) layer to increase the electrical conductivity and facilitate imaging.

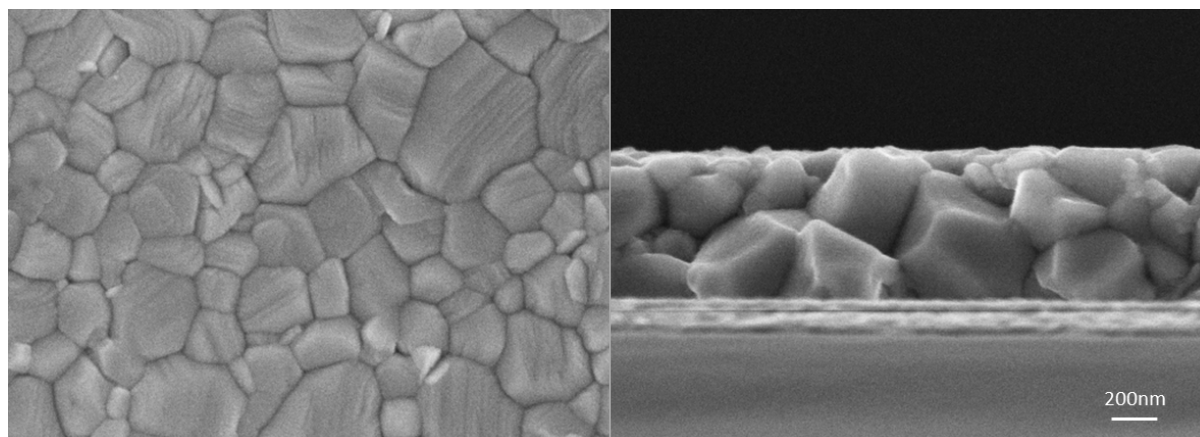


Figure 3.7. Typical SEM top image and cross-section image of a MAPbI_3 perovskite film. Scale bar is the same for both images.

3.4 Optical Characterization

3.4.1 Ultraviolet-visible Spectroscopy (UV-Vis)

Ultraviolet-visible (UV-Vis) absorption spectra were obtained by Shimadzu UV-2600 UV-Vis spectrometer by measuring transmittance spectra of the films (see an example on Figure 3.8).

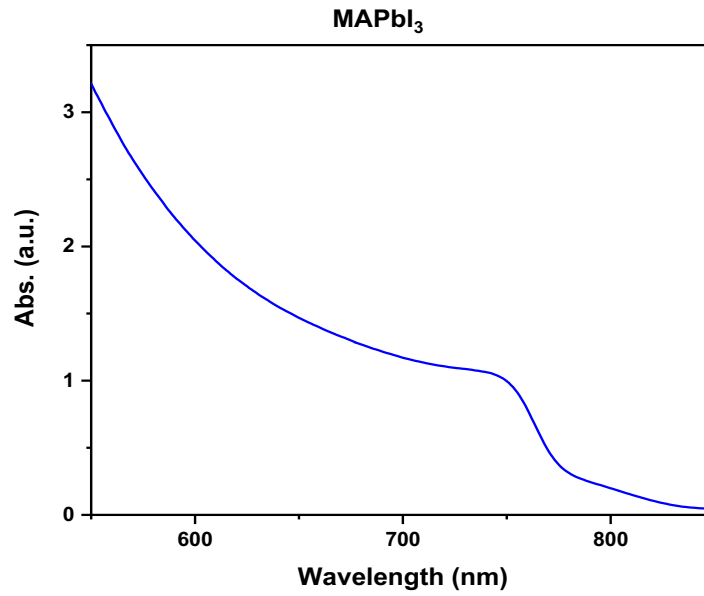


Figure 3.8. UV-Vis absorption spectrum of a MAPbI₃ perovskite film.

Based on the absorption data, the band gap of a semiconductor material can be determined through the Tauc method.²²¹⁻²²³ The Tauc method describes the relationship between the absorption coefficient (α) and band gap energy (E_g) :

$$(\alpha h\nu)^{1/n} = \beta(h\nu - E_g) \quad (15.)$$

Where h is the Planck constant, ν is the photon's frequency, β is the Tauc constant, n is a power factor depending on the nature of the electron transition ($n = 1/2$ for the direct transition band gap, $n = 2$ for the indirect transition band gap).²¹⁶ For example, perovskite materials are direct band gap semiconductors, so the equation becomes:

$$(\alpha h\nu)^2 = \beta(h\nu - E_g) \quad (16.)$$

The band gap energy of a perovskite material can be obtained by a Tauc plot (see an example in Figure 3.9), in which $(\alpha h\nu)^2$ is plotted as a function of photon energy $h\nu$. The linear region of Tauc plot is fitted and the band gap E_g can be estimated from an extrapolation of this linear fit to the x-axis (x-intercept).²¹⁵ Thus, the band gap of a MAPbI₃ thin film is determined to be 1.58 eV by the Tauc method.

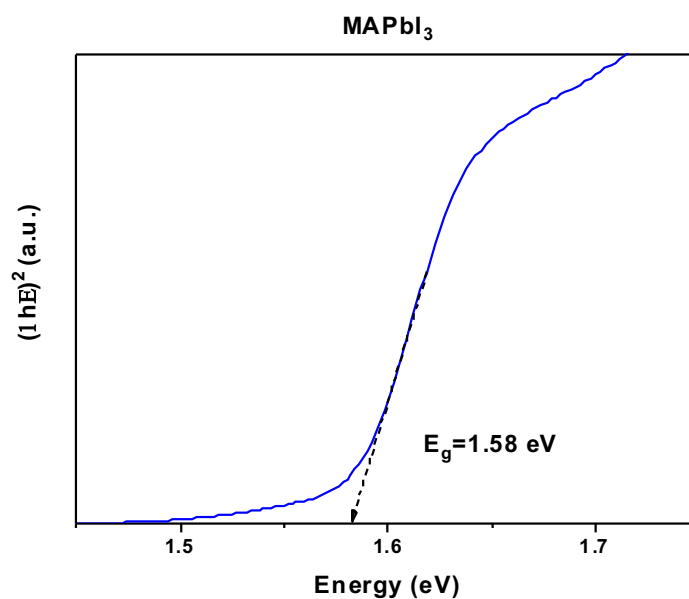


Figure 3.9. The Tauc plot from the absorption data of a MAPbI₃ film. Bandgap E_g is obtained from the x-intercept.

3.4.2 Steady-state Photoluminescence Spectroscopy (Stead-state PL)

Steady state photoluminescence spectra were measured by Fluorolog®-3 with FluorEssence (HORIBA Scientific). For MAPbI₃ thin films, the excitation wavelength is chosen to be 600 nm. A typical example of MAPbI₃ thin film is shown in Figure 3.10,

and the emission peak is determined to be 774 nm. For FA-based perovskite films, the excitation wavelength is set at 450 nm. A typical example of FAPbI₃ thin film is shown in Figure 3.11, and the emission peak is determined to be 804 nm.

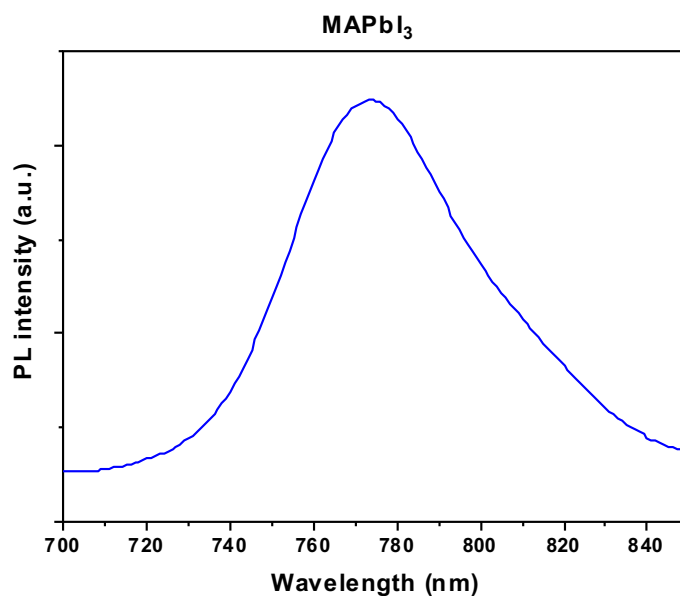


Figure 3.10. Photoluminescence (PL) emission spectrum of a MAPbI₃ thin film. Excitation wavelength is set at 600 nm, the peak position of PL emission is determined to be 774 nm.

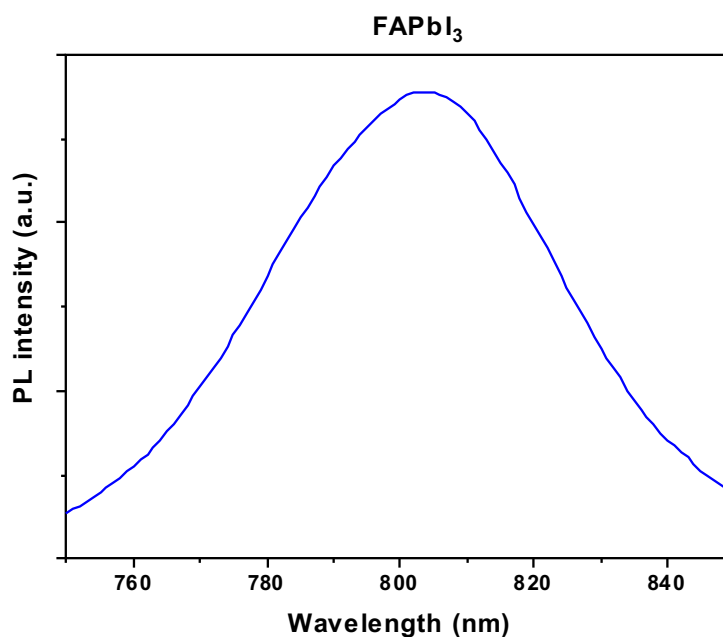


Figure 3.11. Photoluminescence (PL) emission spectrum of a FAPbI₃ thin film. Excitation wavelength is set at 450 nm, the peak position of PL emission is determined to be 804 nm.

3.4.3 Time-resolved Photoluminescence Spectroscopy (TRPL)

Time-resolved photoluminescence spectroscopy (TRPL) is used to study charge recombination or charge transfer dynamics. TRPL measurements were conducted by DeltaFlex time correlated single photon counting (TCSPC) system (HORIBA Scientific) (see setup on Figure 3.12). It is a statistical analysis technique in which the sample is excited by a pulsed laser source with a high repetition rate. The principle of TCSPC is the detection of single photons with periodic excitation and the measurement of their arrival times in respect to the reference light source. The data of PL decay signals in the perovskite films could usually be fitted to biexponential decays: the first fast decay phase is assigned to charge trapping, and the second slow decay phase is assigned to bimolecular recombination of photoexcited electrons and holes.

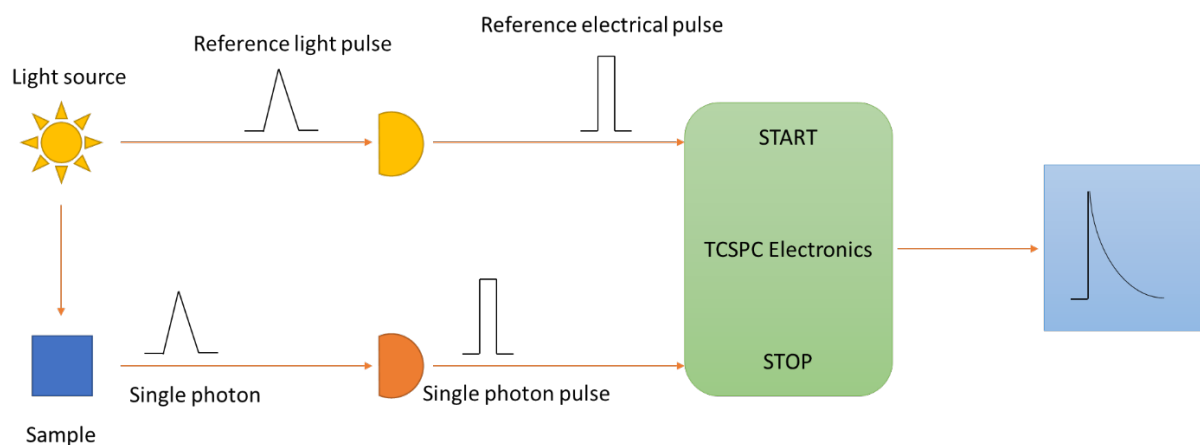


Figure 3.12. Schematic of a TCSPC setup.

3.5 Energetic Characterization

Air Photoemission Spectroscopy (APS) & Kelvin Probe (KP)

Ambient pressure photoemission spectroscopy (APS) and Kelvin probe (KP) measurements were obtained by an APS04 instrument (KP Technology). The VB position was determined by scanning the UV light excitation in the range of 4.8–6.2 eV and extrapolating the cube root photoemission to zero. The Fermi energies were calculated from the contact potential difference measured by the vibrating top Kelvin probe (2 mm, gold tip) and from the work function of the tip (around 4.5–4.6 eV), which was determined using a silver reference.

3.6 Stability Analysis

Environmental Chamber

Stability analysis was determined by XRD patterns of films before and after degradation when the films were kept in ambient air condition either under Xenon lamp or without light (depending on the testing conditions) in an environmental chamber (Figure 3.13). The Xenon lamp is calibrated by silicon reference cell with a light intensity of AM1.5. The humidity levels (RH) were also controlled accordingly, from wet to dry air. The temperature was controlled around 25°C.

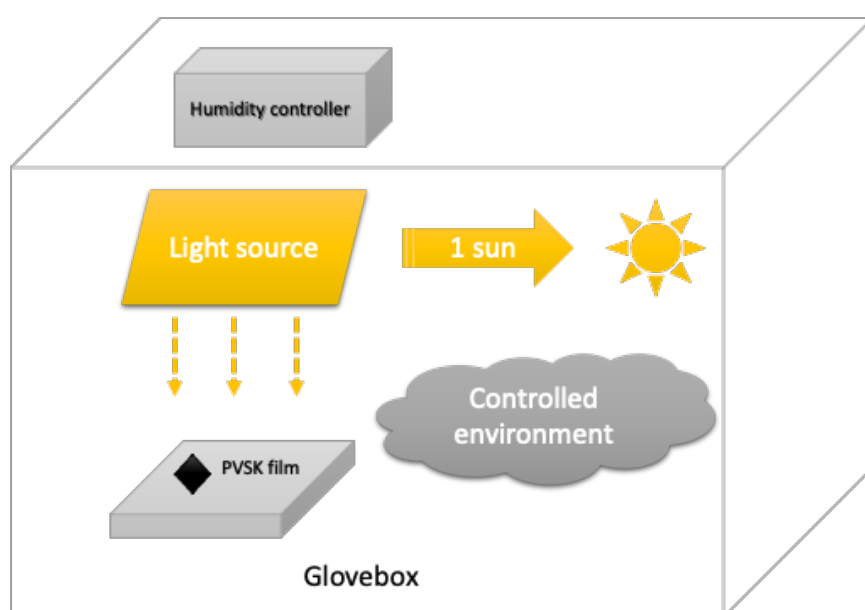


Figure 3.13. Schematic of an environmental chamber.

4. Deciphering the Role of Hole Transport Layer HOMO Level on the Open Circuit Voltage of Perovskite Solar Cells

4.1 Introduction

Numerous research efforts have been made to characterize and optimize metal-halide perovskite solar cells (PSCs) regarding the composition, structure and performance.^{5, 217-220} The multi-layer nature of such devices makes it crucial to evaluate both the individual functional layers and their interfaces. Charge transport layers, which extract charge carriers selectively, including the electron transport layers (ETLs) and hole transport layers (HTLs) are key components in PSCs, leading to reduced interfacial recombination thus enhanced open-circuit voltage (V_{OC}) and fill factor. The interconnection between interfacial recombination and voltage losses has been extensively investigated, where photoluminescence (PL) spectroscopy is widely chosen as a useful tool to interrogate recombination processes.^{223, 224}

One unsolved issue is the correlation between the highest occupied molecular orbital (HOMO) of the HTL ($HOMO_{HTL}$) and the device V_{OC} . Although some researchers demonstrate that V_{OC} is irrelevant to $HOMO_{HTL}$, others report a relationship between $HOMO_{HTL}$ and V_{OC} .^{225, 226} These existing disagreements are reasonable to understand when taking widely common studied organic HTLs into consideration, for instance, poly(triarylamine) (PTAA), poly[N,N'-bis(4-butylphenyl)-N,N'-bisphenylbenzidine] (PolyTPD), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), and poly(3-hexylthiophene-2,5-diyl) (P3HT). Changes in $HOMO_{HTL}$ of these materials

are associated with energy level shifts in the lowest unoccupied molecular orbital (LUMO) simultaneously, along with alterations in film morphology, defect densities and charge carrier concentrations *etc*, all of which have effects on charge carrier recombination and device V_{OC} . Moreover, variations in physicochemical properties of these materials, for instance, surface hydrophobicity and hydrophilicity could have an impact on the morphology and structure of the perovskite layer atop.²²⁷ Therefore, elucidating the relationship between $HOMO_{HTL}$ and device performance is a complicated but meaningful challenge.

Here, the correlation of $HOMO_{HTL}$ and device V_{OC} is studied by analysing the HTL performance of poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA), and a related co-polymer, namely

poly[9,9dioctyl9Hfluorenebis(4phenyl)(2,4dimethylphenyl amine] (PF8TAA).²²⁸

There are many similarities between the two polymers including molecular structures, similar optical band gaps as well as doping levels. However, they do have distinct differences in HOMO levels, and result in different V_{OC} values when applied as HTLs in PSCs. Light-intensity dependent steady-state PL measurement is employed to illustrate the $HOMO_{HTL}$ starts to become the limiting factor of practical V_{OC} as light intensity is increased. To be more specific, it is shown to be a consequence of increases in the magnitude of the quasi-Fermi level splitting (ΔE_F) in the bulk perovskite resulting in greater upward bending of the hole quasi-Fermi level ($E_{F,p}$) in the HTL.

4.2 Results and Discussion

4.2.1 Intrinsic Properties

Figure 4.1 shows the molecular structures of PTAA and PF8TAA respectively, and the introduction of a fluorene unit in PF8TAA is designed to enhance charge carrier mobility. The mobility of PF8TAA is reported to be $\sim 2 \times 10^{-2} \text{ cm}^2/(\text{V s})$, compared to PTAA as $\sim 4 \times 10^{-3} \text{ cm}^2/(\text{V s})$.²²⁸

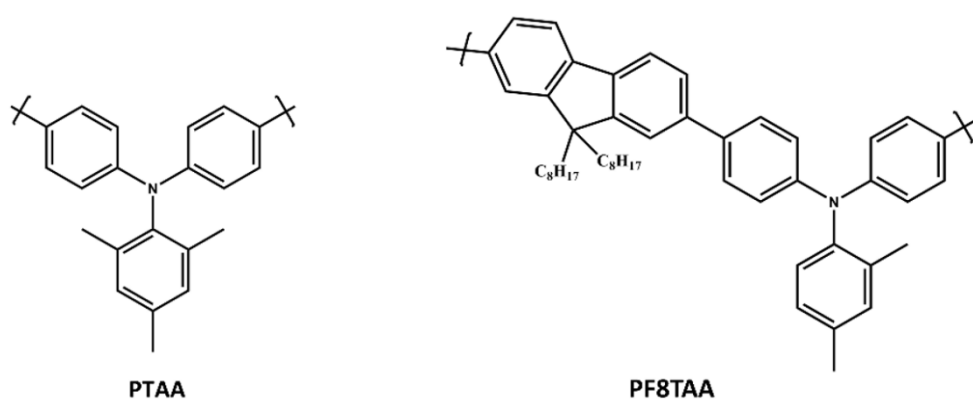


Figure 4.1. The molecular structures of PTAA and PF8TAA.

The HOMO levels of both HTLs were determined by measuring ionization potentials (IP) using ambient pressure photoemission spectroscopy (APS), Figure 4.2a. The valence band (VB) of FA_{0.95}Cs_{0.05}PbI₃ perovskite was also obtained through APS. The HOMO values of PTAA and PF8TAA are -5.03 (± 0.05) eV and -5.24 (± 0.05) eV respectively, and the VB value of FA_{0.95}Cs_{0.05}PbI₃ is -5.61 (± 0.05) eV. The optical band gap energies (E_g) were calculated through Tauc plots,²¹⁵ based on the UV-Vis absorption spectra (Appendix) of individual materials, Figure 4.2b. The equilibrium

dark Fermi levels (E_F) were determined by Kelvin probe. For each of the HTLs, PTAA has an E_g of 2.99 (± 0.03) eV and E_F of 4.67 (± 0.00) eV, and PF8TAA has an E_g of 2.94 (± 0.03) eV and E_F of 4.80 (± 0.00) eV. For perovskite, $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ has an E_g of 1.53 (± 0.03) eV and E_F of 4.79 (± 0.00) eV.

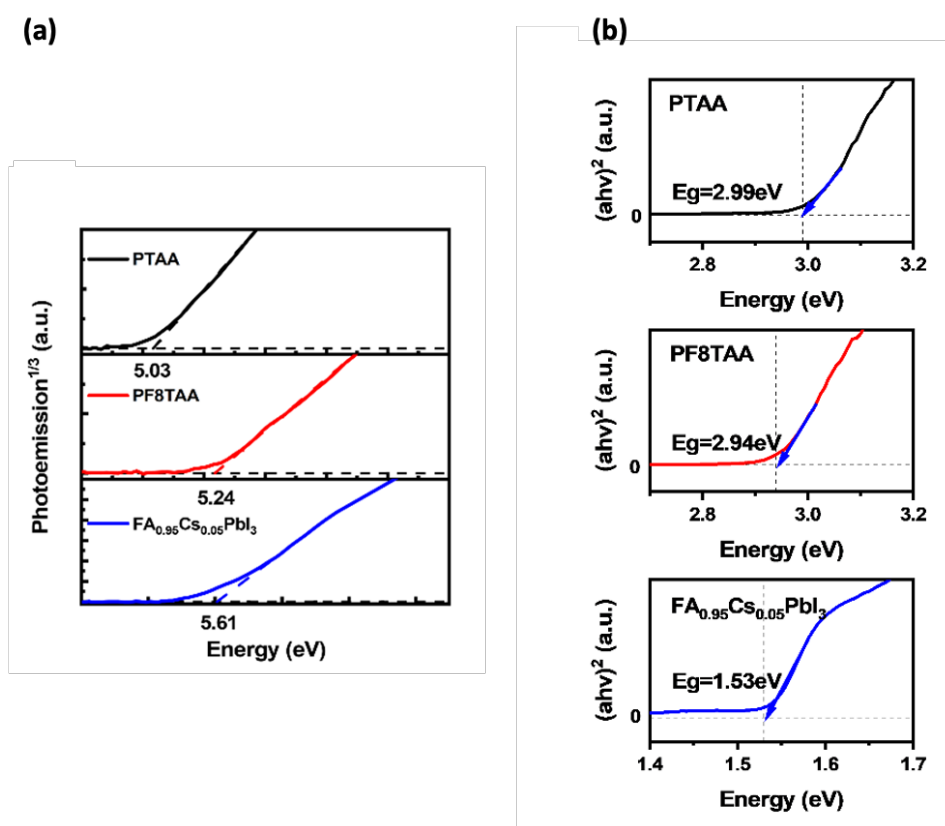


Figure 4.2. (a) Ambient pressure photoemission spectroscopy (APS) spectra of PTAA, PF8TAA and $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ films (three plots at different X, Y scales). (b) Tauc plots from the UV-vis spectra (Appendix) of PTAA, PF8TAA and $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ films.

Figure 4.3 illustrates the flat band energy diagram at the HTL/perovskite interfaces with the above obtained data. All energetic properties of these materials are summarized in Table 4.1. It worth noting the HOMO level shifts by 0.21 eV for PF8TAA compared to PTAA counterpart. According to previous research in our group, p-doping

levels of HTLs can be quantified with the energetic difference between HOMO and E_F values.²²² The doping level of PF8TAA is reduced moderately compared to PTAA with negligible change in E_g values.

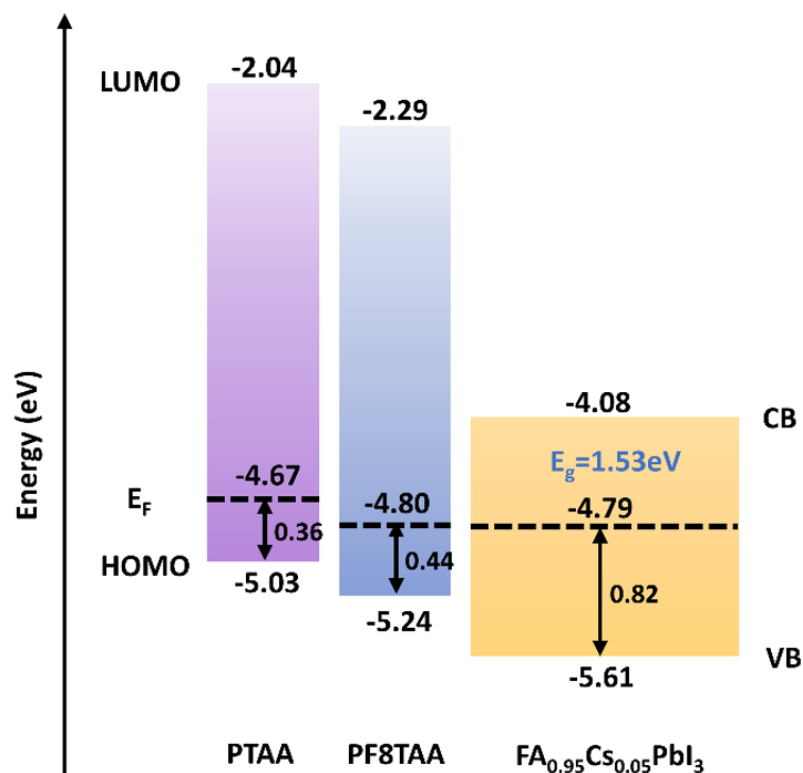


Figure 4.3. Flat band energy diagram at the HTL/perovskite interfaces.

Table 4.1. Energetic properties of PTAA, PF8TAA and $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ obtained from ambient pressure photoemission spectroscopy (APS) and UV-vis spectra, all units given in eV.

	PTAA	PF8TAA	$\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$
LUMO / CB	-2.04 (± 0.05)	-2.29 (± 0.05)	-4.08 (± 0.05)
WF/ E_f	-4.67 (± 0.00)	-4.80 (± 0.00)	-4.79 (± 0.00)
HOMO / VB	-5.03 (± 0.05)	-5.24 (± 0.05)	-5.61 (± 0.05)
Band gap	2.99 (± 0.03)	2.94 (± 0.03)	1.53 (± 0.03)
WF - HOMO	0.36 (± 0.05)	0.44 (± 0.05)	0.82 (± 0.05)

4.2.2 Device Performance

Inverted planar p-i-n PSCs were fabricated with a structure of ITO (150nm) /HTL (20nm) /PFN-Br (<10nm) /perovskite (500nm) /PCBM (60nm) /BCP (<10nm) /Cu (100nm), illustrated in Figure 4.4a. This structure is selected in this work because it can avoid the high temperature processing with negligible hysteresis compared with conventional structure. The HTLs, i.e., PTAA and PF8TAA, were spin-coated onto indium-doped tin oxide (ITO) substrates. Poly(9,9-bis(3'-(N,N-dimethyl)-N-ethylammonium-propyl-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene))dibromide (PFN-Br) acts as a surface modifier sandwiched between the hydrophobic HTL and the hydrophilic perovskite. The amphiphilic nature of PFN-Br can improve the wettability of HTL surface when depositing the perovskite layer.²⁰⁵ Perovskite layers were prepared from a (MAPbI₃ or FA_{0.95}Cs_{0.05}PbI₃) precursor solution by spin-coating with antisolvent dripping approach.⁵⁶ [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is used as electron transport layer (ETL) and was deposited on the perovskite layer. A bathocuproine (BCP) layer was spin-coated as buffer layer prior to the thermal evaporation of Cu electrode. Figure 4.4b shows a cross-section scanning electron microscope (SEM) image of a representative device.

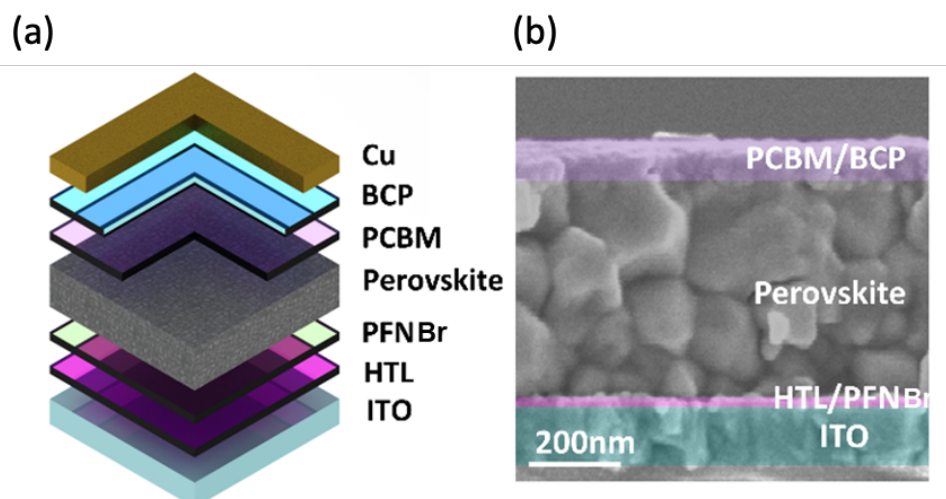


Figure 4.4. (a) Schematic illustration showing the p-i-n device architecture. (b) Cross-section scanning electron microscopy (SEM) image of a typical PSC.

Figure 4.5 demonstrates the surface topography SEM images of $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ on different HTLs, showing polycrystalline perovskite grains in compact structure with full coverage on PTAA and PF8TAA. Comparing the morphology of perovskite on both HTLs, a slight increase in the average grain size is observed with PF8TAA employed as HTL, which is shown in Table 4.3. The average grain size (30 perovskite grains were measured per sample) is determined by ImageJ software, which is 177.9 ± 47.9 nm for $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ deposited on PTAA, compared to the 236.1 ± 79.8 nm for $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ deposited on PF8TAA. Besides, the grain size dispersity also increases slightly in PF8TAA sample.

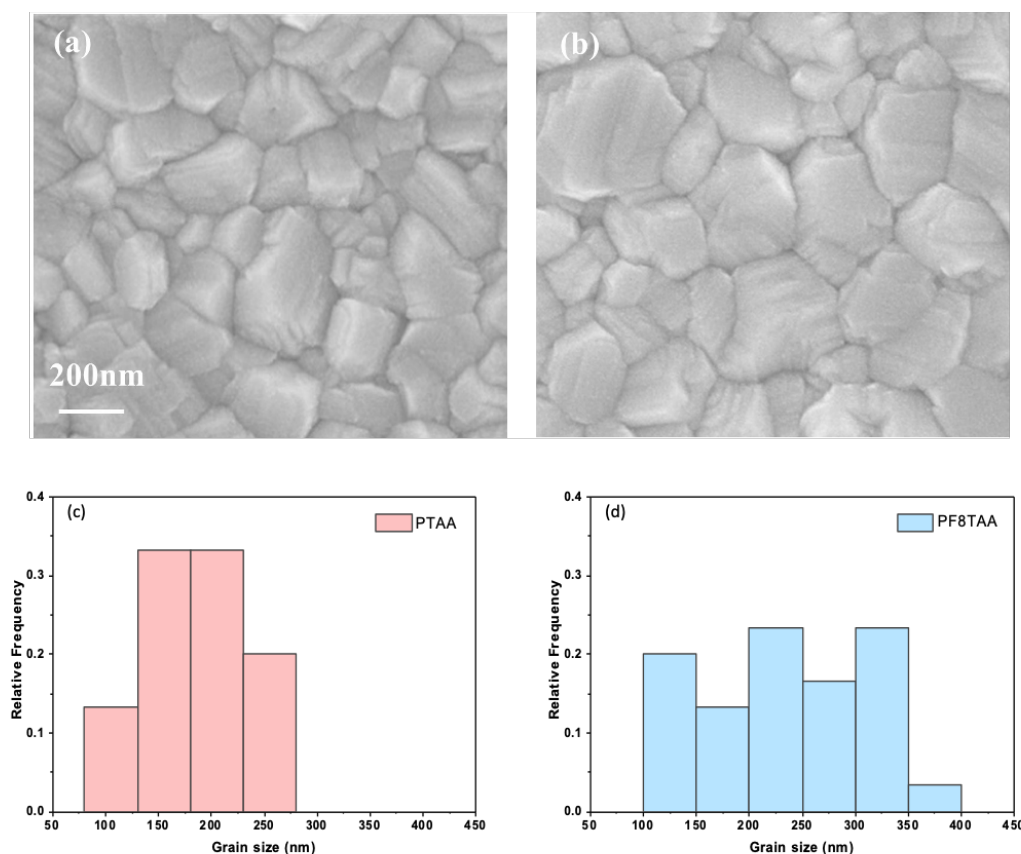


Figure 4.5. Surface topography SEM images of $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ films deposited on (a) PTAA and (b) PF8TAA respectively. Scale bar (200 nm) is the same for PTAA and PF8TAA sample. Grain size analysis obtained from SEM images for $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ films deposited on (c) PTAA and (d) PF8TAA.

Table 4.2. Grain size analyses of perovskite film deposited on PTAA and PF8TAA.

	PTAA/perovskite	PF8TAA/perovskite
Average grain size (nm)	177.9 ± 47.9	236.1 ± 79.8

Nevertheless, more importantly, there is no obvious changes in perovskite crystallinity in both HTLs compared to the reference neat perovskite film, shown in the XRD patterns in Figure 4.6. The major diffraction peak of the cubic structure $\alpha\text{-FAPbI}_3$ (001)

is located at 14.2° . The other diffraction peaks are situated at 20.1° , 24.6° , 28.4° , 31.8° and 35.5° , corresponding to diffraction planes (011), (111), (002), (012) and (112) respectively.²¹² There is a small amount of secondary phase PbI_2 presented on all three films, with its major diffraction peak (001) located at 12.9° .²³¹ The diffraction peak (222) of ITO substrate situated at 30.6° is also marked in the plot.²³²

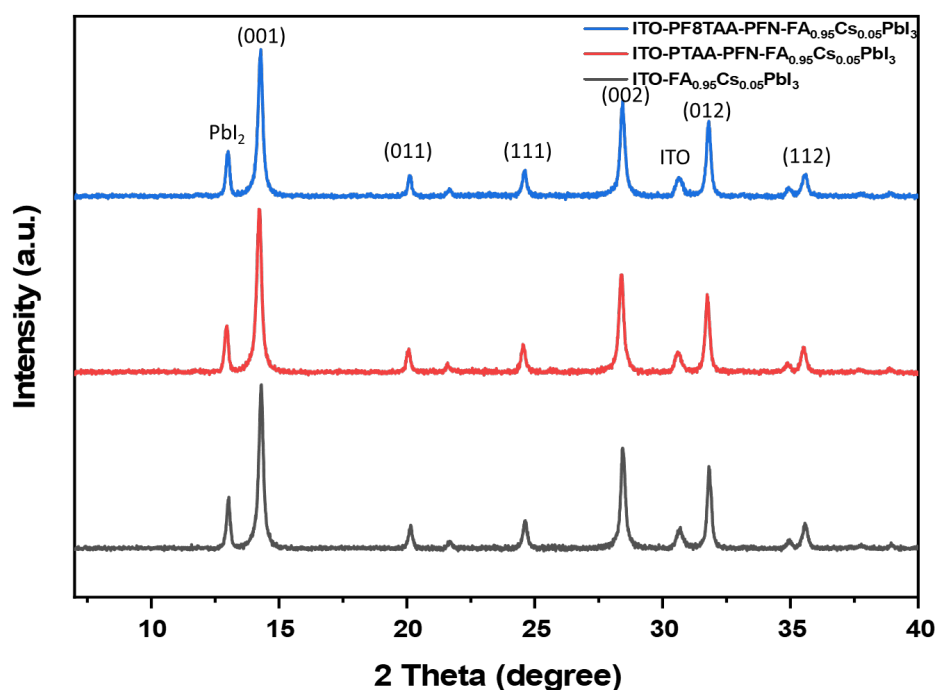


Figure 4.6. XRD patterns for $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ films deposited on ITO, PTAA and PF8TAA layers.

Statistical J-V data for $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ devices employing different HTLs are given in Figure 4.7, and the corresponding J-V parameters listed in Table 4.3. Overall, the performance of PSCs with PF8TAA as a HTL surpass the PTAA counterpart. This is consistent with previous SEM result, in which PF8TAA sample has less grain boundaries.

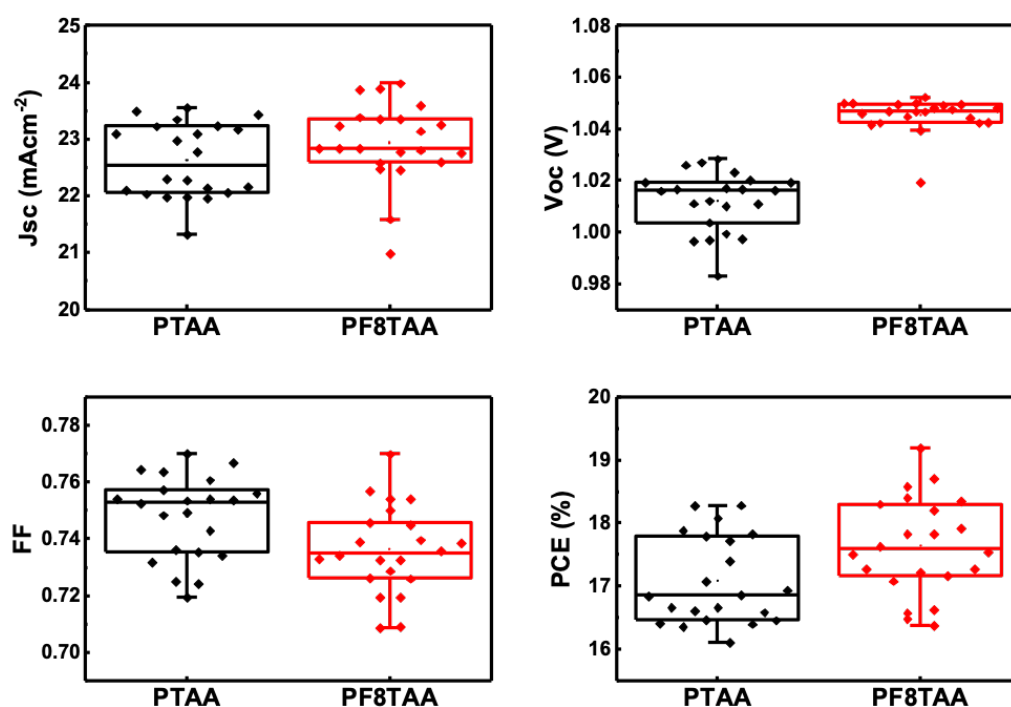


Figure 4.7. Statistical distribution of measured device parameters for PTAA and PF8TAA PSCs.

The average short circuit current (J_{sc}) and fill factor (FF) for PTAA PSCs are determined to be $22.63 (\pm 0.64)$ mA/cm² and $0.748 (\pm 0.014)$, compared to $22.94 (\pm 0.69)$ mA/cm² and $0.736 (\pm 0.015)$ in PF8TAA PSCs, indicating these two HTLs exhibit comparable J_{sc} and FF in devices. However, the average V_{oc} of PTAA PSCs is $1.01 (\pm 0.01)$ V, which increases to $1.05 (\pm 0.01)$ V with PF8TAA, leading to a V_{oc} enhancement of 40 mV. The average PCE is increased from $17.08 (\pm 0.68)$ % in PTAA

devices to 17.64 (± 0.75) % in PF8TAA devices, which is mainly contributed from the improvement of V_{OC} in PF8TAA PSCs.

Table 4.3. Statistical distribution of PV parameters for FA0.95Cs0.05PbI₃ PSCs.

HTL	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
PTAA	22.63 (± 0.64)	1.01 (± 0.01)	0.748 (± 0.014)	17.08 (± 0.68)
PF8TAA	22.94 (± 0.69)	1.05 (± 0.01)	0.736 (± 0.015)	17.64 (± 0.75)

The representative J-V characteristics for champion devices using each of the HTLs are shown in Figure 4.8a. The highest measured V_{OC} for PTAA PSCs was 1.02 V, achieving a PCE of 18.08%. By contrast, an improved V_{OC} of 1.06 V was obtained for PF8TAA PSCs, leading to an increased PCE of 18.26%. The respective external quantum efficiency (EQE) data are shown in Figure 4.8b, where the integrated J_{sc} values are determined to be 20.7 mA/cm² (PTAA) and 21.4 mA/cm² (PF8TAA) respectively, in reasonable agreement with the measured values. Besides, minimal J-V hysteresis was observed on all devices of both HTLs, shown on Figure 4.9. The J-V curves were obtained in reverse and forward scan directions at a scan rate of 50 mV/s under 1 sun illumination, from open circuit to short circuit and vice versa. Hysteresis index can be used to describe the severity degree of hysteresis, as $(HI) = \frac{|PCE_{rev} - PCE_{fwd}|}{PCE_{rev}}$,²³³ where HI (PTAA) is determined to be 0.04, and HI (PF8TAA) to be 0.03. The HI values close to zero, indicating negligible hysteresis shown on both HTL devices.

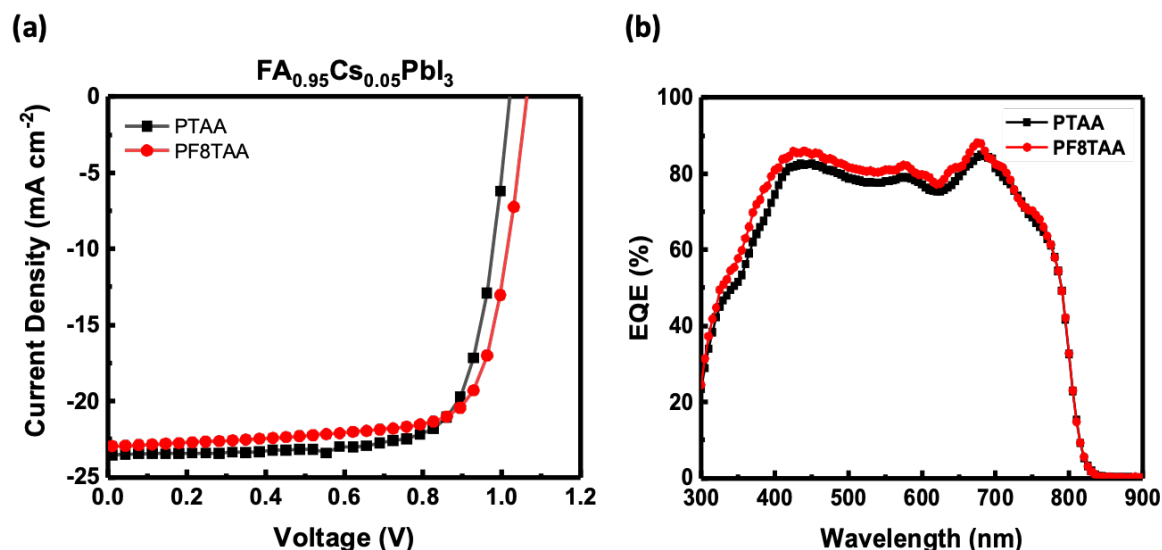


Figure 4.8. (a) J–V curves obtained for devices with the highest V_{OC} values, (b) External quantum efficiency (EQE) spectra of PTAA and PF8TAA PSCs.

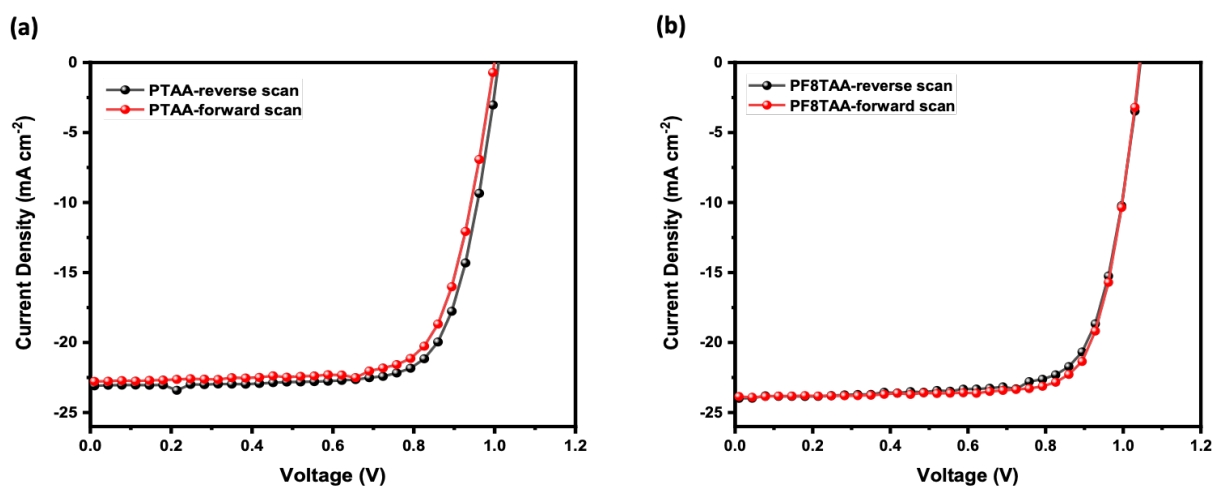


Figure 4.9. The reverse (from open circuit to short circuit) and forward (from short circuit to open circuit) J–V curves of devices employing (a) PTAA and (b) PF8TAA as HTLs.

For MAPbI_3 devices using PTAA or PF8TAA as HTLs, we observe similar V_{OC} trends as in the $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ devices. Figure 4.10 shows the J–V curves of the champion devices employing MAPbI_3 as the active layer. The highest measured V_{OC} for PTAA devices was 1.06 V. In contrast, a V_{OC} enhancement (60 mV) was found in PF8TAA

devices with the highest V_{OC} of 1.12 V. The J_{SC} and FF of PTAA device was 21.67 mA/cm^2 and 0.78, though a slightly decrease was shown on PF8TAA device as 20.58 mA/cm^2 and 0.74 respectively (Table 4.4). The slight reduction in FF is mainly due to the increased series resistance.²³⁴ The resulted PCE of PTAA device was determined to be 17.87% for PTAA device and 17.06% for PF8TAA device. Although there is an enhancement in V_{OC} , the PF8TAA MAPbI₃ device resulted in inferior PCE due to the combination of reduced J_{SC} and FF.

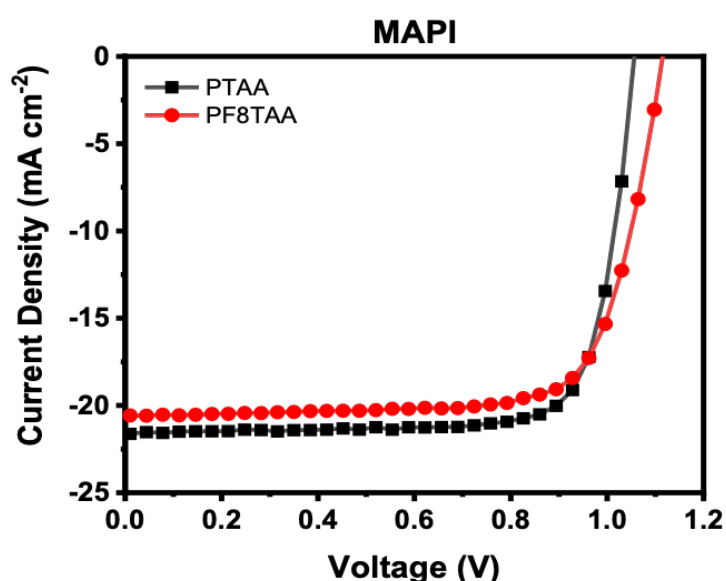


Figure 4.10. J–V curves of champion PTAA and PF8TAA PSCs, employing MAPbI₃ as light absorber.

Table 4.4. PV parameters for champion cells using MAPbI₃ PSCs.

HTL	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	PCE (%)
PTAA	21.67	1.06	0.78	17.87
PF8TAA	20.58	1.12	0.74	17.06

4.2.3 Light-intensity Dependent PL and JV Measurements

The mechanism of HOMO level affecting V_{OC} is studied through measurement of photoluminescence (PL) and V_{OC} of full devices under varying light intensities. Figure 4.11a shows the log-log plot of PL versus light intensity, in which both devices demonstrate a behaviour that can be described as a power law:

$$PL(I) \propto I^k \quad (17.)$$

The exponent k can be obtained as the slope of the fitting curve of the log-log plot, which are $k_{PTAA} = 1.86$ and $k_{PF8TAA} = 1.78$ in this case. The similarity of these values indicate that the dominant recombination mechanisms are similar for both PTAA and PF8TAA. Instead of focusing on the recombination mechanisms, we shift our attention to the differences between relative PL signals (PL_{rel}) along with their variation with incident light intensity. Here, the absolute intensity of steady-state PL is a measurement of the quasi-Fermi level splitting (ΔE_F) in the bulk perovskite layer, described by a generalized Plank's law.^{235, 236} The relationship can be simplified when only the PL_{rel} is measured, as

$$\Delta E_{F,bulk} = kT \ln(PL_{rel}) + C \quad (18.)$$

where C is a calibration factor, and from which we can correlate the change of V_{OC} with the change of PL_{rel} .²³⁷

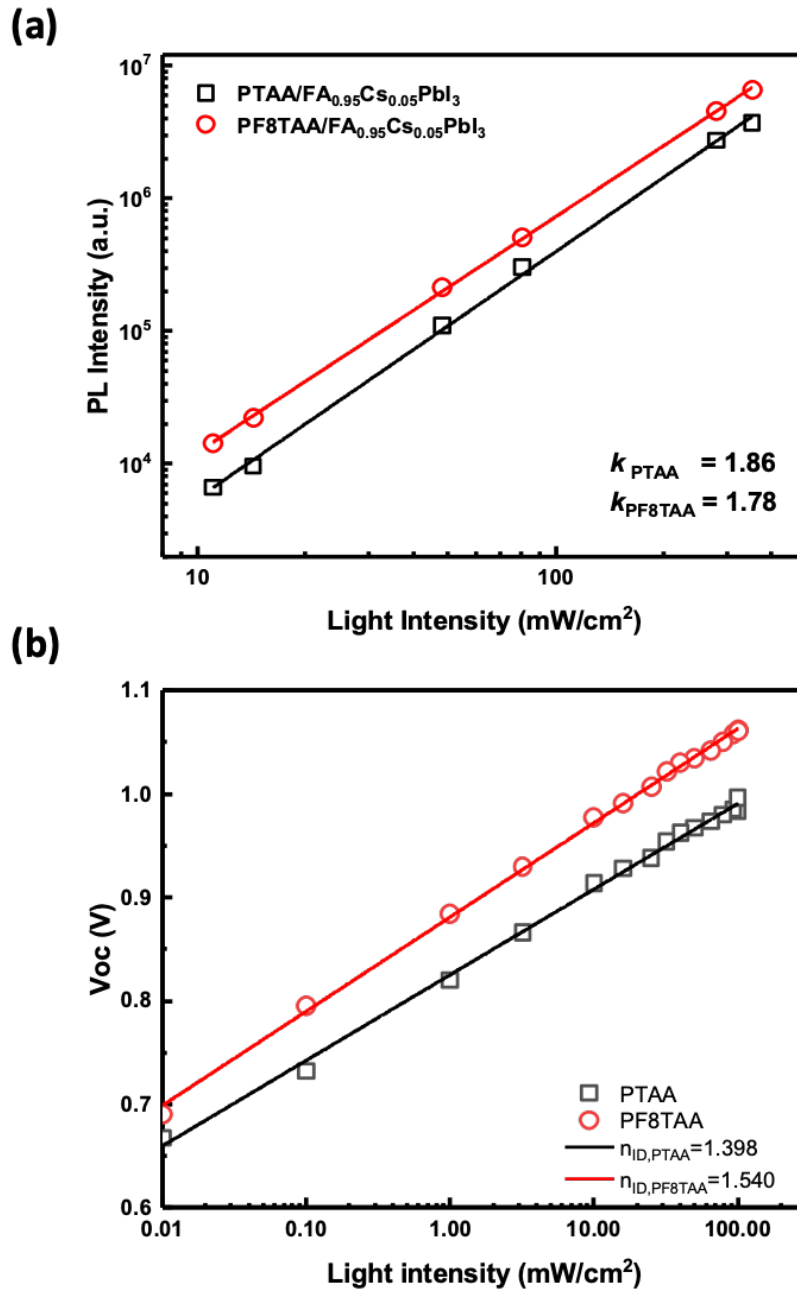


Figure 4.11. **(a)** Light intensity dependent photoluminescence measured on PTAA and PF8TAA PSCs **(b)** Light intensity dependent V_{oc} measured on PTAA and PF8TAA PSCs respectively, with extracted ideality factors.

Several observations can be made from Figure 4.11a. The PL_{rel} difference between the PTAA and PF8TAA devices is greater under low light intensities and smaller under

high light intensities. At all light intensities, the PL_{rel} for PF8TAA device is greater than that for PTAA counterpart. At 1 sun light intensity where the J-V characteristics were usually obtained, the PL_{rel} for PF8TAA device is $\approx 100\%$ greater than that of the PTAA counterpart, corresponding to an increment of $\Delta E_{F,bulk}$ by ≈ 16 meV. However, the measured ΔV_{OC} (80 meV.) is much greater than the difference between $\Delta E_{F,bulk}$. Therefore, it can be concluded that the measured V_{OC} is not equal to the $\Delta E_{F,bulk}$ in the perovskite active layer, which indicates there exists bending of hole quasi-Fermi level ($E_{F,p}$) at the HTL/perovskite interface.^{238, 239}

A semi-log plot of V_{OC} as a function of light intensity is shown in Figure 4.11b. An ideality factor (n_{ID}) can be obtained by fitting these data, which describes the relationship between V_{OC} and light intensity:²²⁶

$$eV_{OC} = E_g - n_{ID}K_B T \ln \frac{I_0}{I} \quad (19.)$$

Where E_g is the bandgap, T is the temperature, K_B is the Boltzmann constant and I_0 is the reverse saturation current. Ideality factor n_{ID} can be derived from the above equation, as

$$n_{ID} = \left(\frac{e}{K_B T} \right) \left(\frac{\Delta V_{OC}}{\Delta \ln I} \right) \quad (20.)$$

The calculated values for the HTLs are n_{ID} (PTAA) = 1.40 and n_{ID} (PF8TAA) = 1.54 respectively. Although recombination mechanism information could be speculated from ideality factor calculation, the ambiguity in interpreting the n_{ID} remains non-

trivial.^{240, 241} Instead, a rather clear trend is that the higher n_{ID} value for PF8TAA PSC leads to greater V_{OC} improvement, compared to PTAA PSC at high light intensities. For example, it can be observed that ΔV_{OC} is 23 mV at intensity of 0.01 mW cm^{-2} , and ΔV_{OC} increases to 80 mV at intensity of 100 mW cm^{-2} (1 Sun illumination). In comparison with related PL_{rel} data at 0.01 mW cm^{-2} , the difference between $PL_{rel, PF8TAA}$ and $PL_{rel, PTAA}$ is fourfold, corresponding to $\Delta V_{OC} = 36 \text{ mV}$, which matches well with the measured $\Delta V_{OC} = 23 \text{ mV}$.

At low light intensities, the changes in PL_{rel} follow and match well with the changes in V_{OC} . In this case, the magnitude of the $\Delta E_{F,bulk}$ is small, thus a small degree of upward bending of $E_{F,p}$ occurs between the HTL and perovskite active layer, Figure 4.12a. In contrast, the trend becomes different when the light intensity is raised up to higher level, when there are smaller differences between PTAA and PF8TAA in $\Delta E_{F,bulk}$ whereas larger differences in V_{OC} . Since V_{OC} represents the ΔE_F between the two electrodes in PSCs, the greater mismatch between V_{OC} and $\Delta E_{F,bulk}$ reveals stronger upward bending of $E_{F,p}$ between the HTL and perovskite active layer. Here, in our case, the PTAA has stronger upward bending than PF8TAA. The dominant limiting factor of V_{OC} becomes the extent of upward bending of $E_{F,p}$ required to align with $HOMO_{HTL}$, Figure 4.12b. Therefore, with increasing light intensity, the magnitude of $\Delta E_{F,bulk}$ becomes greater, by which the upward bending of $E_{F,p}$ at HTL/perovskite interface is more crucial. This results in greater V_{OC} losses and larger mismatch between the V_{OC} and $\Delta E_{F,bulk}$ as well.

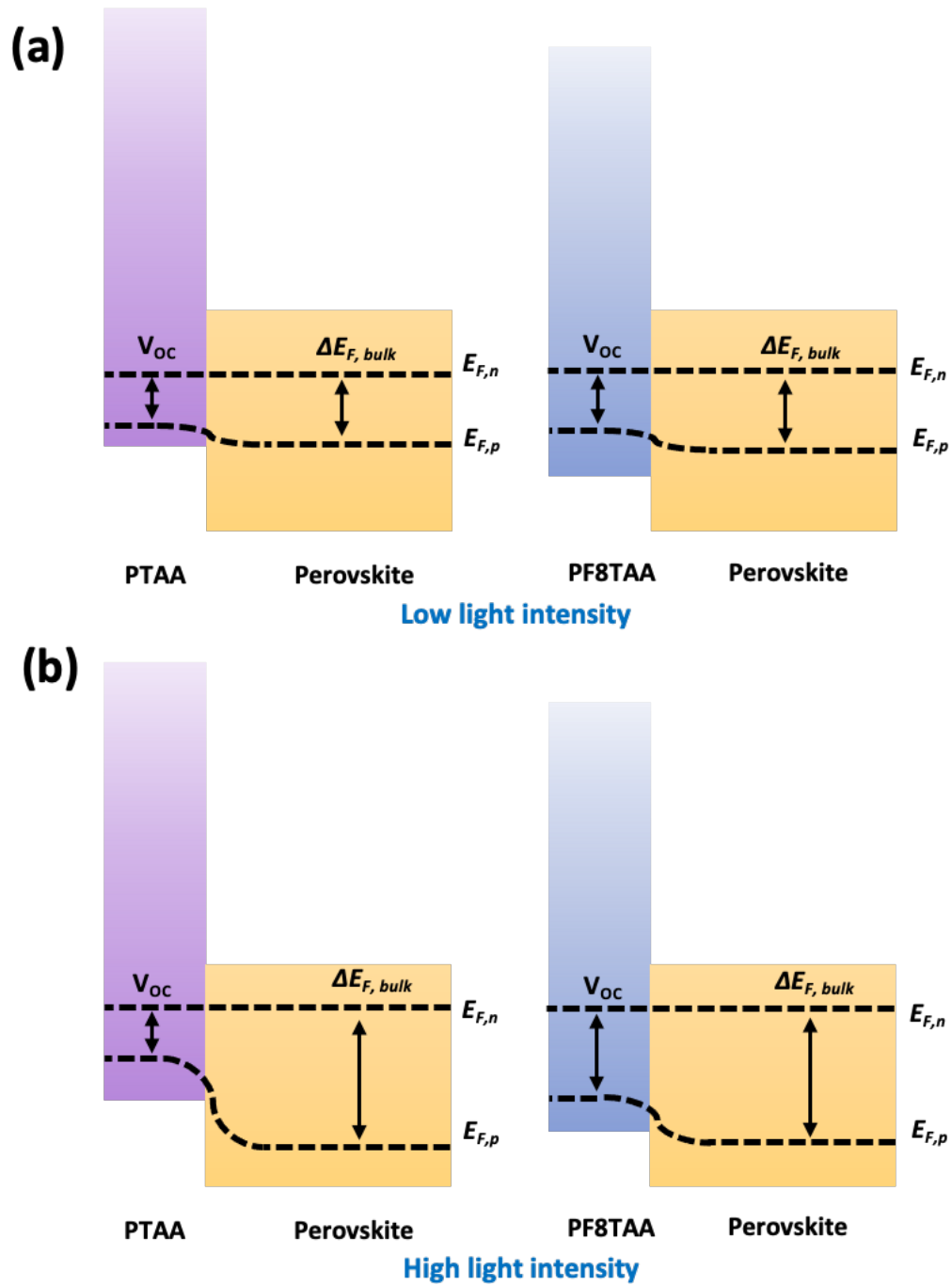


Figure 4.12. Schematic representations of the band diagrams at open circuit, under **(a)** low light conditions and **(b)** high light conditions.

4.2.4 Photoluminescence Studies of Charge Extraction and Recombination Dynamics

Charge extraction and recombination dynamics were investigated using time-resolved PL spectroscopy, the results of which also correlate with device performance, Figure 4.13. The PL decays of perovskite films are measured with time-correlated single-photon counting (TCSPC), probed at the peak position of PL emission spectra.

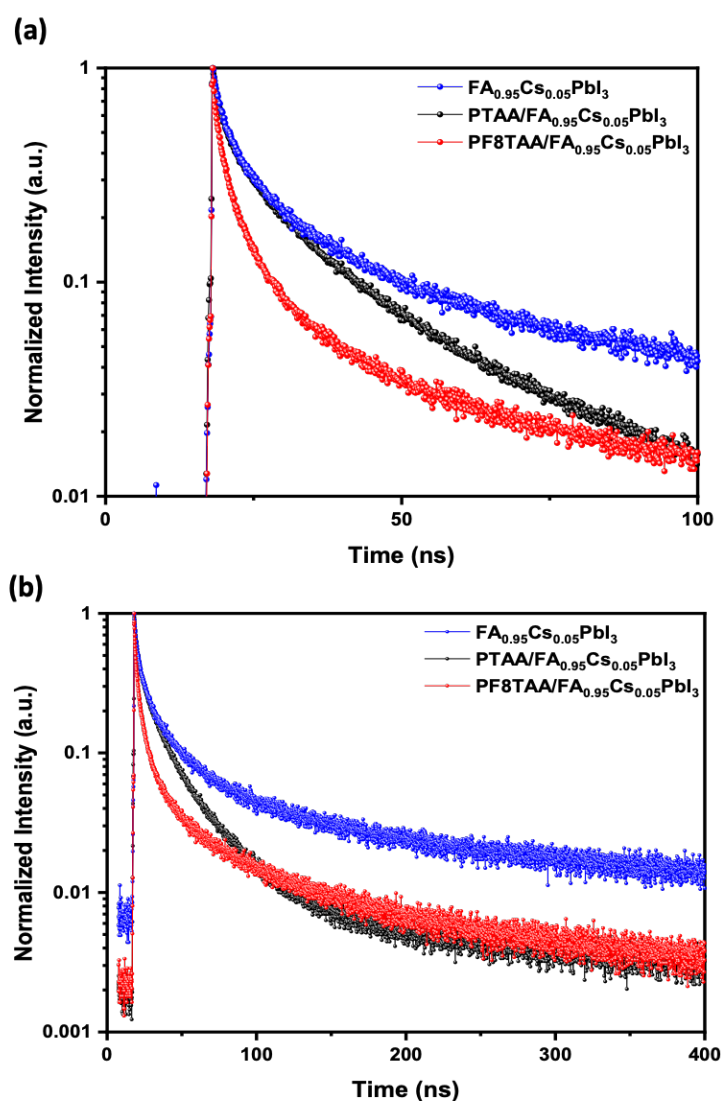


Figure 4.13. Time-resolved photoluminescence spectroscopy of neat, $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$, $\text{PTAA}/\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$, and $\text{PF8TAA}/\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ films over the time ranges (a) 0–100 ns and, (b) 0 – 400 ns.

The neat perovskite film raw data is suitable for fitting as a biexponential decay, where the faster phase is assigned to non-radiative trap-assisted recombination and the slower phase to bimolecular recombination.²⁴² Notable PL quenching can be observed when perovskite layer is interfaced with either of HTLs, with a higher PL quenching in PF8TAA case, which reveals more efficient charge transfer compared to PTAA counterpart.²⁴³ This finding is probably ascribed to a reduced surface/interfacial trap density and also the improved band energy alignment of HTL/perovskite.

The results above emphasize the limiting factors of V_{OC} which originate from the magnitude of the energetic offset between the $HOMO_{HTL}$ and $VB_{perovskite}$. A typical example at relatively high light intensities, $\Delta E_{F,bulk}$ gets close to the magnitude of E_g of the perovskite. This situation agrees with our case at high illumination levels and fit the scenario of high- V_{OC} devices which are made from high-quality perovskite films with defect passivation in perovskite bulk or interfaces. When $\Delta E_{F,bulk}$ becomes smaller than the perovskite E_g , the V_{OC} is predominantly determined by $\Delta E_{F,bulk}$ and less affected by $HOMO_{HTL}$, corresponding to lower illumination levels. This can be extended generally to the situation when non-radiative recombination is the main limitation of $\Delta E_{F,bulk}$. It can be ascribed to insufficient defect passivation in the interlayer/perovskite or high doping levels of HTLs. Thus, it may be a common circumstance in non-state-of-the-art PSCs which lack of correlation between $HOMO_{HTL}$ and V_{OC} thus have considerably low V_{OC} -to- E_g ratio.

4.2.5 Stability of Mixed-Cation Perovskite

The phase stability of mixed-cation perovskite on different HTLs was examined by aging the films under different testing conditions. The stability test was conducted in an environmental chamber (see Chapter 3), which can control the humidity level precisely with ambient air condition (25°C). Perovskite films were put on a sample holder inside the glovebox, with 1 sun light source shining from top to bottom. The humidity controller connected to the glovebox was used to adjust the humidity level quantitatively.

Using this apparatus, four experimental conditions were investigated, namely:

- 1) light and humid (1 sun illumination, 75% RH).
- 2) dark and humid (75% RH).
- 3) light and dry (1 sun illumination, 13% RH).
- 4) dark and dry (13% RH).

Additionally, for each condition three substrates were used, ITO, ITO/PTAA, and ITO/PF8TAA. The perovskite composition $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ was used for all experiments. The structure and composition of the perovskite films were monitored over time using X-ray diffraction (XRD).

Figure 4.14 displays photographs of $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ films aged under four different testing conditions. Except for the perovskite films aged under light and humid condition (1 sun illumination, 75% RH), all other films retained their black colour after 32 hours, suggesting negligible degradation occurred during this time period, which will be further confirmed by XRD. Figure 4.15 shows the XRD patterns of perovskite films at

0 h, confirming that all fresh perovskite films were pure α -FAPbI₃ without a secondary phase of PbI₂. The XRD patterns of perovskite films under different testing conditions are shown in the Figure 4.16, which includes a magnified view of the (001) peak. This peak is commonly used as a characteristic diffraction peak for α -FAPbI₃ due to its strongest intensity at around 14.1° 2 θ , as reported in the literature. Additionally, the peak detected at 12.0° 2 θ corresponds to the diffraction peak of δ -FAPbI₃, and the peak observed at 12.9° 2 θ is attributed to the diffraction peak of PbI₂.²¹²

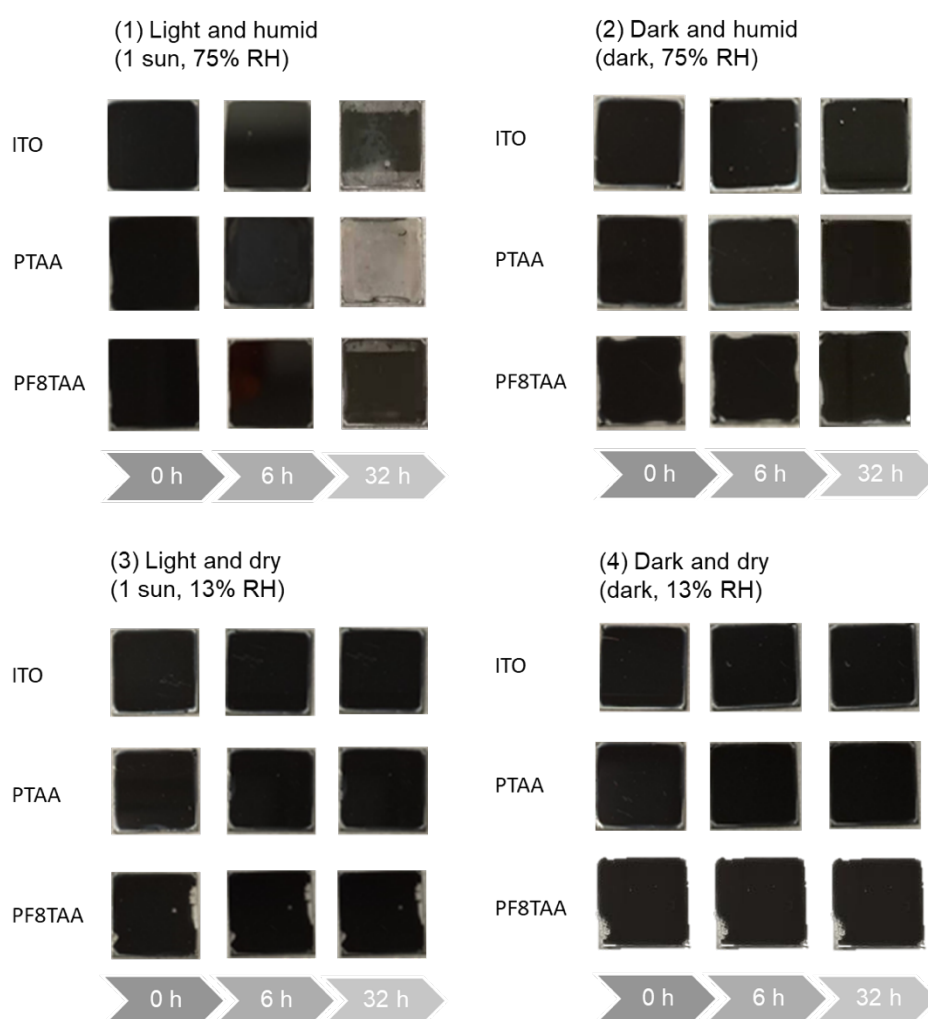


Figure 4.14. Photographs of FA_{0.95}Cs_{0.05}PbI₃ films aged under different testing conditions: (1) light and humid (1 sun illumination, 75% RH), (2) dark and humid (75% RH), (3) light and dry (1 sun illumination, 13% RH), (4) dark and dry (13% RH). The size of each substrate is 1.2 cm × 1.2 cm.

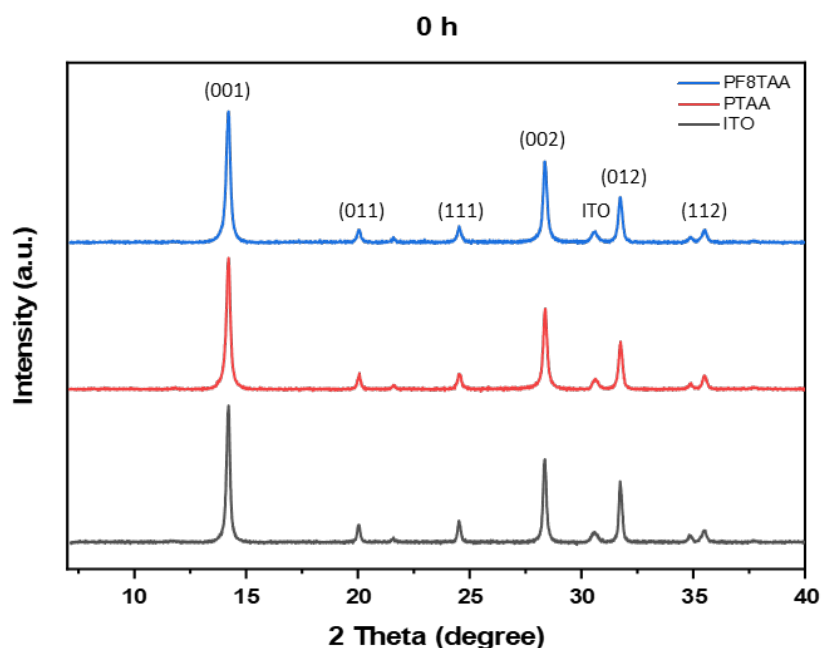


Figure 4.15. X-ray diffraction (XRD) patterns of perovskite films at 0 h (fresh). The diffraction peaks of α -FAPbI₃ are labelled in the plots.

After 32 h, perovskite films aged under (1) light and humid condition (1 sun illumination, 75% RH) showed the appearance of the δ -FAPbI₃ phase, indicating degradation of the films due to a phase transition from the black, photoactive α -phase to the yellow, photoinactive δ -phase. The comparison of perovskite degradation on both HTLs will be discussed in the following section. In (2) dark and humid condition (75% RH), no appearance of PbI₂ or δ -FAPbI₃ was observed. All aged films maintained their black α -FAPbI₃, indicating no degradation had occurred. This will be further confirmed by quantitative analyses. In both (3) light and dry condition (1 sun illumination, 13% RH) and (4) dark and dry condition (13% RH), a small amount of PbI₂ appeared due to the

chemical degradation of α -FAPbI₃, while no sign of δ -FAPbI₃ phase was observed in the XRD patterns.

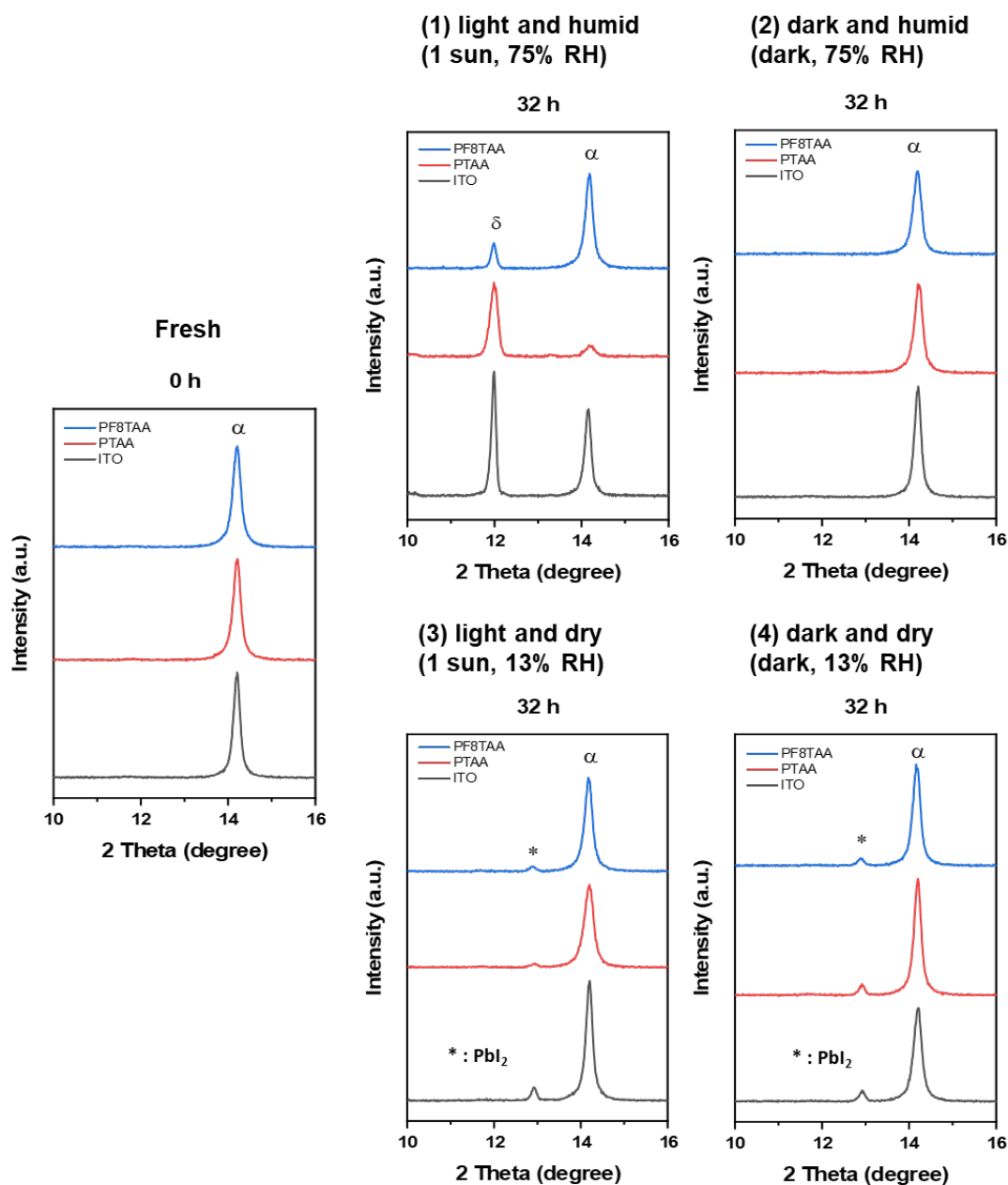


Figure 4.16. XRD patterns of perovskite films aged under different testing conditions: (1) light and humid (1 sun illumination, 75% RH), (2) dark and humid (75% RH), 3) light and dry (1 sun illumination, 13% RH), (4) dark and dry (13% RH). The peaks assigned to α -phase and δ -phase are labelled on the plots, and * denotes PbI_2 peak.

Peak shift: The degradation of perovskite and formation of δ -phase can lead to an increase in the lattice spacing because the δ -phase ($284.6 \text{ \AA}^3$) has a larger unit cell volume compared to the α -phase ($256.0 \text{ \AA}^3$).²⁴⁴ This is due to the distortion of the crystal lattice caused by the rotation of the PbI_6 octahedra in the δ -phase. At 0 h, the peak position of (001) diffraction peak was located at 14.2095° , 14.2002° , and 14.2099° for ITO, PTAA, and PF8TAA respectively. In light and humid condition (1 sun illumination, 75% RH), the peak position of aged film shifts to a smaller angle after 32 h (14.1393° , 14.1811° , and 14.1829°)(Figure 4.17 a), associated with increased lattice spacing d (Figure 4.17 b) according to Bragg's law (Chapter 3). The results indicate that degradation of α -phase occurred under this condition. In the other three conditions, there was no peak shift or lattice spacing change observed on aged films.

Crystallinity: The crystallinity of α -phase can be monitored by the integrated peak area of the (001) diffraction peak. To analyse and compare the severity of degradation, we used the integrated peak area (Figure 4.17 c). Before the stability test (0 h), all pristine films showed a prominent characteristic peak at around $14.1^\circ 2\theta$ for α -FAPbI₃ perovskite phase on different substrates (ITO, PTAA, and PF8TAA) with similar integrated peak areas (31.65, 36.08, and 37.11 respectively).

After 32 h in light and humid condition (1 sun illumination, 75% RH), the integrated peak area of α -FAPbI₃ decreased to different levels: 30.69 for ITO, 3.58 for PTAA, and 27.42 for PF8TAA, owing to phase degradation to δ -FAPbI₃. The ratio of δ -FAPbI₃/ α -FAPbI₃ was calculated as 0.64, 5.07, and 0.16 on ITO, PTAA, and PF8TAA, respectively. The larger the ratio, the more severe the degradation, as more α -FAPbI₃ perovskite phase has degraded and transferred into the δ -FAPbI₃ photoinactive phase.

Notably, the perovskite film on PTAA suffered from the most severe degradation, while the PF8TAA counterpart exhibited enhanced stability.

In the other three conditions, there was no significant change in the integrated peak area of α -FAPbI₃ (001) peak, confirming no notable degradation was seen up to 32 h. It is interesting to note that the perovskite films remained stable under dark and humid condition (75% RH), suggesting that the degradation process is more likely to occur under the condition that involves both light and moisture.

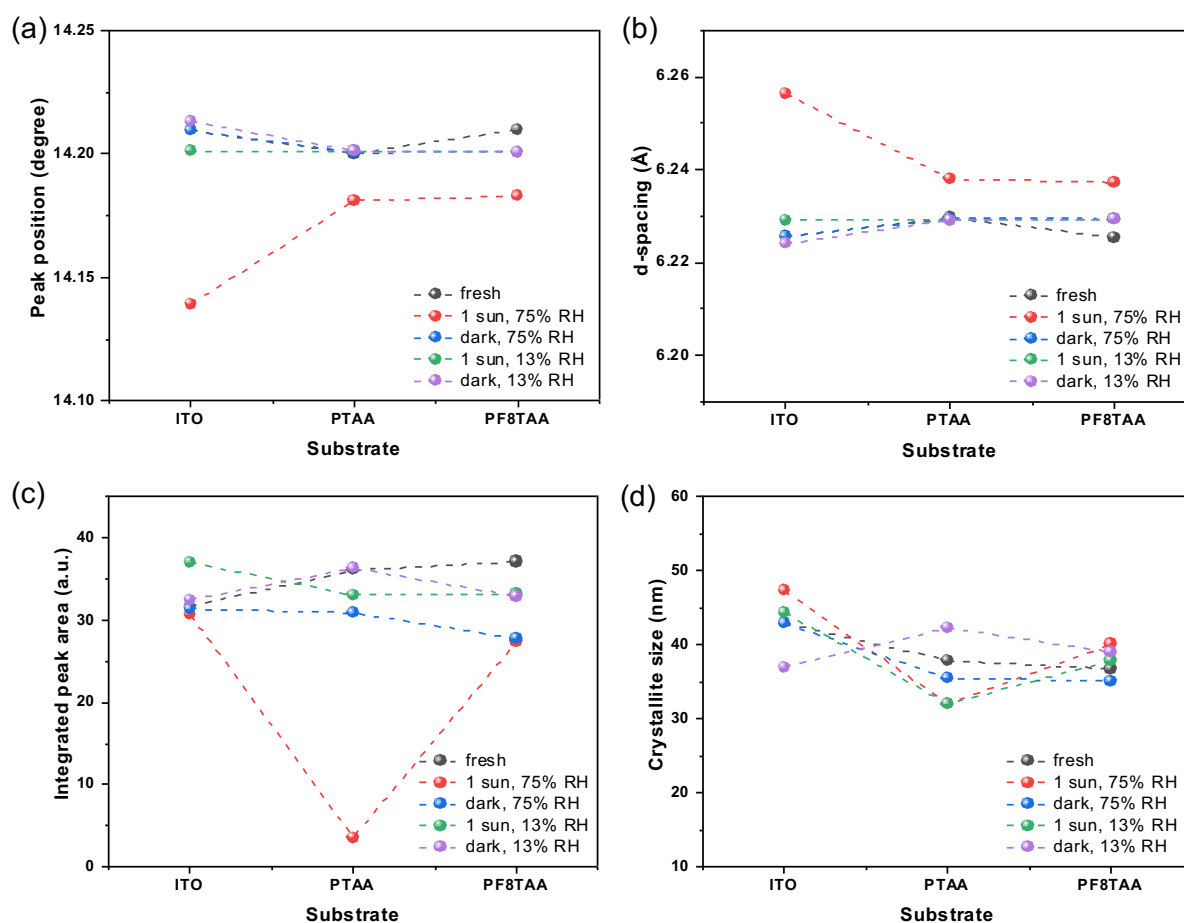


Figure 4.17. XRD analyses of fresh (0 h) and aged (32 h) films on the α -phase (001) peak: (a) perovskite peak position, (b) d-spacing, (c) integrated peak area, (d) corresponding crystallite size of perovskite on three different substrates, ITO, PTAA, and PF8TAA.

Crystallite size:

Crystallite size relates the full width at half maximum (FWHM) and can be estimated by Scherrer equation (Chapter 3). From Figure 4.17 d, the crystallite size of (001) peak ranges from 36.7 - 42.9 nm for fresh films, and 32.0 - 47.3 nm for all aged films. The crystallite size of the perovskite films remains relatively consistent, with a small degree of variation observed between the fresh and aged films, indicating no significant change in the average crystallite size. Table 4.5 lists the calculated (001) α -phase peak parameters of fresh and aged films.

The mixed-cation perovskite $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ is found to be vulnerable to degradation under the influence of light and moisture, resulting in the formation of $\delta\text{-FAPbI}_3$ as a major degradation product. However, the perovskite on PF8TAA exhibits superior stability compared to PTAA under identical conditions.

Table 4.5. Calculated XRD parameters of the α -phase (001) peak, for fresh (0 h) and aged (32 h) perovskite films on different testing conditions.

Substrates	Conditions	Peak position 2θ (degree)	d-spacing (Å)	Integrated peak area	FWHM (degree)	Crystallite size (nm)
ITO	Fresh	14.2095	6.226	31.65	0.1865	42.9
	1 sun, 75% RH	14.1393	6.256	30.69	0.1692	47.3
	dark, 75% RH	14.2095	6.226	31.36	0.1866	42.9
	1 sun, 13% RH	14.2013	6.229	37.05	0.1806	44.3
	dark, 13% RH	14.2131	6.224	32.47	0.2167	36.9
PTAA	Fresh	14.2002	6.230	36.08	0.2115	37.8
	1 sun, 75% RH	14.1811	6.238	3.58	0.2501	32.0
	dark, 75% RH	14.2006	6.229	30.89	0.2256	35.5
	1 sun, 13% RH	14.2013	6.229	33.04	0.2501	32.0
	dark, 13% RH	14.2013	6.229	36.30	0.1893	42.3
PF8TAA	Fresh	14.2099	6.225	37.11	0.2179	36.7
	1 sun, 75% RH	14.1829	6.237	27.42	0.1997	40.1
	dark, 75% RH	14.2008	6.229	27.77	0.2284	35.0
	1 sun, 13% RH	14.2009	6.229	33.16	0.2115	37.8
	dark, 13% RH	14.2008	6.229	32.92	0.2053	39.0

4.3 Conclusion

In summary, p-i-n planar perovskite solar cells have been fabricated and characterized. PTAA and its related co-polymer PF8TAA were used as HTLs, with structural, device characterization and device performance analysis presented for both. The HTLs have similar molecular structures, along with similar band gaps and doping levels, which allows a more focused study on the correlation between HOMO_{HTL} on device performance, especially V_{OC} .

The distinct differences in HTL HOMO levels are characterized by APS, highlighting PF8TAA has a HOMO level of $-5.24 (\pm 0.05)$ eV, which is 0.21 eV deeper than PTAA counterpart. The surface morphology of perovskite films, characterized by SEM, shows a slight increase in the average grain size when PF8TAA is employed, accompanied by an increase in the grain dispersity. The increased average grain size on PF8TAA sample is favorable for perovskite devices and may also contribute to enhanced device performance.²²⁴ More importantly, no significant differences in crystallinity were detected on PTAA and PF8TAA, characterized by XRD. It can be excluded that the variations in device performance are induced by structural variations in the perovskite layers on PTAA and PF8TAA. The PL decays, characterized by TCSPC, show that more efficient charge transfer from the perovskite to the HTL occur in the PF8TAA sample compared to PTAA counterpart.

For both $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ and MAPbI_3 perovskite, devices applying PF8TAA as HTL show higher V_{OC} than the ones relying on PTAA as HTL. The enhanced device V_{OC} of PF8TAA is about 40 mV for $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ PSC, and 60 mV in MAPbI_3 PSC. Light-intensity dependent PL and JV measurements were applied to study and understand

this phenomenon. Numerous significant observations have been made through our investigation. When $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ is interfaced with different HTLs, significant different PL behaviours can be noticed, where the PL_{rel} for PF8TAA device is always higher than PTAA counterpart at all light intensities, more so at low light intensities region. At low light intensities, PL_{rel} variations follow the changes in V_{OC} , when the magnitude of the $\Delta E_{F,bulk}$ is small, there is a small degree of upward bending of $E_{F,p}$ between the active layer and HTL. At high light intensities, PSCs reliant on PF8TAA and PTAA as HTLs show less variation in $\Delta E_{F,bulk}$ whereas greater differences in V_{OC} . In this case, the dominant limiting factor for V_{OC} becomes the extent of upward bending of $E_{F,p}$ which is required to align with $\text{HOMO}_{\text{PTAA}}$ compared with $\text{HOMO}_{\text{PF8TAA}}$ at the interface between HTL and perovskite. Therefore, the magnitude of $\Delta E_{F,bulk}$ becomes larger when light intensity increases, and $E_{F,p}$ bending at the HTL/perovskite interface more prominent, leading to greater V_{OC} losses.

This work sheds light on undetermined question regarding the role of the HTL HOMO level on device V_{OC} , illustrating that it is critical to minimize the energetic offset between the HTL and perovskite to further reduce V_{OC} losses to pursue the cutting-edge perovskite solar cells.

Additionally, thin film stability study shows that mixed-cation perovskite is prone to degradation when exposed to light and moisture, leading to the α -to- δ phase transition. However, it was found that perovskite films on PF8TAA display better stability than those on PTAA under the same conditions. The stability experiments conducted so far have only been on perovskite films, with device stability yet to be investigated due to time limitations, which will be examined in future studies.

5. Methylammonium Chloride Treatment with Wide Processing Window for Highly Efficient Perovskite Solar Cells

5.1 Introduction

Background Information

Organic-inorganic hybrid perovskite materials are comparatively attractive as light absorbers because of their tunable band gap from 1.48 eV to 2.3 eV via mixing different cations or halides into the systems. Among the perovskite materials, formamidinium (FA)-based perovskites have been extensively studied recently owing to the ideal band gap which is closer to the optimal value in Shockley–Queisser(S-Q) limit, and they exhibit a broader light absorption spectrum extending to 840nm.²⁴⁹⁻²⁵¹ For FAPbI₃, there are two phases, yellow non-perovskite (δ -phase) and black perovskite (α -phase), the later being photoactive hence useful for solar cells. Generally, the FA-based perovskite materials have phase instability at room temperature in ambient conditions, whereby the α -phase can readily transform into δ -phase owing to the large size of FA⁺ cation.²⁵³ Since the large ionic radius of FA⁺ (2.79 Å) results in a large tolerance factor (>1) for pure FAPbI₃, which is more stable to form hexagonal structure (δ -phase) according to Goldschmidt's rule (Chapter 2).⁷ Studies have shown that the introduction of smaller cations, such as MA⁺ (2.70 Å)/ Cs⁺ (1.81 Å), can effectively inhibit the phase instability, with proper tuning the tolerance factor of perovskite into ideal region (0.8 - 1) to form cubic structure (α -phase).

To achieve high performance solar cells, it is of great importance to control perovskite films to form highly crystalline and dense-grained uniform morphology.^{56, 255} Considerable efforts have been made to achieve these objectives using various approaches, such as selecting different perovskite precursors, adapting fabrication methods, using alternative antisolvents, adjusting annealing conditions, applying surface passivation, and introducing additives. Several groups have reported the effective use of methylammonium chloride (MACl) as an additive that can stabilise the α -phase via the formation of intermediate adducts with Pb^{2+} , through which the perovskite crystal growth can be slowed down and be able to grow into larger grains with higher crystallinity.^{48, 260, 261} More recently, Xie *et al.* reported a novel method using MACl to control the vertical recrystallization process of FA-based perovskite, in which MACl is spin-coated as post-treatment on as-deposited perovskite film prior to annealing.⁴⁹ Upon annealing, MACl would vertically diffuse into the δ -phase perovskite film and then assist the recrystallization of FAPbI_3 to α -phase, resulting in compact and large-sized grains with minimized grain boundaries. Pre-deposited δ -phase perovskite films can be phase transformed into α -phase with MACl as stabilizer to achieve homogeneous nucleation and smooth uniform grain growth.⁴⁹

The Buried Interfaces

With these efforts, the compact morphologies of perovskite thin films, which are generally observed by top view SEM, can be obtained. Nevertheless, the compact surface of perovskite film cannot always guarantee efficient device performance. Further enhancement of state-of-the-art PSCs has been predominantly hampered by a lack of thorough comprehension of the heterojunction interfaces between perovskite and CTLs and interfacial optimization designs.²⁶²⁻²⁶⁴ Previous studies have put a large

number of efforts on the top surfaces of perovskite films, where researchers have gained lots of understanding towards the correlations of perovskite surface morphology and device performance.²⁶⁵⁻²⁶⁷ However, the buried interfaces of perovskite films can cause dramatic performance losses in photovoltaics, which are comparatively lack of investigation than the top surface of perovskite. It is found that sub-microscale imperfections and inhomogeneities are accumulated at the buried interfaces, limiting device performance as a result.²⁷⁰ Recently Yang *et al.* proposed a facile and effective method to uncover the mystery of the buried interfaces characteristics via a lift-off process in FA-based PSCs. They showed those imperfections and inhomogeneities originate from complex phases which are directly correlated to undesirable non-radiative losses.²⁷⁰ Therefore, efficient passivation approaches are needed to mitigate the imperfections and inhomogeneities, minimize the undesirable losses and boost the PCEs.

Widening the Processing Window of PSCs

Apart from the above, selection of antisolvents, and dripping time should be controlled precisely to achieve high PCEs. One of the main challenges in the field is the narrow processing window of perovskite fabrication, making it difficult to reproduce among the labs. Among the literature, several approaches to widen the processing window of PSCs have been reported.²⁷¹⁻²⁷³ Chen *et al.* demonstrated an approach of additive engineering in antisolvent to promote the seed growth in perovskite thin film, which can widen the processing window during the antisolvent dripping process.²⁷¹ Employing anisole as an alternative antisolvent resulted in improved tolerance to antisolvent dripping time (from 2 to 40 s) and solvent ratio (DMF/DMSO v/v from 7:3 to 0:10) of precursor solution.²⁷¹ Some research groups turn their considerations to the solvents

in perovskite precursor solutions. For example, Huang *et al.* reported the antisolvent dripping time window can be broaden (from 9 to 90 s) by replacing DMSO with tetrahydrothiophene 1,1-dioxide (sulfolane) in the mixed solvent DMF/DMSO of perovskite precursor.²⁷² Yang *et al.* employed a mixed solvent DMF/NMP rather than DMF/DMSO in precursor solution to enable a wide processing window (up to 8min).²⁷³ However, most of the work on widening the processing window is focused on methylammonium lead iodide (MAPbI₃) and triple cation perovskites with moderate band gap (>1.5 eV). Such effort has not been extended to FA-based perovskites with narrower band gap (<1.6 eV).

The Focus of This Study

Here, a novel sequential dynamic deposition (SDD) approach is investigated to mitigate the microstructural defects and inhomogeneities at the buried interfaces of FA-based perovskite. The SDD approach consists of the antisolvent dripping method and MACl treatment. Different from traditional methods of adding MACl as additives in precursor solutions or static spin-coating on as-deposited perovskite films, MACl is added via a dynamic spin-coating approach, in which the MACl solution is deposited on the spinning perovskite substrate prior to annealing (see Chapter 3). The addition of MACl can effectively eliminate microstructural defects and inhomogeneities at the buried interfaces of perovskite films, with improved crystallinity, increased grain sizes and reduced grain boundaries, leading to reduced interfacial recombinations and significantly enhanced device performance. In addition, the perovskite fabrication processes become less sensitive to different types of antisolvents and antisolvent dripping times. This approach can be extensively used in perovskite films with a range of thicknesses (500 nm ~ 1 μ m), resulting in remarkable device performance

improvements. The results demonstrate this SDD approach can achieve considerably enhanced PCEs and widen the processing window of narrow bandgap FA-based PSCs.

5.2 Results and Discussion

5.2.1 Modification of Perovskite Film Processing

Figure 5.1 shows a schematic illustration of traditional deposition and sequential dynamic deposition (SDD) approaches. In both cases, diethyl ether is added as antisolvent on the spinning substrate with perovskite precursor solution. For traditional deposition method, the as-deposited film is then directly placed on hotplate for thermal annealing, to remove the remaining solvents and crystallize the perovskite film. For SDD method, a MACl layer is added on the as-deposited perovskite film by dynamic spin-coating of MACl in IPA solution, followed by thermal annealing.

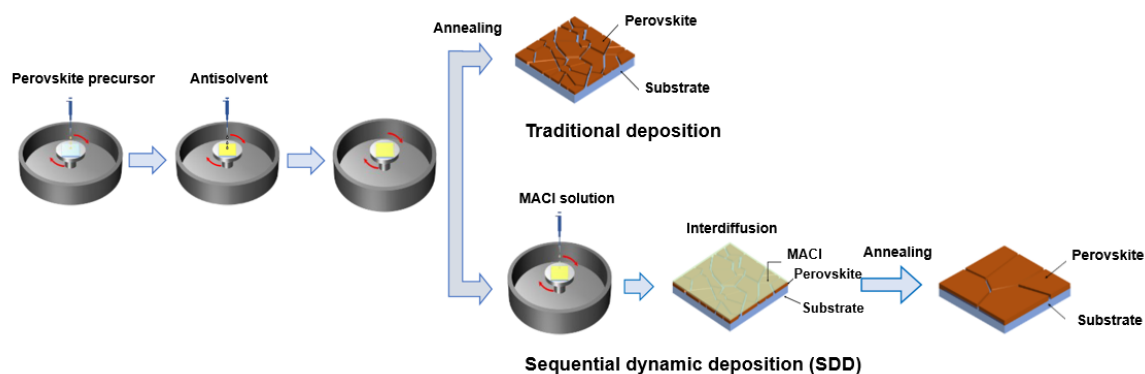


Figure 5.1. Schematic illustration of traditional deposition method and sequential dynamic deposition (SDD) method for preparing the perovskite film.

A peel-off method (developed by Chieh-Ting Lin) is presented in Figure 5.2 to obtain and uncover the bottom side of the perovskite film *i.e.*, the buried interface. The perovskite precursor solution is spin-coated on a glass substrate through either traditional deposition or SDD approach, and polycrystalline perovskite film is formed via thermal annealing. Transparent epoxy UV curable glue is added on top of

perovskite layer, following by sealing with a cover glass using UV light. Afterwards, the perovskite layer is carefully peeled off from the bottom glass substrate, exposing the buried interface.

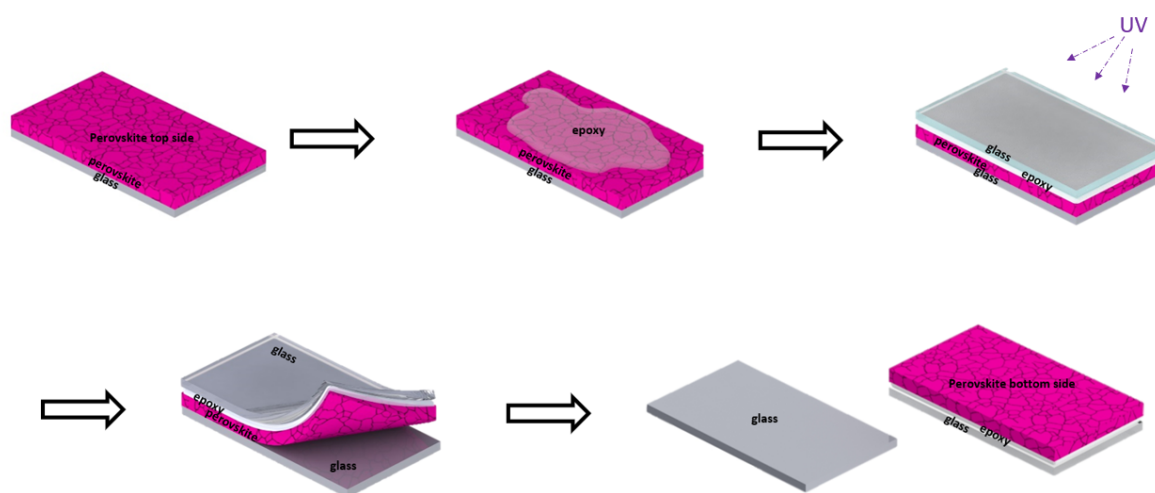


Figure 5.2. Schematic illustration of peel-off method to obtain the bottom-side of perovskite films.

5.2.2 Morphological Analyses

Figure 5.3 (a-b) displays photographs of pristine perovskite film on a glass substrate. The top side of perovskite film shows a characteristic black, shiny and smooth surface. In contrast, the bottom side (imaged through the substrate) appears foggy. The surface morphology of perovskite film is important for device performance. Surface scanning electron microscopy (SEM) images of the pristine perovskite film, top side and bottom side are shown in Figure 5.3 (c-d). Crystalline and uniform grains are seen on the top side, however, voids and defects are observed on the bottom side.

Such voids and defects create microstructural inhomogeneities and imperfections that may induce interfacial recombination and be detrimental to device performance.²⁷⁶

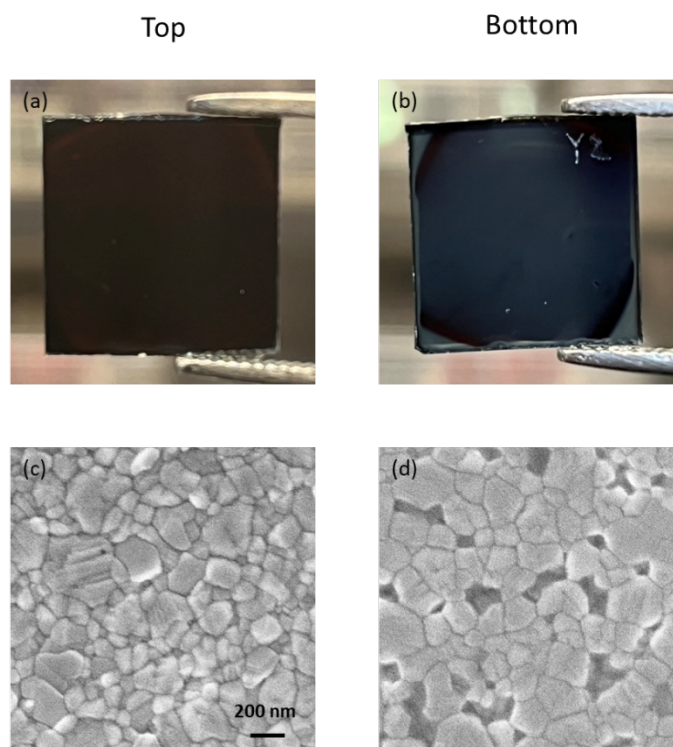


Figure 5.3. (a-b) Photographs of perovskite films from the (a) top side and (b) bottom side. The size of the substrate is 1.2 cm $\times$ 1.2 cm. (c-d) Corresponding surface scanning electron microscopy (SEM) images from (c) top side and (d) bottom side. The scale bar (200 nm) is the same for both images.

$\text{FA}_{0.95}\text{MA}_{0.05}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$ is chosen as the reference perovskite. Adding 5% MAPbBr_3 into FAPbI_3 can help to form and efficiently stabilize the α -phase at relatively low temperature process (100°C).^{277, 278} The morphology of the perovskite films with differing MACl treatments were investigated by SEM.

Figure 5.4 (a-f) show the surface SEM images of perovskite films from the top side with increasing MACl concentrations (16 μl MACl in IPA solution is added on each film,

more details in Chapter 3). It can be seen that the average grain size of perovskite increases with increasing MACl concentration, suggesting the this treatment can facilitate the growth of perovskite grains. The grain size of pristin film without MACl (Ref-0) was about 160 ± 24 nm in average. A larger average grain size of 237 ± 57 nm was obtained with 1 mg/ml MACl, and the average grain size was 646 ± 138 nm with 3 mg/ml MACl. The grain size was further increased to 1207 ± 218 nm for 9 mg/ml MACl. Figure 5.4 g shows the grain size distribution on the top side as a function of MACl concentration. It is worth noting that small voids were observed on 9 mg/ml MACl, resulting in microstructural defects in perovskite film, which is likely to cause interfacial recombination losses and unfavourable to photovoltaic energy conversion.²⁷⁶

Top side

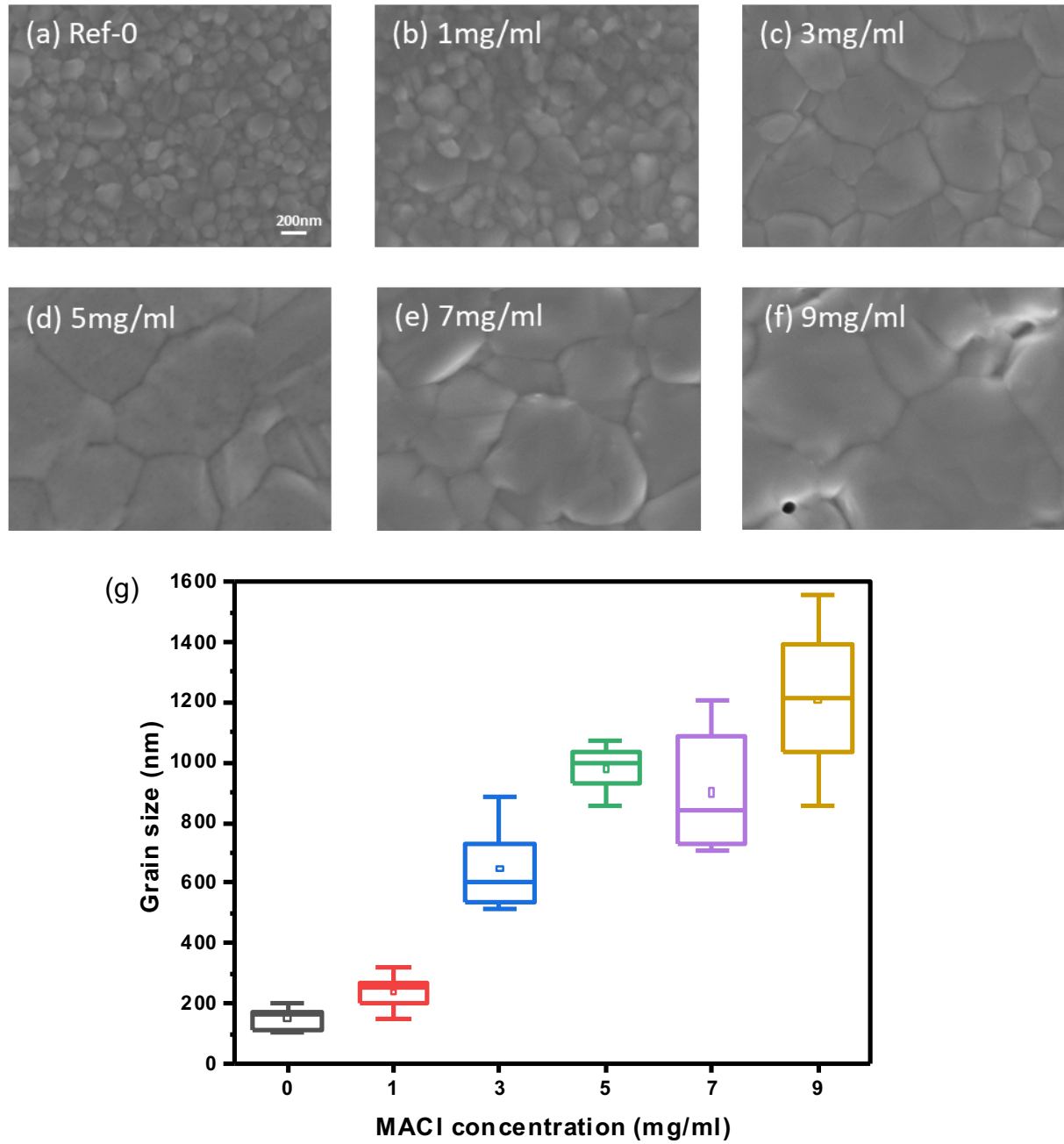


Figure 5.4. Surface topography and grain size distribution of perovskite films from the top side. (a-f) Surface SEM images of $\text{FA}_{0.95}\text{MA}_{0.05}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$ films with different amount of MACl: (a) pristine (without addition), (b) 1 mg/ml MACl, (c) 3 mg/ml MACl, (d) 5 mg/ml MACl, (e) 7 mg/ml MACl, and (f) 9 mg/ml MACl. The scale bar (200 nm) is the same for all images. (g) Grain size distribution of the films as a function of MACl concentration (0, 1 mg/ml, 3 mg/ml, 5 mg/ml, 7 mg/ml, and 9 mg/ml).

Figure 5.5 (a-f) show the surface SEM images of perovskite films from the bottom side with increasing MACl concentrations. By exposing the buried interfaces of perovskite, undetected microstructural inhomogeneities and imperfections can be identified. Voids as microstructural defects were observed throughout the pristine film (Ref-0) without MACl. With the addition of MACl, voids were reduced in 1 mg/ml film and completely eliminated in 3 mg/ml film. Such features were absent in 5 mg/ml and 7 mg/ml films, confirming the effective defect elimination and improvement on structural coherence by MACl treatment. However, excess amount of MACl (9 mg/ml) would lead to the new appearance of voids on the grain boundaries and in the bulk film.

The average grain size of perovskite is increased with MACl concentration, and this trend is consistent with previous results from the top side. The pristine perovskite (Ref-0) grains showed a relatively small average size about 190 ± 47 nm, which were increased to 205 ± 53 nm with 1 mg/ml MACl. With the further addition of MACl, the average grain size continued to increase from 585 ± 126 nm (3 mg/ml MACl) to 755 ± 94 nm (5 mg/ml MACl), 812 ± 185 nm (7 mg/ml MACl), and 1070 ± 191 nm (9 mg/ml MACl). Figure 5.5 g shows the grain size distributions on the bottom side as a function of MACl concentration.

The grain size analyses from both the top side and bottom side suggest that MACl treatment can facilitate perovskite to form larger grains with less grain boundaries.

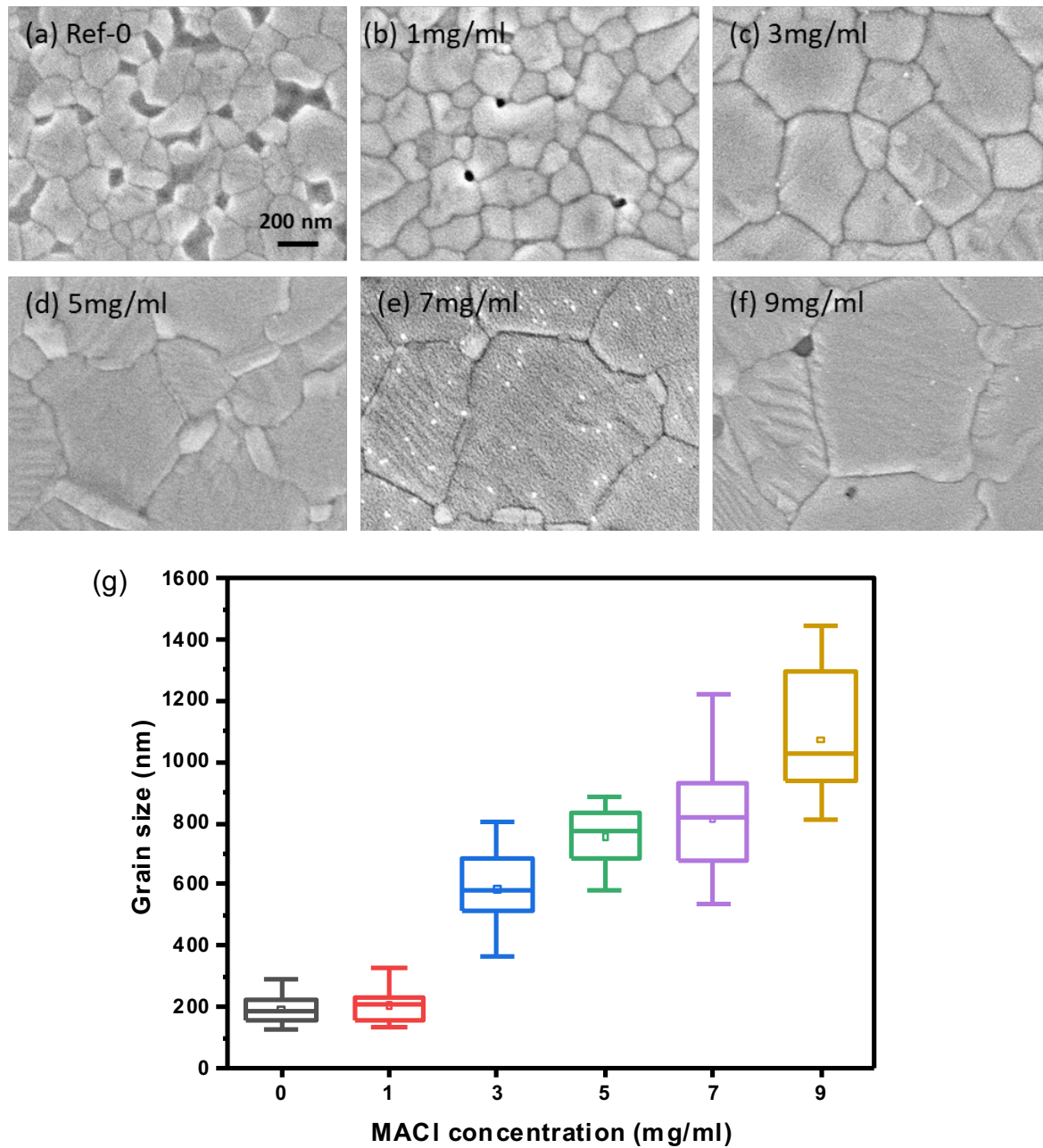
Bottom side

Figure 5.5. Surface topography and grain size distribution of perovskite films from the bottom side. (a-f) Surface SEM images of $\text{FA}_{0.95}\text{MA}_{0.05}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$ films with different amount of MACI: (a) pristine (without addition), (b) 1 mg/ml MACI, (c) 3 mg/ml MACI, (d) 5 mg/ml MACI, (e) 7 mg/ml MACI, and (f) 9 mg/ml MACI. The scale bar (200 nm) is the same for all images. (g) Grain size distribution of the films as a function of MACI concentration (0, 1 mg/ml, 3 mg/ml, 5 mg/ml, 7 mg/ml, and 9 mg/ml).

Cross section SEM images of the same films are shown in Figure 5.6 (a-f). Using ImageJ the film thickness is determined to be about 650 nm for all conditions, however the lateral grain size increases with the addition of MACl. It was also observed that small voids present at the bottom interface – shown in the red boxes in Figure 5.6 a-b. These correlate with those seen in Figure 3 b. At higher MACl concentrations, these defects are eliminated. At the highest MACl concentration, 9 mg/ml MACl (Figure 5.6 f), voids in the bulk of the perovskite film are observed (highlighted in the red box). Thus for subsequent analysis and characterisation, the MACl concentration range 1 - 7 mg/ml were further investigated.

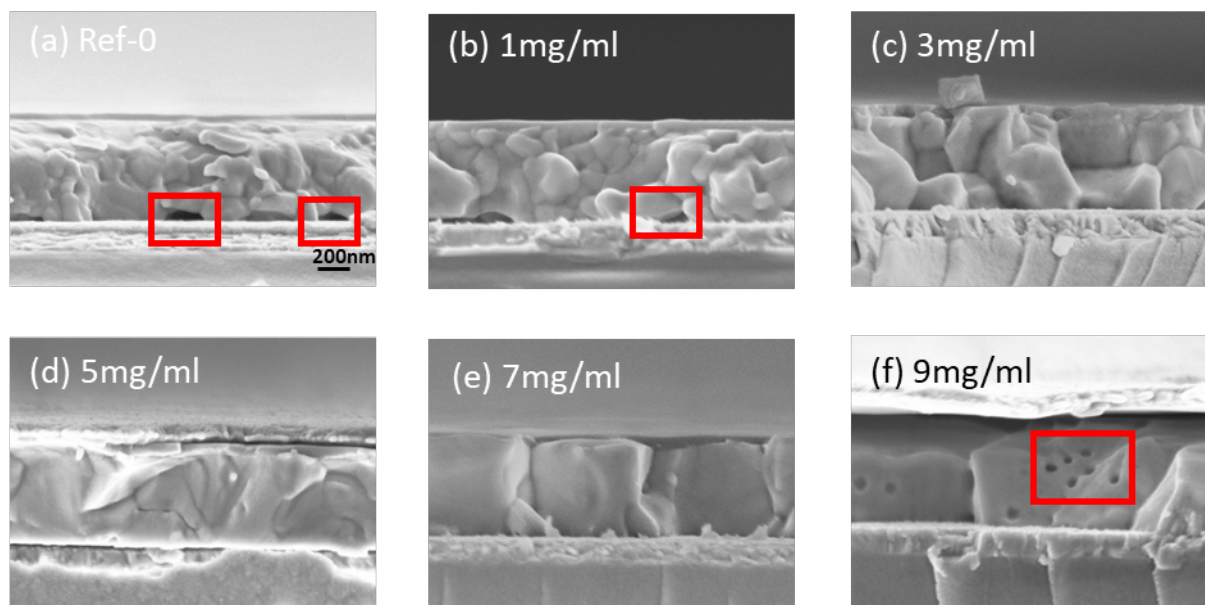


Figure 5.6. Cross-section morphology of vertical crystallization and the schematic of perovskite formation. (a-f) Cross-section SEM images of $\text{FA}_{0.95}\text{MA}_{0.05}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$ films with different amount of MACl: (a) pristine (without addition), (b) 1 mg/ml MACl, (c) 3 mg/ml MACl, (d) 5 mg/ml MACl, (e) 7 mg/ml MACl, and (f) 9 mg/ml MACl. The scale bar is the same for all images.

5.2.3 Optical Characterisations

Steady state photoluminescence (PL) measurements were applied to study charge carrier recombination processes in the films following MACl treatment (Appendix). It can be observed that the PL emission peak position gradually blue shifts with the addition of MACl then remains relatively stable beyond 3 mg/ml, Figure 5.7 a. This indicates the trap state density is reduced on adding MACl to the system.²⁷⁹ In perovskite films with trapping, emission usually occurs on average from energy states closer together owing to the unfilled trap states. If passivation on trap states happens, the emission occurs on average further apart in energy states. In addition, the PL peak intensity increases with increasing MACl concentration from 0 to 5 mg/ml, then yet remains higher than the reference (Figure 5.7 b). The change in peak intensity suggests that the introduction of MACl leads to a suppression of non-radiative recombination process.

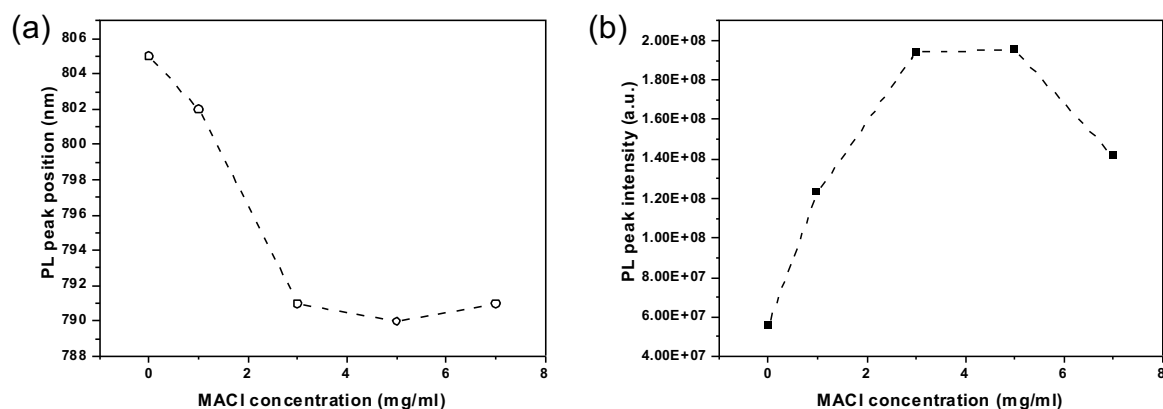


Figure 5.7. (a) Perovskite PL peak position as a function of MACl concentration, (b) Perovskite PL peak intensity as a function of MACl concentration.

Ultraviolet-visible (UV-vis) absorption spectra of the as-prepared films are presented Figure 5.8. These show a blue shift of their absorption onset with increasing MACl concentration. Through Tauc method calculation (see more details in Chapter 3), the band gap of perovskite increases slightly with the addition of MACl, indicating MA incorporation to the perovskite system.²⁸⁰ Table 5.1 summarizes the corresponding band gap energy with different MACl concentrations.

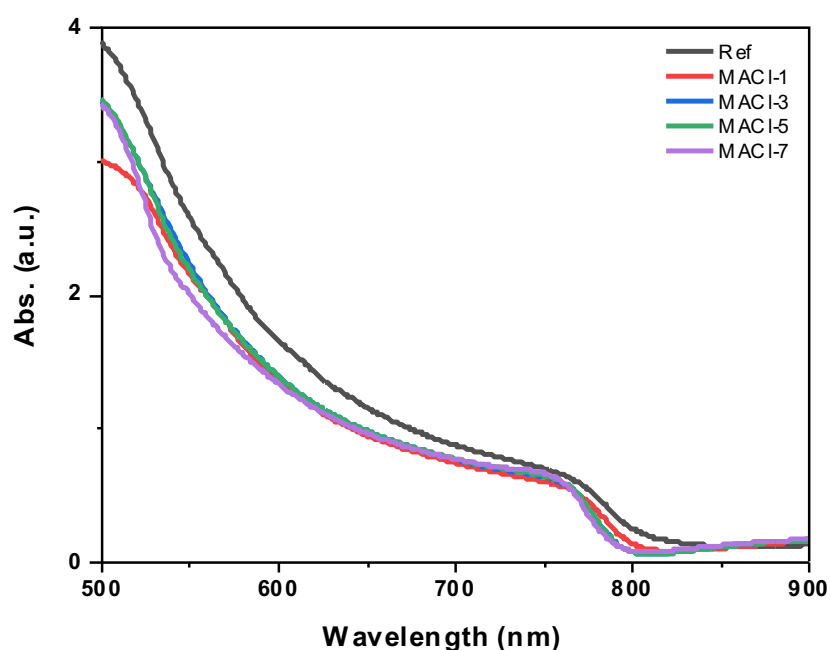


Figure 5.8. Ultraviolet-visible (UV-vis) absorption spectra of perovskite with different MACl concentrations

Table 5.1. Corresponding band gap energy obtained from Tauc method.

	Band gap (eV)
Ref.	1.52 (± 0.01)
MAcI-1	1.54 (± 0.01)
MAcI-3	1.55 (± 0.01)
MAcI-5	1.55 (± 0.01)
MAcI-7	1.56 (± 0.01)

5.2.4 Structural Characterisations

The structural of perovskite films was studied by X-ray diffraction (XRD), shown in Figure 5.9 a. For the reference film, the diffraction peaks of photoactive α -phase (001), (011), (111), (002), (012) and (112) are located at 14.2° , 20.1° , 24.6° , 28.4° , 31.8° and 35.5° respectively. The trend of an increase in peak intensity would indicate a greater degree of crystallinity. With a closer analysis of α -phase (001) diffraction peak in Figure 5.9 b, the peak intensity increases with the addition of MAcI, indicating the improved crystallinity of α -phase by MAcI treatment compared to the reference.

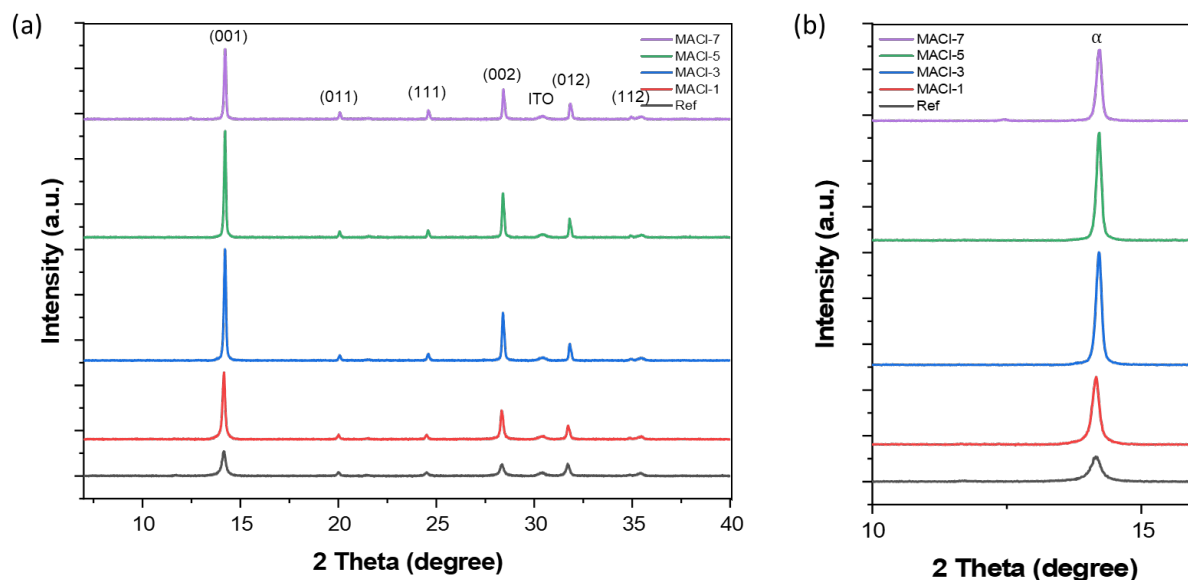


Figure 5.9. (a) X-ray diffraction (XRD) pattern of perovskite with different MACl concentrations, and (b) Zoom-in figure of the (001) peak.

Peak shift: Figure 5.10 a shows the α -phase (001) diffraction peak position as a function of MACl concentration. The peak position for α -phase shifts to a higher angle with the addition of MACl. According to Bragg's law (see Chapter 3), the lattice interplanar spacing d (Figure 5.10 b) decreases with increasing MACl concentration, which may be due to the incorporation of MA^+ into the crystal lattice. The increased amount of smaller MA cation in the FA-based perovskite would lead the contraction of the lattice with compression stress, thus decreasing d -spacing. The results fit well with the existing literature.^{48, 49, 280} The Cl^- ion is speculated to be removed from the film due to the volatile nature of MACl, which would undergo decomposition during the thermal annealing process.^{49, 281}

Crystallinity: Figure 5.10 c shows the integrated peak area of (001) peak as a function of MACl concentration. The peak area can indicate the crystallinity of perovskite, which increases from 0 to 3 mg/ml MACl, reaching the highest point at 3 mg/ml MACl. Then the peak area starts to decrease from 5 to 7 mg/ml MACl. The highest value was obtained at 3 mg/ml MACl, indicating the best crystallinity achieved at this point.

Crystallite size: Figure 5.10 d shows the corresponding crystallite size of as a function of MACl concentration. There is an increase in crystallite size when perovskite is treated with MACl, as FWHM decreases with MACl concentration, which can be calculated by Scherrer equation (see Chapter 3). All the corresponding calculated XRD parameters are listed on the Table 5.2.

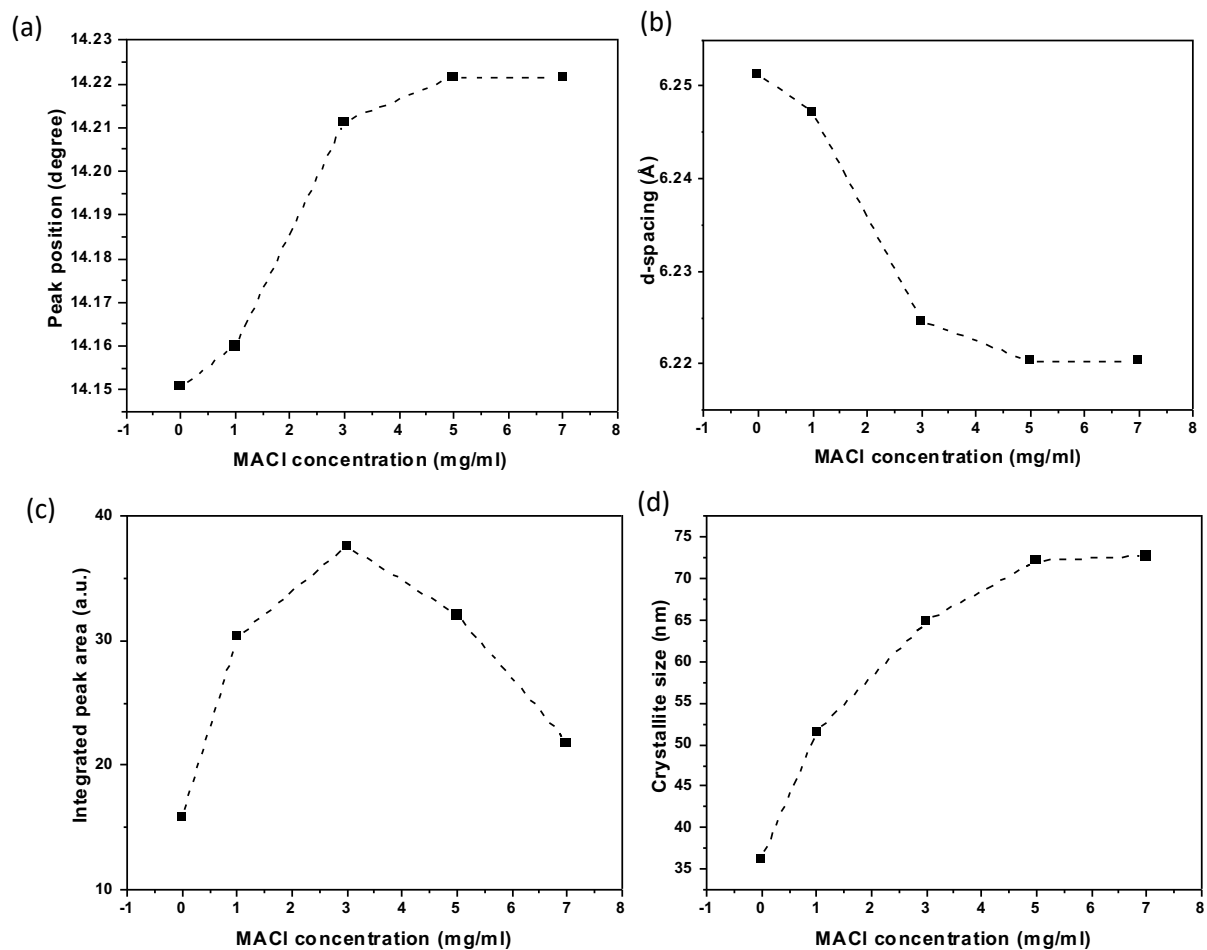


Figure 5.10. X-ray diffraction (XRD) analyses on the α -phase (001) peak. (a) Perovskite peak position as a function of MACl concentration. (b) d spacing as a function of MACl concentration. (c) Integrated peak area of the (001) peak as a function of MACl concentration. (d) Corresponding crystallite size as a function of MACl concentration.

Table 5.2. Calculated X-ray diffraction (XRD) parameters of the α -phase (001) peak.

MACl concentration (mg/ml)	Peak				
	position	d-spacing	Integrated	FWHM	Crystallite
	2θ	(Å)	peak area	(degree)	size (nm)
	(degree)				
0 (ref.)	14.1507	6.251	15.8416	0.2206	36.3
1	14.1600	6.247	30.2779	0.1553	51.5
3	14.2114	6.225	37.5993	0.1233	64.9
5	14.2216	6.220	32.0564	0.1109	72.2
7	14.2216	6.220	21.8616	0.1100	72.8

5.2.5 Device Performance

The device performance of PSCs with different MACl concentrations was investigated. The typical device structure is ITO (150 nm)/ PTAA (10 nm)/ PFN-Br (<10 nm)/ $\text{FA}_{0.95}\text{MA}_{0.05}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$ (~650 nm)/ PCBM (60 nm)/ BCP (<10 nm)/ Cu (100 nm) (see Chapter 3). Figure 5.11 shows the representative J-V characteristics of devices with and without MACl treatment, prepared in a p-i-n planar architecture.

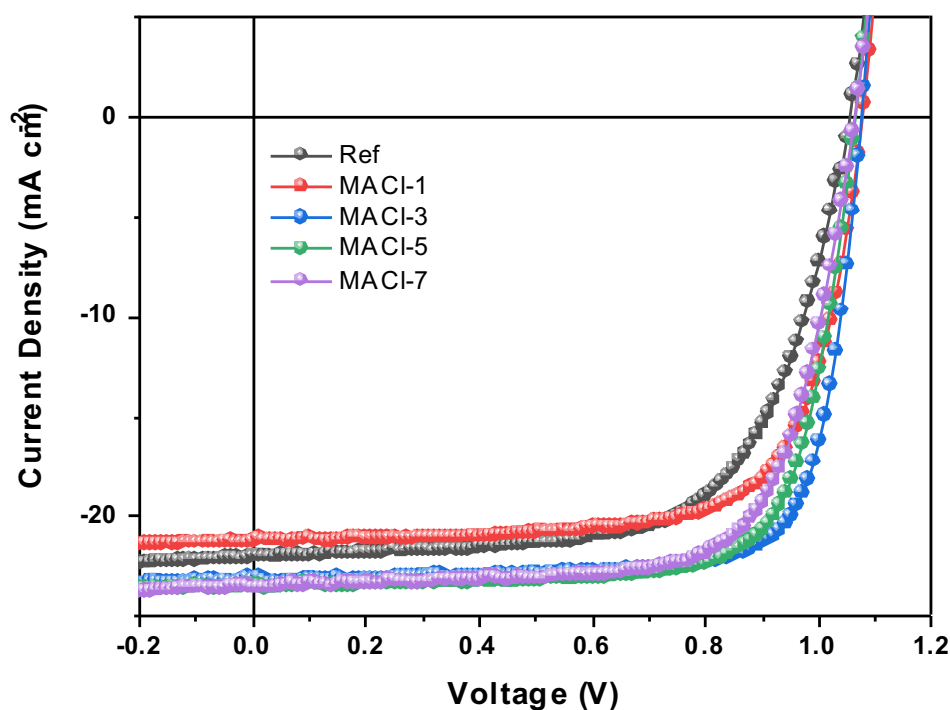


Figure 5.11. Representative J-V curves of PSCs with different MACl concentrations, measured with reverse scan (scan rate of 50 mV s^{-1}).

Figure 5.12 plots the statistical distribution of J_{sc} , V_{oc} , FF and PCE of PSCs with different MACl concentrations. The pristine device shows an inferior power conversion efficiency (PCE) of $12.49 (\pm 1.49) \%$, with a short circuit current (J_{sc}) of $18.85 (\pm 1.74) \text{ mA cm}^{-2}$, open circuit voltage (V_{oc}) of $1.036 (\pm 0.017) \text{ V}$ and fill factor (FF) of 0.639

(± 0.037). With 1 mg/ml MACl treatment, the device PCE increases to 15.46 (± 0.66) % due to improved photovoltaic parameters (J_{SC} , V_{OC} and FF). A greatly enhanced device performance is observed when 3 mg/ml MACl is added to the device, and the device shows a J_{SC} of 23.46 (± 0.42) mA cm⁻², V_{OC} of 1.073 (± 0.003) V and FF of 0.754 (± 0.020), and a PCE of 18.99 (± 0.29) %. The enhanced PCEs of MACl-treated devices compared to the control devices are attributed to the improved J_{SC} , V_{OC} and FF. However, the PCE starts to drop to 17.28 (± 0.70) % when MACl is increased to 5 mg/ml. And the PCE of the 7 mg/ml MACl device is further reduced to 15.57 (± 1.63) % due to the losses of V_{OC} and FF. Therefore, excess amount of MACl treatment is not beneficial to device performance and the optimal condition is determined to be 3 mg/ml, which is consistent with previous PL and XRD results. The photovoltaic parameters of PSCs with different MACl concentrations are listed in Table 5.3.

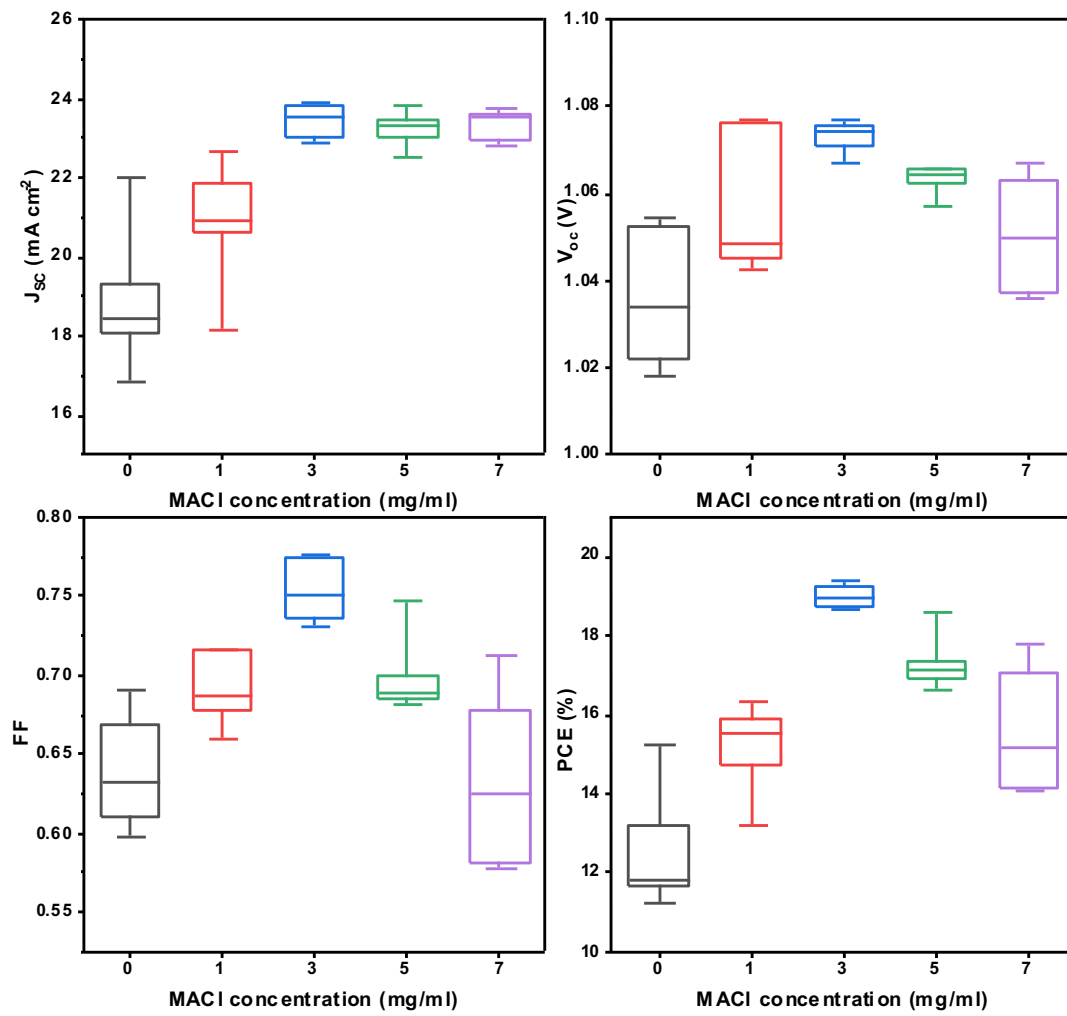


Figure 5.12. Statistical distribution of (a) short circuit current density (J_{sc}), (b) open circuit voltage (V_{oc}), (c) fill factor (FF), and (d) power conversion efficiency (PCE) on PSCs with different MACl concentrations.

Table 5.3. Photovoltaic parameters of PSCs with different MACl concentrations. Measured from 6 devices for each condition.

MACl concentration (mg/ml)	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF	PCE (%)
0	18.85 (±1.74)	1.036 (±0.017)	0.639 (±0.037)	12.49 (±1.49)
1	21.19 (±0.95)	1.056 (±0.016)	0.691 (±0.022)	15.46 (±0.66)
3	23.46 (±0.42)	1.073 (±0.003)	0.754 (±0.020)	18.99 (±0.29)
5	23.27 (±0.45)	1.063 (±0.003)	0.699 (±0.025)	17.28 (±0.70)
7	23.37 (±0.39)	1.051 (±0.013)	0.634 (±0.059)	15.57 (±1.63)

5.2.6 Versatility of SDD Approach

5.2.6.1 Different perovskite active layer thicknesses

We now turn to explore the versatility of this treatment with different thicknesses of perovskite films (500 nm ~ 1 μ m), by using precursor concentration as a means of controlling thickness. The 500 nm, 650 nm and 1 μ m FA_{0.95}MA_{0.05}Pb(I_{0.95}Br_{0.05})₃ perovskite films were prepared from 1.3 M, 1.5 M, and 1.8 M precursor solutions respectively (see Chapter 3). Figure 5.13 demonstrates the cross-section SEM images of perovskite films in varied thicknesses, without and with MACl treatment (using the optimal 3 mg/ml MACl in IPA).

Without MACl treatment, it can be clearly seen that there are some voids present at the bottom sides of perovskite films in all conditions (shown in the red boxes in Figure 5.13 a-c), correlating with the microstructural features observed previously in Figure 5.5 a. With MACl treatment, for the 500 nm perovskite film, the overall grain sizes are increased. What's more, the voids are eliminated with the addition of MACl. For the 650 nm film, the grains also become larger and the voids at the bottom side are eliminated. In terms of the 1 μ m film, the voids at the bottom side are reduced but not fully eliminated. This may be due to the amount of MACl added (using the same volume of 16 μ l MACl solution as for the 500 nm and 650 nm films) is not sufficient to eliminate a larger number of voids present in the 1 μ m film.

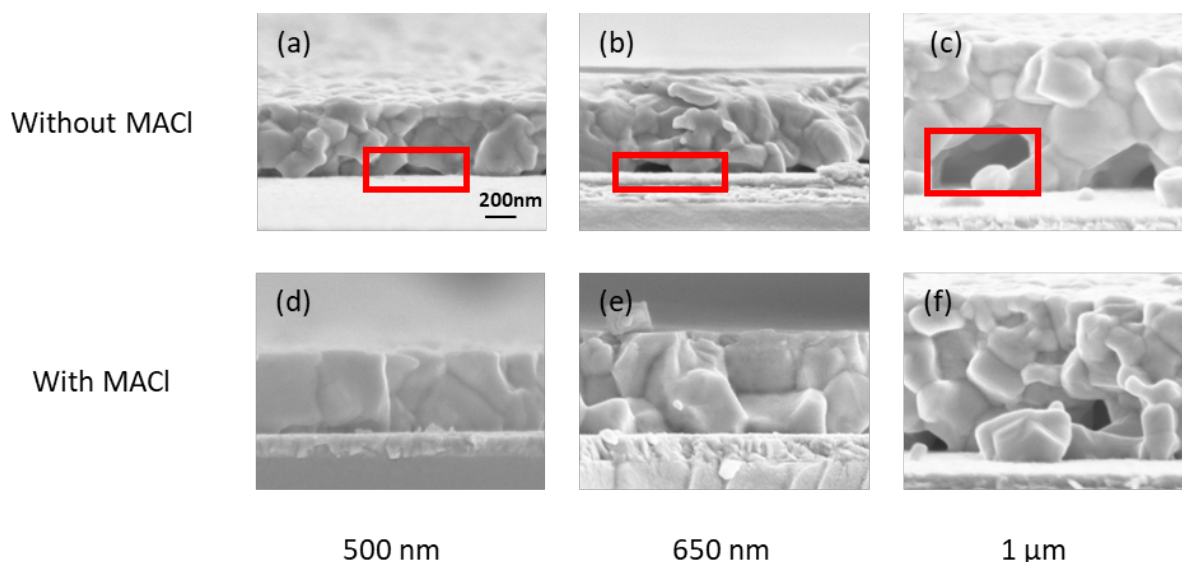


Figure 5.13. Cross-section SEM images of the 500nm (1.3M), 650nm (1.5 M) and 1 μ m (1.8 M) perovskite films (a-c) without MACI treatment, and (d-f) with MACI treatment respectively. Scale bar (200 nm) is the same for all images.

In addition, the device performance of different perovskite layer thicknesses (500 nm, 650 nm, 1 μ m) was studied, without and with MACI treatment. Figure 5.14 shows the PCEs of typical devices as a function of perovskite thickness. Without MACI treatment, there is a decrease in average PCEs from 15.28 (± 1.20) % to 13.28 (± 1.23) % and 8.23 (± 1.67) % when perovskite thickness is increased from 500 nm to 650 nm and 1000 nm (i.e., 1 μ m), due to the reduced V_{OC} and FF (shown in Figure 5.15). This may be associated with increased interfacial recombination losses and series resistances. With MACI treatment, in contrast, higher average PCEs over 17 % are observed in all devices. The average PCEs of 500 nm, 650 nm and 1 μ m device are determined to be 18.09 (± 0.34) %, 20.20 (± 0.18) % and 17.01 (± 0.51) % respectively. Compared to the control devices without MACI treatment (of the same perovskite thickness), the enhanced PCEs of MACI-treated devices are driven by the improvement in J_{SC} , V_{OC}

and FF (shown in Figure 5.15). The statistical data with MACI treatment also show less variations in photovoltaic performance parameters. Table 5.4 summarizes the average photovoltaic parameters of PSCs with different perovskite thicknesses. Consequently, these results not only demonstrate the validity of MACI treatment, but also reveal the versatility of our SDD methodology.

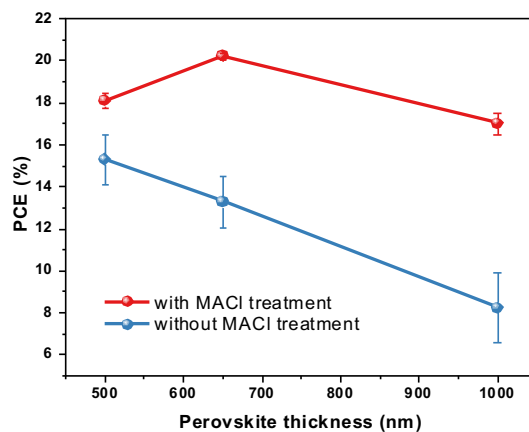


Figure 5.14. Power conversion efficiency (PCE) of PSCs as a function of perovskite layer thickness (500nm, 650nm, and 1 μ m), without and with MACl post treatment. Measured from 6 devices for each condition.

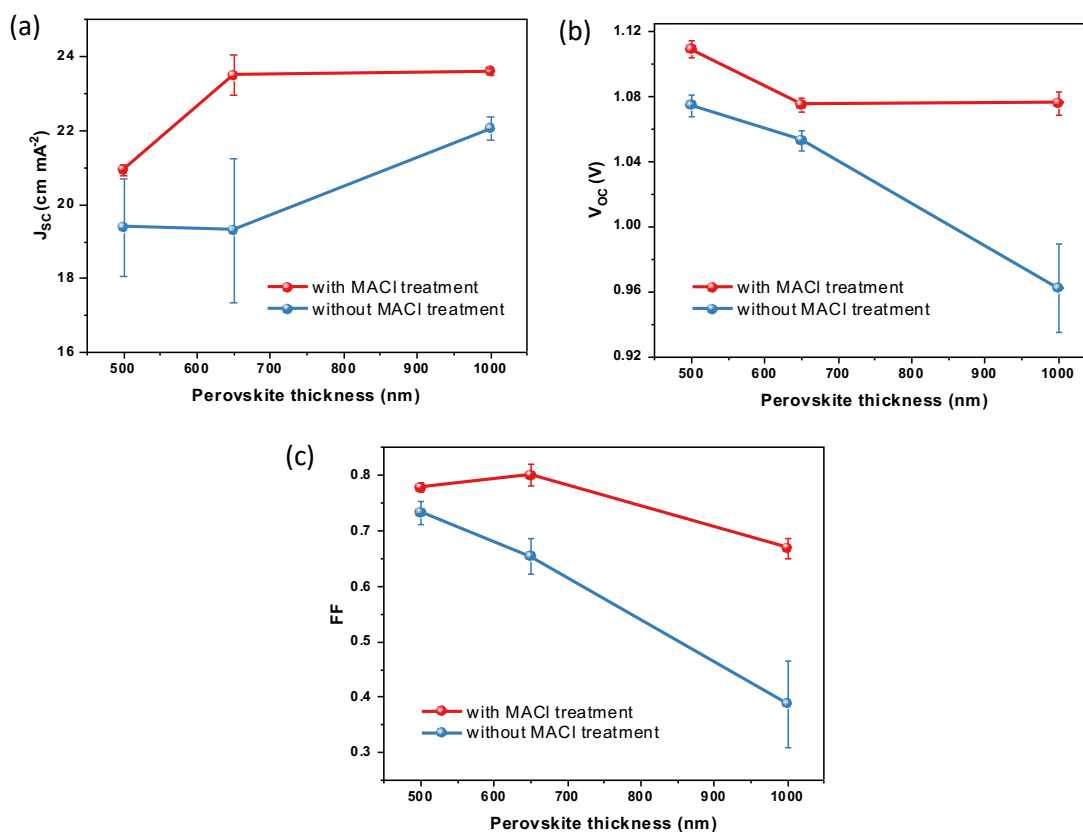


Figure 5.15. Photovoltaic parameters of PSCs as a function of perovskite layer thickness (500nm, 650nm, and 1 μ m), without and with MACl post treatment. (a) short circuit current density (J_{sc}); (b) open circuit voltage (V_{oc}); (c) fill factor (FF).

Table 5.4. Photovoltaic parameters of PSCs with different perovskite thicknesses (500nm, 650nm, and 1 μm), without and with MACl post treatment. Measured from 6 devices for each condition.

Perovskite thickness (nm)	MACl treatment	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
500	Without	19.38 (± 1.33)	1.074 (± 0.007)	0.733 (± 0.021)	15.28 (± 1.20)
	With	20.95 (± 0.14)	1.109 (± 0.005)	0.778 (± 0.009)	18.09 (± 0.34)
650	Without	19.30 (± 1.95)	1.053 (± 0.006)	0.654 (± 0.032)	13.28 (± 1.23)
	With	23.49 (± 0.54)	1.075 (± 0.005)	0.800 (± 0.019)	20.20 (± 0.18)
1000	Without	22.06 (± 0.33)	0.962 (± 0.027)	0.388 (± 0.079)	8.23 (± 1.67)
	With	23.59 (± 0.08)	1.076 (± 0.007)	0.669 (± 0.018)	17.01 (± 0.51)

5.2.6.2 Different types of antisolvents and dripping time

To investigate the versatility of MACl treatment on device performance with different types of antisolvents and antisolvent dripping times, PSCs were fabricated with three commonly used antisolvents (diethyl ether (DE), chlorobenzene (CB), and toluene) under four different antisolvent dripping times (8 s, 10 s, 15 s, and 20 s). The antisolvent is dripped onto the spinning substrate with perovskite precursor solution at specific time, and the total spin-coating time is set as 30s. For devices without MACl, the perovskite layer is formed through traditional deposition method (see Figure 5.1 in previous section). For devices with MACl treatment, MACl (3 mg/ml in IPA) is added on the as-deposited perovskite by dynamic spin-coating, as described in SDD method. Figure 5.16 a-b shows the measured PCEs as a function of antisolvent dripping time, with respect to DE, CB, and toluene, without and with MACl treatment.

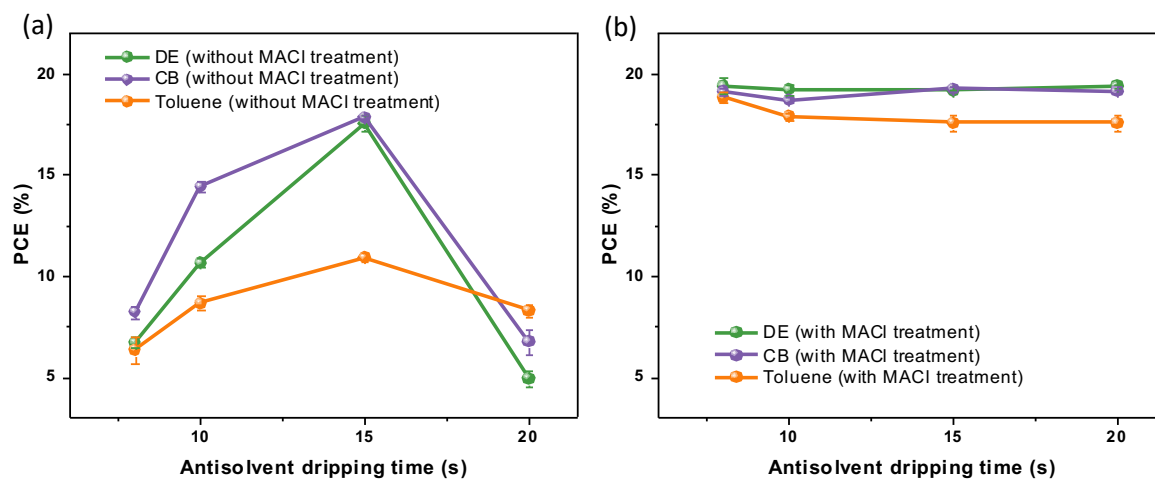


Figure 5.16. Power conversion efficiency (PCE) of PSCs as a function of antisolvent dripping time (8 s, 10 s, 15 s, and 20 s), with respect to three different antisolvents: diethyl ether (DE), chlorobenzene (CB), and toluene; (a) without and (b) with MACl treatment. Measured from 6 devices for each condition.

Without MACI treatment:

Without MACI treatment, the antisolvent dripping time significantly affects the device performance (shown in Figure 5.16 a). The PCEs of all three antisolvents demonstrate similar trends, which increase up to 15 s and then decline. For examples, the average PCE of DE devices increase significantly from 6.70 (± 0.25) % (8 s) to 10.65 (± 0.21) % (10 s), and 17.56 (± 0.43) % (15 s), mainly contributed from the increased V_{OC} and FF (shown in Figure 5.17). However, extending the dripping time to 20 s results in a PCE decrease to 4.94 (± 0.39) %, due to the reduced J_{SC} , V_{OC} and FF. These results indicate there is a specific processing window for DE as the optimal dripping time is 15 s. Table 5.5 summarizes the average photovoltaic parameters of PSCs using DE as antisolvent.

Similar trends can be observed for CB and toluene devices, the average photovoltaic parameters of PSCs for them are summarized in Table 5.6 and Table 5.7 respectively. For CB devices, the average PCE increases from 8.23 (± 0.31) % (8 s) to 14.42 (± 0.24) % (10 s), reaching the highest as 17.83 (± 0.12) % (15 s), then drops to 6.74 (± 0.65) % (20 s). The overall enhanced PCE of CB devices up to 15 s is owing to improved V_{OC} and FF. However, further extending the dripping time to 20 s would greatly reduce the V_{OC} and FF, thus reducing the PCE. The processing window for CB is determined to be 15 s as the optimal condition.

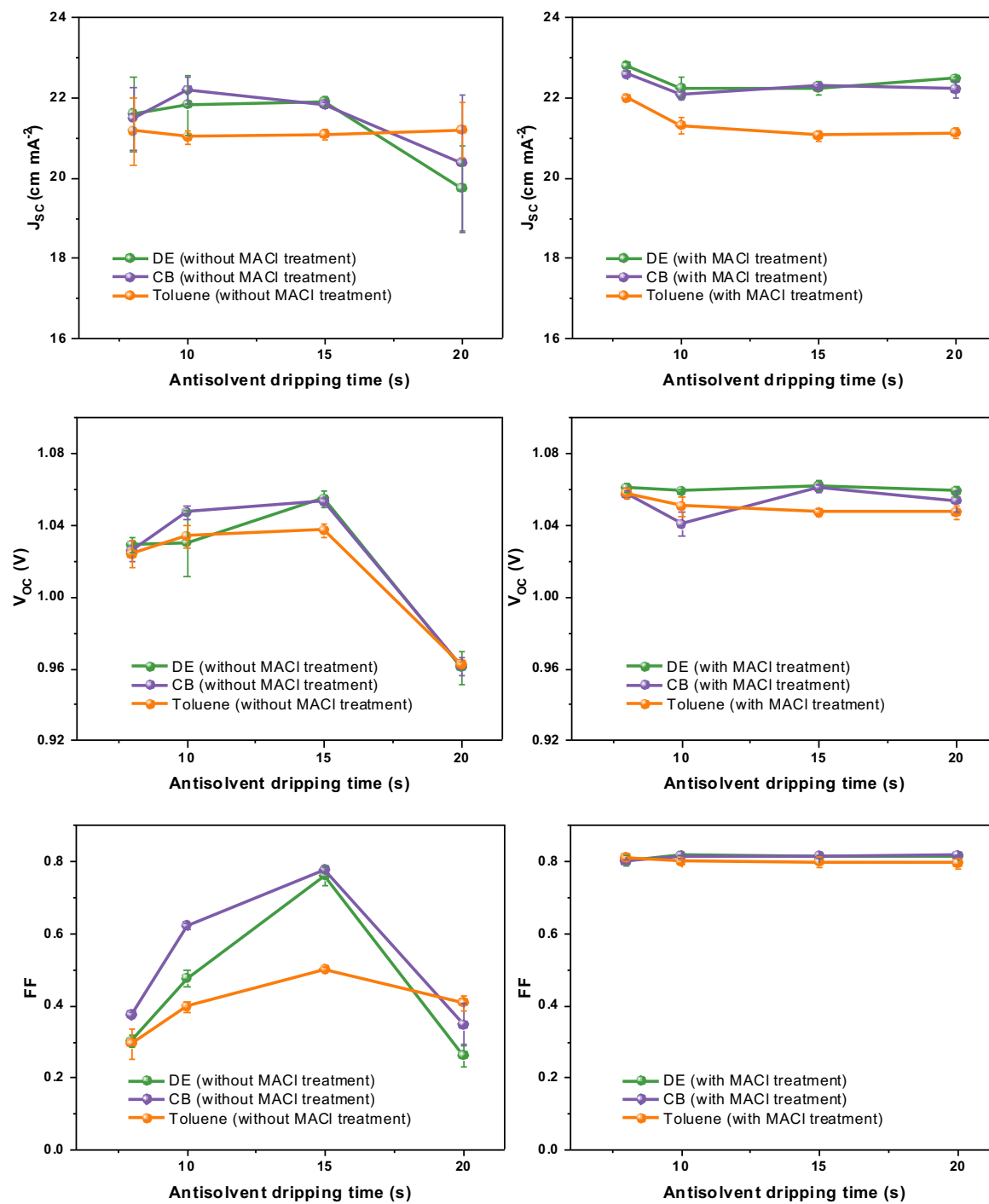


Figure 5.17. Photovoltaic parameters of PSCs as a function of perovskite layer thickness (500nm, 650nm, and 1 μm), without and with MACl post treatment. Top panel: short circuit current density (J_{sc}); Middle panel: open circuit voltage (V_{oc}); Bottom panel: fill factor (FF).

For toluene devices, the average PCE increases from 6.36 (± 0.66) % (8 s) to 8.64 (± 0.36) % (10 s) and 10.91 (± 0.20) % (15 s), then decreases to 8.30 (± 0.33) % (20 s). The overall performance of toluene devices is inferior to DE devices and CB devices, due to the relatively low FF in all conditions. The increase in PCE of toluene device up to 15 s is mostly contributed from improved FF, while the decline in PCE at a longer time (20 s) is attributed to the loss in V_{OC} and FF. Thus, dripping at 15 s is the optimal condition for toluene as the best processing window, which is consistent with existing literature.²⁸²

With MACI treatment:

In contrast, with MACI treatment, all devices demonstrate considerably high and consistent performance with PCEs over 17.5 % at all processing conditions (shown in Figure 5.16 b). The average photovoltaic parameters are also summarized in Table 5.5, Table 5.6, and Table 5.7 for comparison. For example, DE devices exhibit high average PCEs of 19.39 (± 0.39) % (8 s), 19.22 (± 0.25) % (10 s), 19.17 (± 0.02) % (15 s), and 19.38 (± 0.12) % (20 s), contributed from high J_{SC} , V_{OC} and FF in all antisolvent dripping times (shown in Figure 5.17). This suggests that MACI treatment can widen the processing window of antisolvent dripping time.

For CB devices, the average PCEs also keep relatively consistent at 19.11 (± 0.18) % (8 s), 18.68 (± 0.12) % (10 s), 19.26 (± 0.13) % (15 s) and 19.11 (± 0.08) % (20 s). Moreover, the average PCEs of toluene devices are also largely enhanced with MACI treatment, resulting in comparable efficiencies with DE and CB device, which are 18.83 (± 0.29) % (8 s), 17.88 (± 0.16) % (10 s), 17.58 (± 0.40) % (15 s) and

17.57 (± 0.38) % (20 s). In contrast to the devices without MACI treatment, the improved PCEs for both CB and toluene devices with MACI treatment are driven by considerable improvement of V_{OC} and FF. These results show that all three antisolvents (DE, CB, and toluene) demonstrate comparable and highly consistent device performance with MACI treatment.

In combination with the results above, it can be summarized that MACI treatment provides a wider processing window for the use of different antisolvents and antisolvent dripping times, towards achieving highly efficient PSCs.

Table 5.5. Photovoltaic parameters of PSCs using DE as antisolvent. Measured from 6 devices for each condition.

Antisolvent	Dripping time (s)	MACl treatment	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
DE	8	Without	21.59 (±0.93)	1.029 (±0.004)	0.302 (±0.016)	6.70 (±0.25)
		With	22.78 (±0.12)	1.061 (±0.003)	0.803 (±0.013)	19.39 (±0.39)
	10	Without	21.82 (±0.75)	1.030 (±0.018)	0.476 (±0.021)	10.65 (±0.21)
		With	22.23 (±0.29)	1.059 (±0.001)	0.817 (±0.001)	19.22 (±0.25)
	15	Without	21.90 (±0.13)	1.055 (±0.005)	0.760 (±0.026)	17.56 (±0.43)
		With	22.23 (±0.16)	1.062 (±0.003)	0.812 (±0.005)	19.17 (±0.02)
	20	Without	19.74 (±1.06)	0.961 (±0.009)	0.262 (±0.032)	4.94 (±0.39)
		With	22.46 (±0.06)	1.059 (±0.003)	0.815 (±0.004)	19.38 (±0.12)

Table 5.6. Photovoltaic parameters of PSCs using CB as antisolvent. Measured from 6 devices for each condition.

Antisolvent	Dripping time (s)	MACl treatment	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
CB	8	Without	21.48 (±0.79)	1.026 (±0.006)	0.374 (±0.007)	8.23 (±0.31)
		With	22.58 (±0.07)	1.057 (±0.002)	0.801 (±0.006)	19.11 (±0.18)
	10	Without	22.18 (±0.34)	1.047 (±0.004)	0.621 (±0.009)	14.42 (±0.24)
		With	22.06 (±0.10)	1.040 (±0.007)	0.814 (±0.004)	18.68 (±0.12)
	15	Without	21.81 (±0.07)	1.053 (±0.002)	0.776 (±0.007)	17.83 (±0.12)
		With	22.29 (±0.04)	1.061 (±0.002)	0.815 (±0.004)	19.26 (±0.13)
	20	Without	20.36 (±1.72)	0.961 (±0.005)	0.347 (±0.059)	6.74 (±0.65)
		With	22.21 (±0.21)	1.053 (±0.006)	0.817 (±0.001)	19.11 (±0.08)

Table 5.7. Photovoltaic parameters of PSCs using toluene as antisolvent. Measured from 6 devices for each condition.

Antisolvent	Dripping time (s)	MAI treatment	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
Toluene	8	Without	21.16 (±0.84)	1.024 (±0.008)	0.294 (±0.041)	6.36 (±0.66)
		With	21.99 (±0.07)	1.058 (±0.003)	0.810 (±0.010)	18.83 (±0.29)
	10	Without	21.02 (±0.16)	1.034 (±0.006)	0.398 (±0.015)	8.64 (±0.36)
		With	21.30 (±0.21)	1.050 (±0.005)	0.799 (±0.007)	17.88 (±0.16)
	15	Without	21.07 (±0.13)	1.037 (±0.003)	0.499 (±0.007)	10.91 (±0.20)
		With	21.06 (±0.12)	1.047 (±0.002)	0.798 (±0.015)	17.58 (±0.40)
	20	Without	21.19 (±0.69)	0.962 (±0.002)	0.407 (±0.022)	8.30 (±0.33)
		With	21.11 (±0.13)	1.047 (±0.003)	0.795 (±0.013)	17.57 (±0.38)

5.2.7 Stability of MACI-Treated Perovskite

The phase stability of $\text{FA}_{0.95}\text{MA}_{0.05}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$ was examined by aging the thin films in ambient air environment with 30% RH. Perovskite films were prepared with the addition of MACI from 1 mg/ml to 7 mg/ml, and MACI-free one was taken as reference.

The photographs in

Figure 5.18 show perovskite films at various aging stages, ranging from 0 to 666 hours. At 0 hours, all the fresh films exhibited black color, indicating the presence of photoactive $\alpha\text{-FAPbI}_3$. Upon aging, the films did not exhibit any significant color change and remained predominantly black in color.

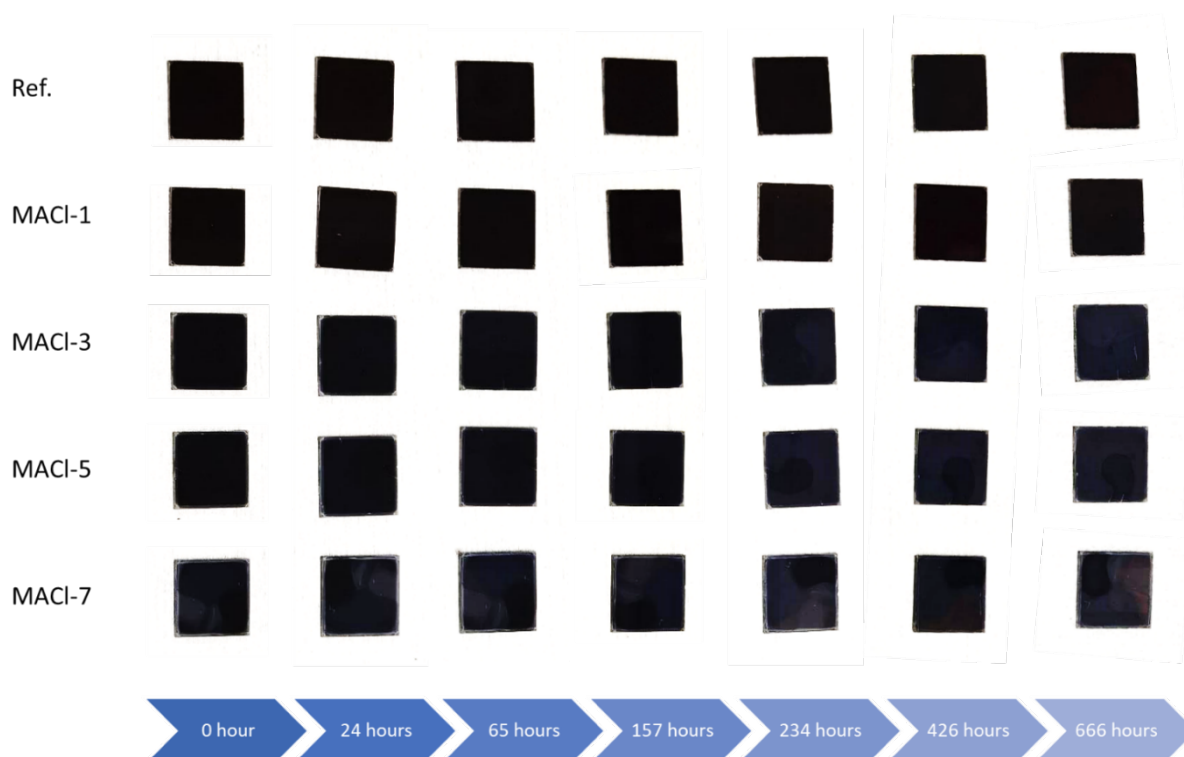


Figure 5.18. Photographs of perovskite films with different MACI concentrations (x mg/ml, $x=1, 3, 5, 7$) aging in ambient air (30% RH) for different times (0 – 666 h). The corresponding perovskite films are termed as MACI- x for convenience. The substrate size is 1.2 cm $\times$ 1.2 cm for each film.

However, comparing the XRD pattern before and after aging (Figure 5.19 a and c), there was still a small amount of degradation from α -FAPbI₃ to secondary phase PbI₂. The major diffraction peaks for α -FAPbI₃ (001) and PbI₂ are at 14.2° 2 θ and 12.9° 2 θ respectively. The increased peak intensity of PbI₂ in all films is due to the material decomposition of FAPbI₃, which was degraded thus the (001) peak intensity was reduced accordingly.⁷

It is noticeable that only the MACl-free reference film showed a major diffraction peak of δ -FAPbI₃ at 12.0° 2 θ , while no appreciable sign of photoinactive δ -FAPbI₃ phase was observed in other aged films with MACl except the 7 mg/ml one. This is consistent with previously reported phase instability nature of FAPbI₃ due to α -to- δ phase transition. After aging, compared to the MACl-free reference, the incorporation of appropriate MACl can effectively inhibit formation of photoinactive δ -FAPbI₃. With MACl treatment, the degradation of FAPbI₃ in ambient air at low moisture level (30% RH) is predominantly driven by material decomposition to PbI₂ rather than phase transition to δ -FAPbI₃.²⁴⁴

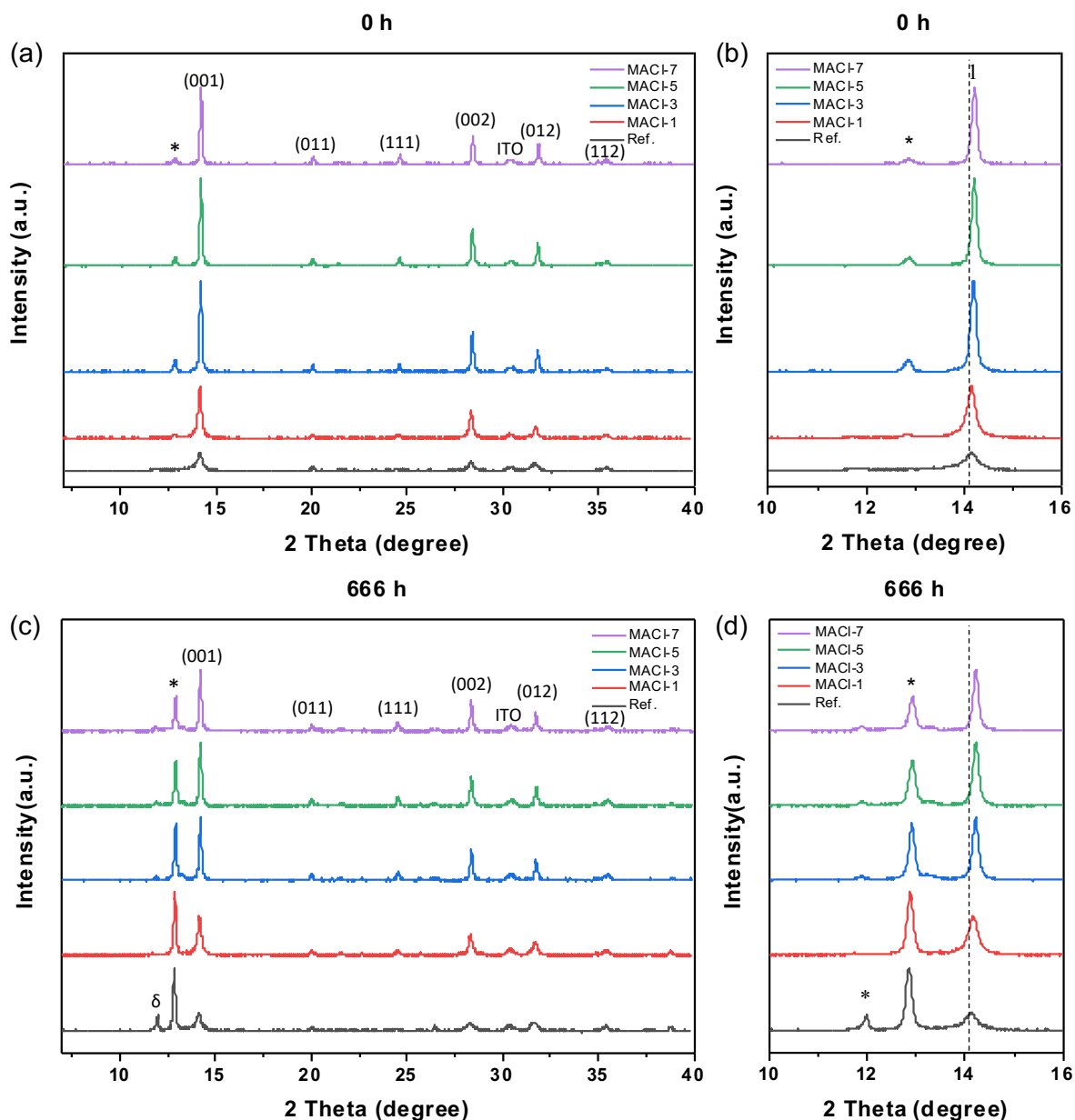


Figure 5.19. XRD patterns of perovskite films with different MACl concentrations before (0 h) and after (666 h) aging. (a) Fresh films (0 h). (b) Zoom-in figure of the (001) peak of fresh films. (c) Aged films (666 h). (d) Zoom-in figure of the (001) peak of aged films. δ denotes δ -FAPbI₃, α denotes α -FAPbI₃ and * denotes PbI₂. The diffraction peaks of α -FAPbI₃ are labelled in the plots (a) and (c).

Peak shift: Upon closer inspection of the α -phase (001) peak in Figure 5.19 b, it is evident that the peak position shifts to a higher angle with increasing MACl

concentration, indicating the incorporation of MA cations into the lattice, consistent with previous analyses.^{49, 280} The incorporation of smaller MA cations induces lattice contraction, resulting in a decrease in lattice spacing, d .

Compared to the fresh films (0 h), aged films (666 h) show no significant change in peak position except for the reference and 7 mg/ml MACl-treated films (Figure 5.20 a). A noticeable shift towards a lower angle is observed in the peak position of the reference and 7 mg/ml MACl-treated aged films (666 h), corresponding to a decrease in lattice spacing, d (Figure 5.20 b), due to the lattice expansion during α -to- δ phase degradation.²⁴⁴

Crystallinity: The crystallinity of perovskite films can be assessed by examining the integrated peak area. Before aging (0 h), all fresh films exhibited a pronounced characteristic peak of the α -phase. The integrated peak area of the α -phase increases as MACl concentration increases from reference to 1 mg/ml and 3 mg/ml (measured as 10.65, 20.92, and 23.36, respectively), and then decreases from 5 to 7 mg/ml (measured as 20.59 and 17.29, respectively), with the highest value obtained at 3 mg/ml MACl (Figure 5.20 c). This finding indicates that MACl treatment can enhance the crystallinity of perovskite films, which is consistent with previous research. Additionally, the integrated peak area ratio of $\text{PbI}_2/\alpha\text{-FAPbI}_3$ for fresh films before aging (0 h) was determined to be 0.08, 0.08, 0.14, 0.11, and 0.10 for reference, 1 mg/ml, 3 mg/ml, 5 mg/ml, and 7 mg/ml MACl-treated films, respectively. This indicates the presence of PbI_2 under similar conditions in all fresh films.

After aging for 666 hours, an overall reduction in integrated peak area of the α -phase was observed in all aged films, indicating a reduction in crystallinity due to perovskite

degradation. As shown in the Figure 5.19 d, the main degradation product PbI_2 was observed in all cases, with an overall increase in the peak area of the PbI_2 diffraction peak. As a result, the integrated peak area ratio of $\text{PbI}_2/\alpha\text{-FAPbI}_3$ for aged films (666 h) was measured to be 1.71, 0.99, 0.85, 0.77, and 0.61 for the same films, respectively. The larger the ratio, the more severe the degradation, as more perovskite material decomposes to PbI_2 . Therefore, the MACI-treated films show enhanced stability compared to the reference film.

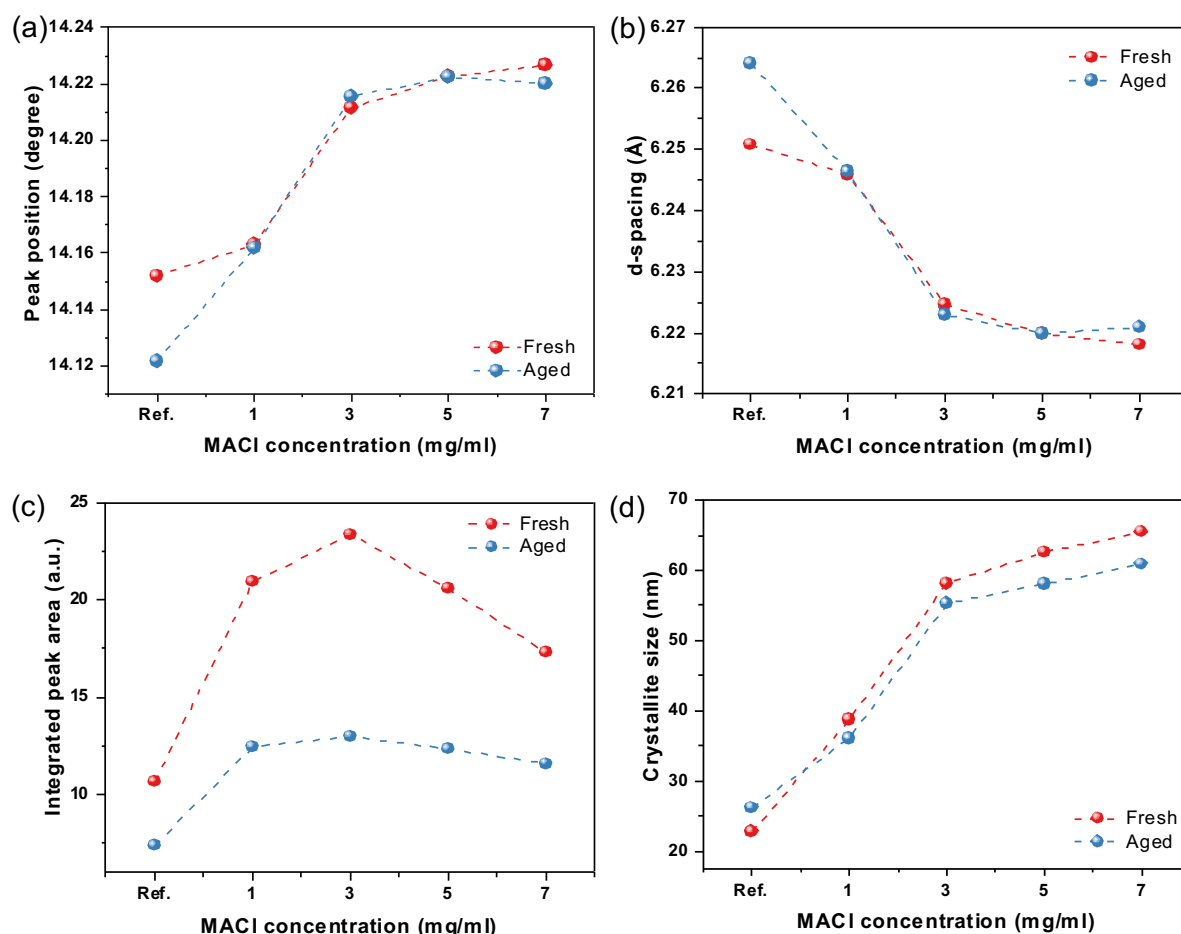


Figure 5.20. XRD analyses of fresh (0 h) and aged (666 h) films on the α -phase (001) peak: (a) Perovskite peak position as a function of MACI concentration. (b) d spacing as a function of MACI concentration. (c) Integrated peak area as a function of MACI concentration. (d) Corresponding crystallite size of perovskite as a function of MACI concentration.

Furthermore, the presence of the δ -FAPbI₃ phase was observed in both the MACl-free reference film and the 7 mg/ml MACl treated film, whereas no δ -FAPbI₃ peak was detected in other MACl treated films (1 mg/ml, 3 mg/ml, 5 mg/ml). As a result, the integrated peak area ratio of δ -FAPbI₃/ α -FAPbI₃ after aging was 0.36 and 0.09 for the reference and 7 mg/ml MACl, respectively. This indicates that suitable amount of MACl (1 - 5 mg/ml) can also lead to suppression of α -to- δ phase degradation and improve the thin film stability.

Crystallite size: The addition of MACl leads to an increase in crystallite size (Figure 5.20 d), which can be determined by Scherrer equation as the full width at half maximum (FWHM) decreases with increasing MACl concentration. This finding is in agreement with previous studies. The α -phase (001) peak of the perovskite films shows an increase in crystallite size from 22.8 nm (in the reference sample) to 65.5 nm (in MACl-7) for the fresh films, and from 26.2 nm (in the reference sample) to 60.9 nm (in MACl-7) for the aged films. However, the crystallite size of perovskite films is relatively consistent across the different MACl concentrations, with only small variations observed between fresh and aged films. The results indicate that there is no significant change in the crystallite size after aging. Table 5.8 lists the calculated peak parameters of fresh and aged films with different MACl concentrations.

Table 5.8. Calculated XRD parameters of the α -phase (001) peak, for fresh (0 h) and aged (666 h) perovskite films with different MACl concentrations.

	Conditions	Peak				
		position	d-spacing	Integrated	FWHM	Crystallite
		2θ (degree)	(Å)	peak area	(degree)	size (nm)
Reference	Fresh	14.1519	6.251	10.65	0.3513	22.8
	Aged	14.1217	6.264	7.37	0.3057	26.2
MACl 1mg/ml	Fresh	14.1631	6.246	20.92	0.2064	38.8
	Aged	14.1619	6.246	12.44	0.2219	36.1
MACl 3mg/ml	Fresh	14.2116	6.225	23.36	0.1377	58.1
	Aged	14.2155	6.223	12.99	0.1448	55.3
MACl 5mg/ml	Fresh	14.2226	6.220	20.59	0.1279	62.6
	Aged	14.2225	6.220	12.53	0.1379	58.0
MACl 7mg/ml	Fresh	14.2267	6.218	17.29	0.1222	65.5
	Aged	14.2201	6.221	11.59	0.1315	60.9

Figure 5.21 displays the XRD patterns of perovskite films with varying MACl concentrations for different times. The PbI_2 peak intensity of the MACl-free reference film increased over time, while MACl-treated films showed less pronounced increases in PbI_2 , and the amount of PbI_2 decreased with higher MACl concentrations. The MACl-free reference film exhibited photoinactive δ -FAPbI₃ starting at 157 h, and the intensity increased with time. However, there was no significant sign of δ -FAPbI₃ in MACl-treated films (1 mg/ml to 5 mg/ml) until 666 h, suggesting that the addition of MACl (up to 5 mg/ml) can suppress the phase transition to δ -phase and improve the stability of α -phase.

The optimal MACl concentration was found to be 3 mg/ml, which not only enhanced the perovskite with highest crystallinity but also improved the stability of α -phase. Interestingly, excess MACl (7 mg/ml) resulted in the appearance of δ -FAPbI₃ from 157 h, indicating that an excessive amount of MACl may not benefit the phase stability of FA-based perovskite films. This finding is consistent with our previous study on the optimization of the corresponding PSCs.

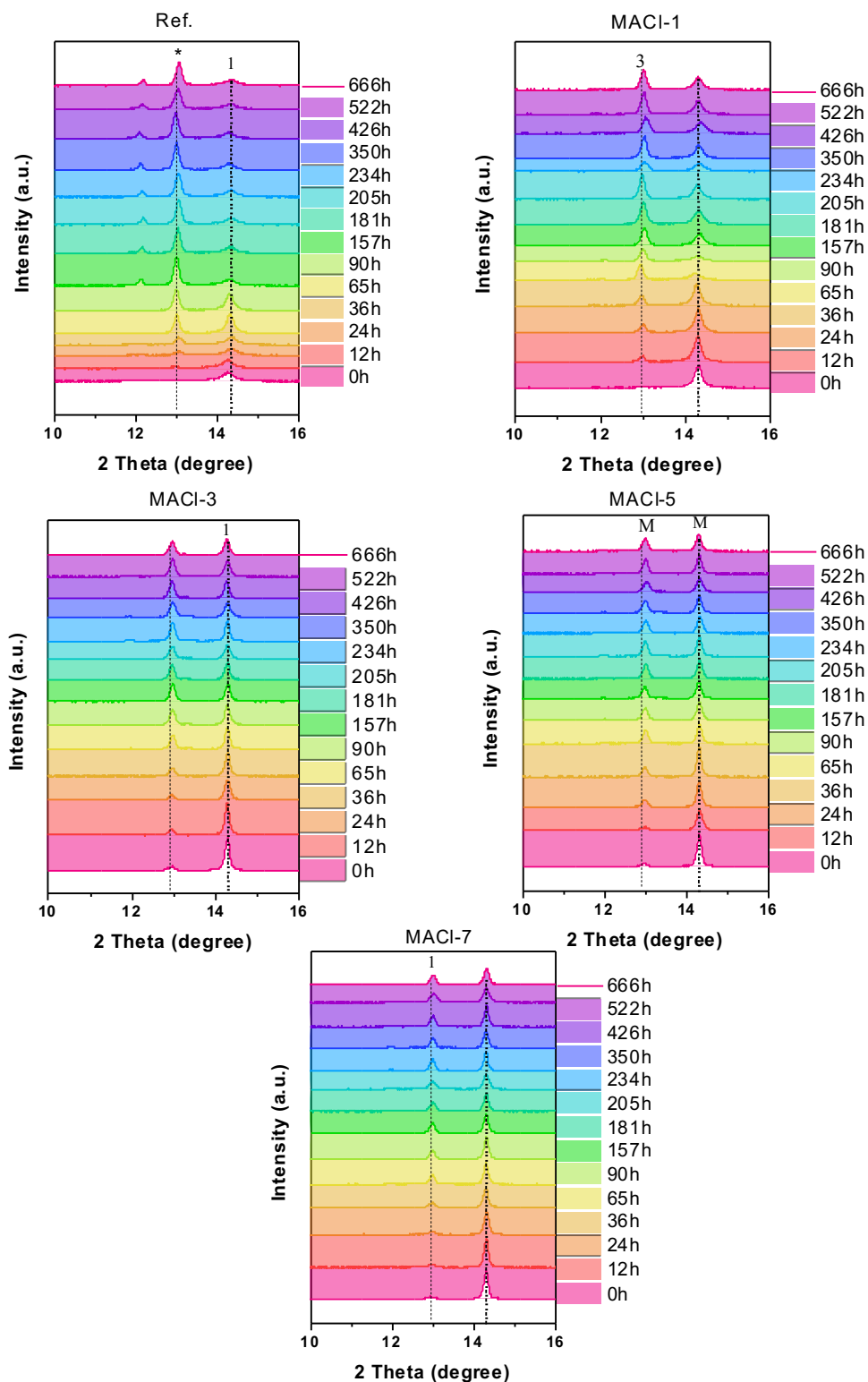


Figure 5.21. XRD patterns of perovskite films with different MACI concentrations for different times.

5.3 Conclusions

We have proposed an innovative sequential dynamic deposition (SDD) approach with MACl treatment in contrast to traditional additive engineering methods to mitigate the imperfections and inhomogeneities of FA-based perovskite at the buried interfaces. By applying a peel-off method, the bottom side of perovskite films can be obtained and voids as microstructural defects are present at the pristine film without MACl treatment. In contrast, with MACl treatment, these microstructural defects can be effectively removed. The treated perovskite films demonstrate greatly enhanced structural coherence on perovskite grains, leading to continuous and uniform films both on the top and bottom sides. In addition to that, increased grain sizes and crystallinity of perovskite can be achieved, with a reduction of HTL/perovskite interfacial recombination, and corresponding devices show significantly improved performance.

Based on microstructural observations, structural analyses, steady-state PL measurements, and absorption spectra, 3 mg/ml MACl in IPA solution was proved to be the optimal condition for $\text{FA}_{0.95}\text{MA}_{0.05}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$ perovskite, resulting in the champion device with a PCE of 20.5 %. With MACl treatment, there is also a reduction in batch-to-batch variability in all photovoltaic performance parameters (i.e., J_{sc} , V_{oc} , FF and PCE).

In addition, the versatility of MACl treatment is demonstrated for narrow bandgap FA-based PSCs with active layer thicknesses ranging from 500 nm to 1 μm . Without MACl treatment, PSC performance shows a thickness dependence feature as reduced device efficiency in thicker photoactive layer device. With MACl treatment, the PSC

performance becomes less sensitive to thickness, achieving largely improved efficiencies in all devices with different thicknesses.

Furthermore, to demonstrate the universality of MACI treatment, different antisolvents (DE, CB, and toluene) and antisolvent dripping times (8 s, 10 s, 15 s, and 20 s) are explored as different processing conditions for PSCs fabrication. Without MACI treatment, different antisolvents have individual processing windows of antisolvent dripping times to achieve the best performing devices. With MACI treatment, the PSC performance becomes insensitive to different antisolvents and antisolvent dripping times, yielding significant improvements in all processing conditions.

We have also investigated the phase stability of MACI-treated perovskite at various concentrations. Our findings suggest that the incorporation of MACI can enhance the stability of the perovskite films by effectively inhibiting the formation of the photoinactive δ -phase.

Therefore, the SDD approach with MACI treatment is demonstrated to be an effective method to enhance device efficiency and reproducibility. More importantly, the versatility of this treatment for a wide range of perovskite layer thicknesses, antisolvents, and antisolvent dripping times can open the wide processing window of narrow bandgap PSCs in future.

6. Conclusions and Future Work

6.1 Conclusions

The aim of this chapter is to provide a comprehensive summary of the novel insights presented in this thesis for the development of state-of-the-art perovskite solar cells (PSCs). Researchers have devoted significant efforts over the years to improve PSCs, with the ultimate goal of achieving high efficiency and stability for commercialization. Various strategies have been proposed here to improve device performance, including composition engineering, interface engineering and additive engineering, *etc.* Moreover, the stability issue of perovskite materials has also been highlighted which will have a significant impact on long-term operating devices. Unlike previous studies that mainly focused on conventional perovskite methylammonium lead iodide (MAPbI_3), this thesis places more emphasis on formamidinium lead iodide (FAPbI_3), which has a promising future in commercialization due to its more suitable band gap and superior thermal stability. Both chapter 4 and 5 ultimately aim to enhance the device performance through different approaches. The overall idea is to develop a systematic strategy to make proper selections and wise modifications on different layer materials of PSCs, from charge transport layer to perovskite layer.

In Chapter 4, the work mainly focuses on composition and interface engineering. The study investigates the correlation between the highest occupied molecular orbital (HOMO) of the hole transport layers (HTLs) and the device open-circuit voltage (V_{oc}) to understand the non-radiative recombination losses in perovskite solar cells (PSCs). By employing comparable HTL materials, namely PTAA and PF8TAA, it is discovered that minimizing the energetic offset between HTLs and perovskite is of paramount

importance to further reduce V_{OC} losses and promote device efficiency. Furthermore, analyses of the thin film stability indicate that FA-based perovskite exhibits susceptibility to degradation upon exposure to light and moisture, resulting in the α -to- δ phase transition. Nevertheless, it is observed that perovskite films on PF8TAA exhibit superior stability in comparison to those on PTAA under equivalent conditions.

Chapter 5 focuses on the use of additive engineering to widen the processing window of perovskite solar cells (PSCs). To achieve this objective, methylammonium chloride (MACl) is incorporated into FA-based perovskite using a proposed sequential dynamic deposition (SDD) approach. The MACl treatment helps to optimize and mitigate imperfections and inhomogeneities of FA-based perovskite at the buried interfaces, resulting in a uniform morphology and high crystallinity on both the top and bottom sides. Additionally, the phase stability of MACl-treated perovskite is examined at different concentrations. The results indicate that the addition of MACl can improve the stability of the perovskite films by effectively preventing the formation of the photoinactive δ -phase. Notably, the versatility of the MACl treatment for various perovskite layer thicknesses, antisolvents, and antisolvent dripping times presents a promising approach to widen the processing window of narrow bandgap perovskite solar cells (PSCs) in the future.

In summary, chapter 4 has studied HTLs in similar molecular structures, with similar band gaps and doping levels. Unlike previous research on HTLs which may have distinct variations in physicochemical properties, our research allows a more focused study between HTL HOMO and device V_{oc} . With understanding the role of HTL HOMO, this research has guiding meanings to HTL materials selection in PSCs. Chapter 5 has introduced a peel-off method to reveal the bottom side of perovskite

films, giving direct evidence of microstructural defects which relates to inferior device performance. MACI treatment can improve perovskite film quality, by removing these defects and increasing grain sizes and crystallinity. Besides, with this treatment, devices become insensitive to different processing parameters including perovskite thicknesses, antisolvents and dripping times. This allows repeatable preparation of perovskite layers, therefore, PSCs can be fabricated in a highly reproducible way.

6.2 Future Work

Various strategies have been proposed for enhancing the performance of perovskite solar cells (PSCs) through materials characterization and device optimization. Despite the progress made, there remain some unresolved issues that should be addressed in future research due to the diverse directions of investigation and limited research time.

Chapter 4 proposes a principle for minimizing the energetic offset between HTL and perovskite. Based on this principle, we recommend designing cost-effective HTL alternatives, including novel inorganic materials, to enable low-cost and high-efficient PSCs that can be commercialized in the future. In addition to investigating the correlation between the HTL HOMO and the perovskite VB, further research should explore the relationship between the ETL LUMO and the perovskite CB in terms of their impact on device performance.

In Chapter 5, the effectiveness and universality of the SDD approach with MACI treatment have been demonstrated in enhancing perovskite morphology and device performance. Nonetheless, the spin coating fabrication technique is limited to lab-scale processes, which may not be feasible for large-scale manufacturing in the industry. Future studies should aim to replicate these results in larger scale experiments by employing more compatible fabrication techniques, such as inkjet printing, doctor blade printing, and slot-die coating, *etc.*

Both chapters highlight the importance of perovskite phase stability, which presents a promising avenue for future research. However, the underlying degradation

mechanisms under different conditions are not fully understood. Further systematic studies should be conducted using various characterization techniques, including morphological and optical analyses, as well as operational stability studies. In addition, effective strategies should be sought to improve the perovskite phase stability against light and moisture, particularly for FA-based perovskite to increase durability under high humidity conditions. Achieving commercialization of highly efficient and stable PSCs will require joint efforts from researchers.

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8. Appendix

Supplementary Figures

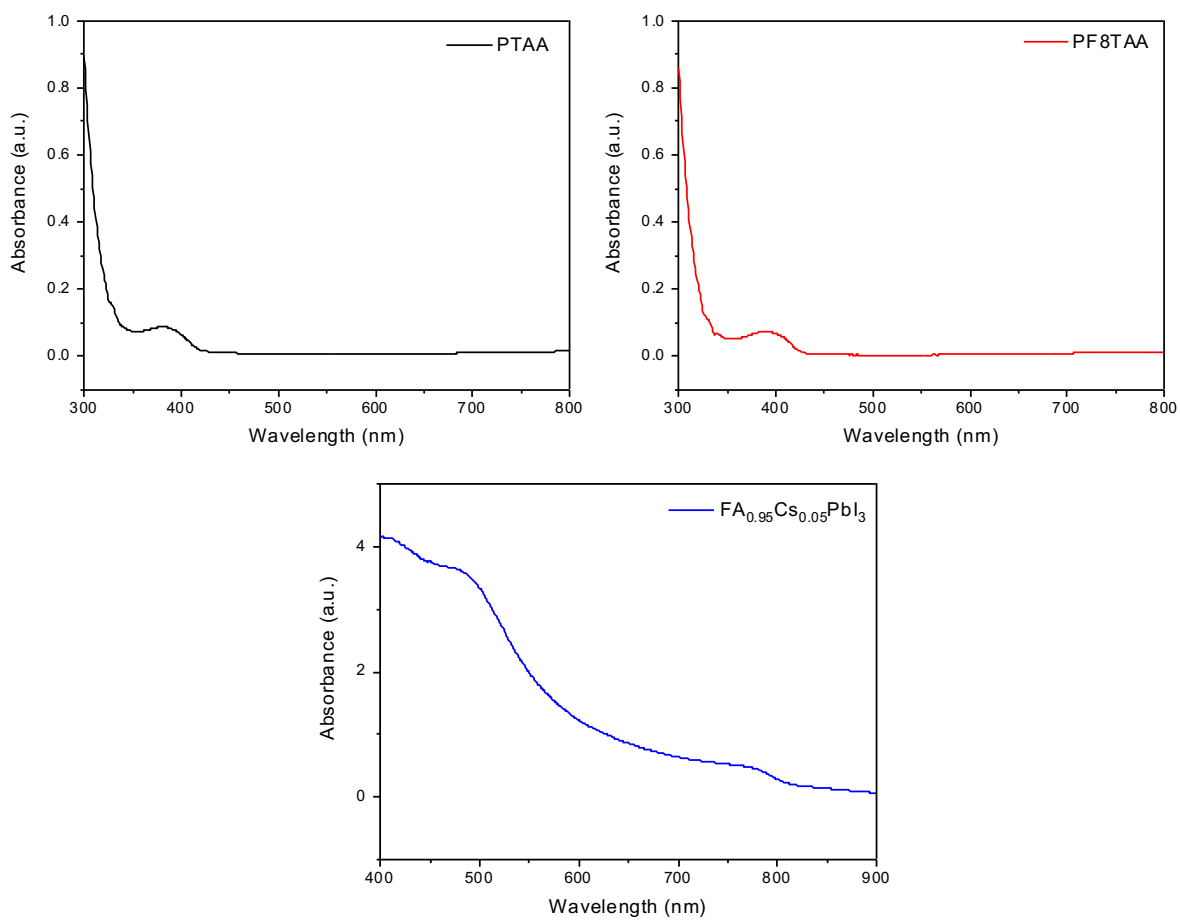


Figure 8.1. Ultraviolet-visible (UV-vis) absorbance spectra for PTAA, PF8TAA and $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ respectively.

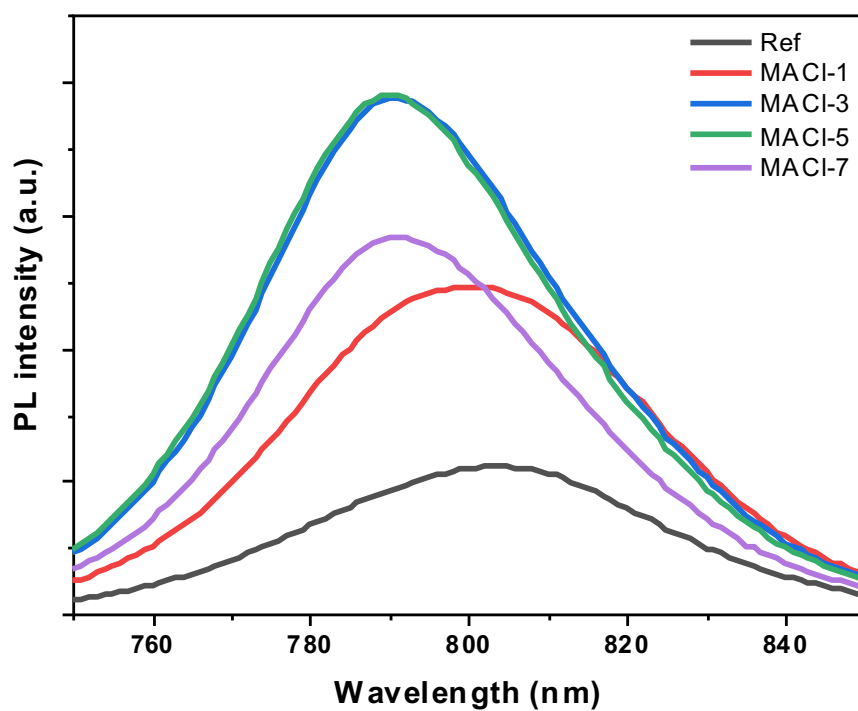


Figure 8.2. Steady state photoluminescence (PL) spectra of perovskite with different MACl concentrations (Reference, 1 mg/ml, 3 mg/ml, 5 mg/ml, and 7 mg/ml).

Stability of Pure FAPbI₃ Perovskite

Varying environmental conditions

The effects of different external environmental conditions on FAPbI₃ degradation were investigated in the environmental chamber. Humidity level was set to 75% RH in all conditions during the stability test. Three testing conditions were investigated, namely:

- 1) light (1 sun illumination).
- 2) dark.
- 3) heating.

Before stability test (0 h), all fresh films showed prominent peak at $14.2^\circ 2\theta$ for α -FAPbI₃ perovskite phase without the presence of other phases as PbI₂ or δ -FAPbI₃. The photographs for fresh and aged films are shown in Figure 8.3, where no visible colour changes were seen after 4 hours, corresponding to no obvious changes on the XRD patterns in Figure 8.4.

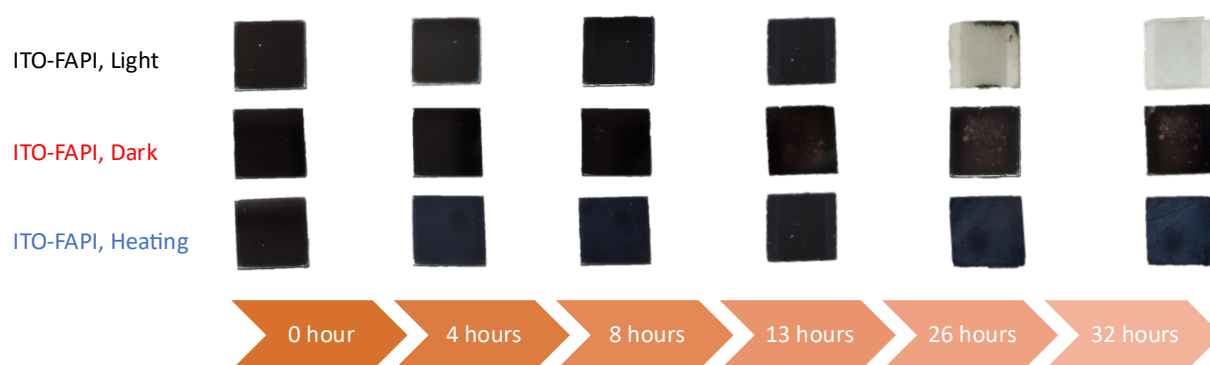


Figure 8.3. Photographs of FAPbI₃ films at different environmental conditions (light, dark, and heating) with 75% RH. The size of each substrate is 1.2 cm × 1.2 cm.

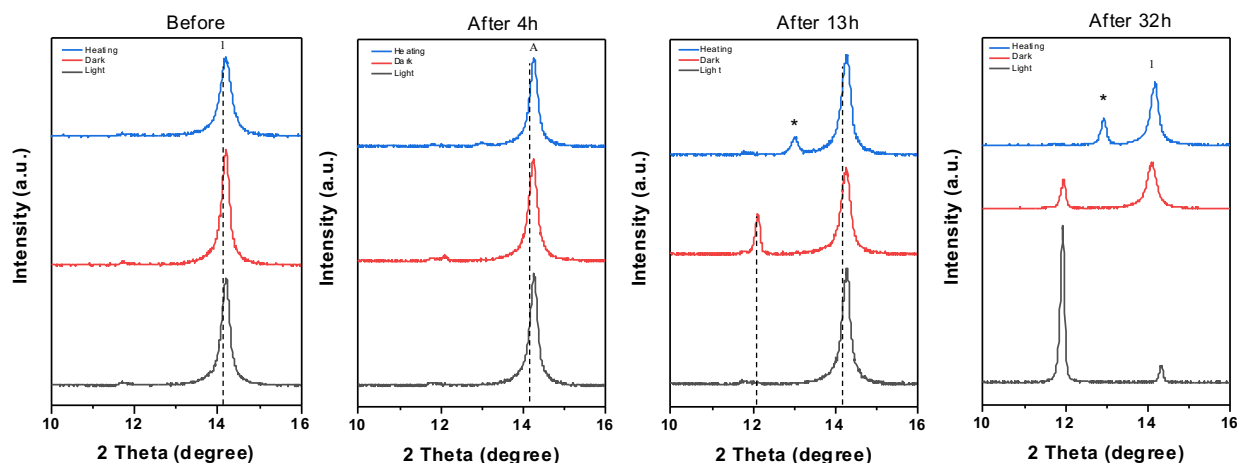


Figure 8.4. XRD patterns of FAPbI₃ films aged at different environmental conditions (light, dark, and heating) with 75% RH. The peaks assigned to α -phase and δ -phase are labelled on the plots, and * denotes Pbl₂ peak.

Aged films on 1) light or 2) dark conditions showed no appearance of additional diffraction peaks. On 3) heating condition, a small amount of Pbl₂ started to appear, resulting in integrated peak area ratio of Pbl₂/ α -FAPbI₃ to be 0.04. After 13 hours, there was no visible colour changes on photographs. There was still just pure α -FAPbI₃ phase on 1) light condition. The appearance of δ -FAPbI₃ was observed on 2) dark condition, resulting in integrated peak area ratio of δ -FAPbI₃/ α -FAPbI₃ as 0.21. On 3) heating condition, the Pbl₂ secondary phase kept accumulating to a larger amount with the peak area ratio of Pbl₂/ α -FAPbI₃ growing to 0.12. After 32 hours, the black films degraded with colour changes to different extents on three conditions. The films became transparent on 1) light condition, brown on 2) dark condition, and greyish on 3) heating condition. Looking on XRD pattern, δ -FAPbI₃ phase started to show on the 1) light condition, with the peak area ratio of δ -FAPbI₃/ α -FAPbI₃ became 10.4. On the 2) dark condition, photoinactive δ -FAPbI₃ phase continued to increase, with peak

area ratio of δ -FAPbI₃/ α -FAPbI₃ became 0.32. It is interesting to find that there was no trace of PbI₂ until this stage. On the 3) heating condition, instead, PbI₂ secondary phase increased to 3 times more than 13 hours, whereas no trace of δ -FAPbI₃ phase could be found until this stage. The resulted peak area ratio of δ -FAPbI₃/ α -FAPbI₃ became 0.28. Comparing the final result, under 75% RH, the severity of degradation was: light > dark ~ heating. The aged film on 1) light condition has been relatively stable before 13 hours, however, it degraded dramatically in the last stage from black to transparent. The aged films on 2) dark and 3) heating conditions degraded at an earlier stage with a slower degradation speed. The results suggested there might be different degradation mechanisms under different environmental conditions. From above, light/dark tends to enhance the emergence of δ -FAPbI₃ peak, while heating is more likely to induce the appearance of PbI₂ peak.

Investigating the role of substrates

The effects of different substrate on FAPbI_3 degradation were investigated. Using environmental chamber, four testing conditions were investigated, namely:

- 1) light and humid (1 sun illumination, 75% RH).
- 2) dark and humid (75% RH).
- 3) light and dry (1 sun illumination, 13% RH).
- 4) dark and dry (13% RH).

X-ray diffraction (XRD) analysis was applied to study the structural stability of perovskite film. FAPbI_3 perovskite on different substrates were compared in above testing conditions: neat ITO, ITO/PTAA, ITO/PF8TAA, ITO/PEDOT: PSS.

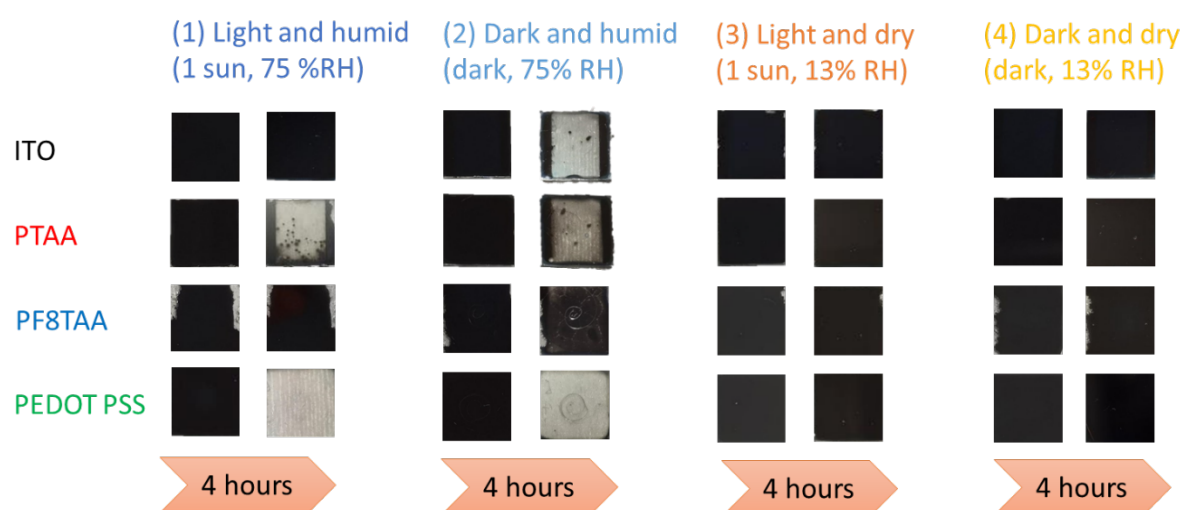


Figure 8.5. Photographs of FAPbI_3 films aged under different testing conditions: (1) light and humid (1 sun illumination, 75% RH), (2) dark and humid (75% RH), 3) light and dry (1 sun illumination, 13% RH), (4) dark and dry (13% RH). The size of each substrate is 1.2 cm $\times$ 1.2 cm.

In the 1) light and humid condition (1 sun illumination, 75% RH), there were obvious colour changes on the photographs before and after aging (Figure 8.5), as aged films become greyish on 1) ITO, faded to semi-transparent on 2) PTAA, greyish on 3) PT8AA, and transparent on 4) PEDOT: PSS. Before stability test, all fresh films were pure α -FAPbI₃ phase in XRD patterns (Figure 8.6). After 4 hours, the emergence of δ -FAPbI₃ indicated perovskite degradation to photoinactive phase (Figure 8.7). The resulted integrated peak area ratio of δ -FAPbI₃/ α -FAPbI₃ for aged films became 0.03, 2.9, 0.03 and 21.19 on 1) ITO, 2) PTAA, 3) PF8TAA, and 4) PEDOT: PSS respectively. The severity of degradation was compared as: PEDOT: PSS > PTAA > ITO ~ PF8TAA.

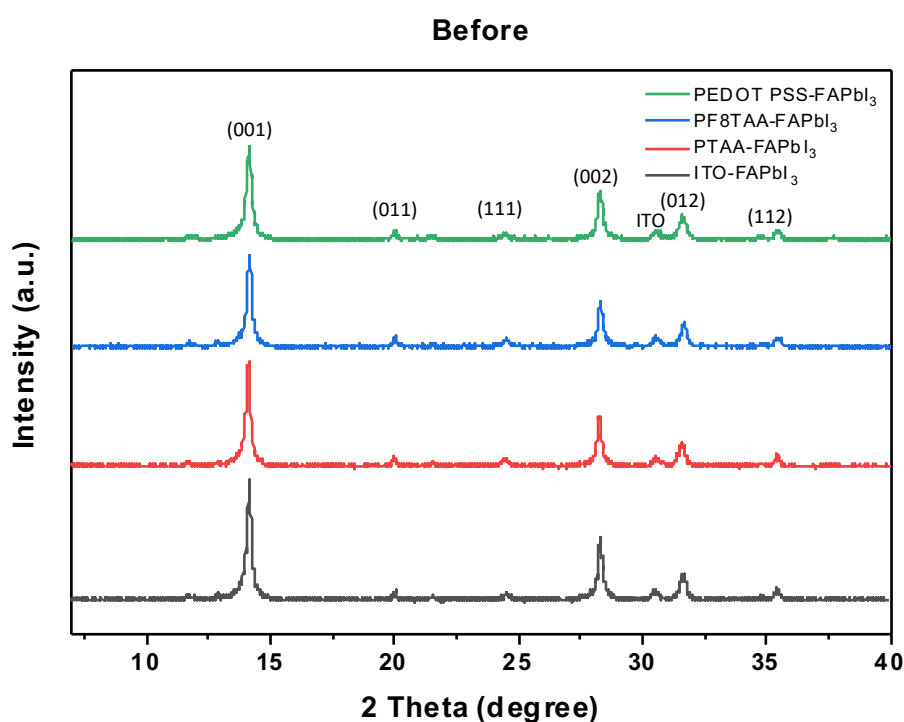


Figure 8.6. X-ray diffraction (XRD) patterns of perovskite films before aging at 0 h (fresh). The diffraction peaks of α -FAPbI₃ are labelled in the plots.

In the 2) dark and humid condition (75% RH), colour changes could be seen on the photographs before and after stability test, with aged films faded to different extents (Figure 8.5). The degradation of perovskite corresponded to peak changes in XRD pattern. Before stability test, fresh films were pure α -FAPbI₃ photoactive phase. After 4 hours stability test, however, the appearance of δ -FAPbI₃ was observed in all conditions (Figure 8.7). Perovskite suffered from phase transition from photoactive α -FAPbI₃ black phase to photoinactive δ -FAPbI₃ yellow phase, resulting in integrated peak area ratio of δ -FAPbI₃/ α -FAPbI₃ as 2.85, 4.75, 0.78 and 38.96 for 1) ITO, 2) PTAA, 3) PF8TAA, and 4) PEDOT: PSS respectively. The severity of degradation was compared as: PEDOT: PSS > PTAA > ITO > PF8TAA.

In the 3) light and dry condition (1 sun illumination, 13% RH), no obvious colour changes were observed on the photographs after stability test (Figure 8.5). In XRD pattern, there was no apparent degradation on all films. Although there was a small amount of PbI₂ appeared on aged films, they are relatively stable under this condition. No sign of δ -FAPbI₃ on XRD pattern was found (Figure 8.7). The integrated peak area ratios of PbI₂/ α -FAPbI₃ on aged films were relatively small, as 0.07, 0.06, 0.078 and 0.03 for 1) ITO, 2) PTAA, 3) PF8TAA, and 4) PEDOT: PSS respectively. Overall, the degradation was mild and similar on all substrates.

In the 4) dark and dry condition (13% RH), the results were similar to 3) condition. There were no obvious colour changes on the photographs after aging, all films kept black after 4 hours (Figure 8.5). Although a small amount of PbI₂ appeared on aged films, they were considerably stable with no obvious degradation to δ -FAPbI₃ (Figure 8.7). As a result, the integrated peak area ratio of PbI₂/ α -FAPbI₃ were 0.08, 0.08, 0.08

and 0.03 for 1) ITO, 2) PTAA, 3) PF8TAA, and 4) PEDOT: PSS respectively. The film degradation was mild and similar on all substrates.

In summary, we investigated the phase stability of FAPbI₃ films on various substrates under different environmental conditions. Our results indicate that different degradation mechanisms may occur under different conditions. Specifically, exposure to light/dark is found to enhance the emergence of the δ -FAPbI₃ peak, while heating is more likely to induce the appearance of the PbI₂ peak. Additionally, we observed that the black photoactive α -phase is vulnerable to moisture and can easily be degraded to the yellow photoinactive δ -phase in high humidity environments. Moreover, we found that the choice of underlying layer plays a crucial role in determining the phase stability of perovskite.

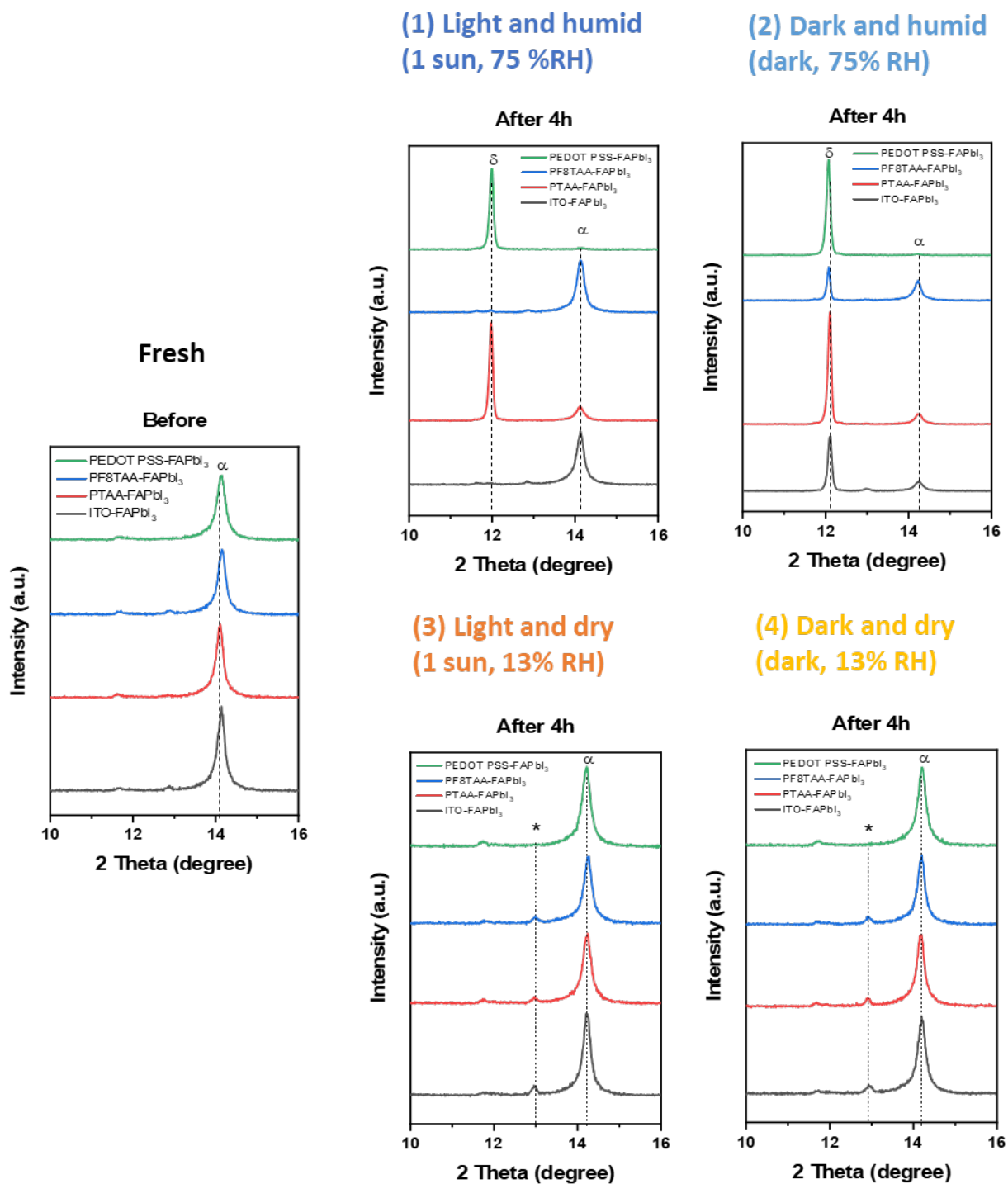


Figure 8.7. XRD patterns of fresh and aged perovskite films under different testing conditions: (1) light and humid (1 sun illumination, 75% RH), (2) dark and humid (75% RH), 3) light and dry (1 sun illumination, 13% RH), (4) dark and dry (13% RH). The peaks assigned to α -phase and δ -phase are labelled on the plots, and * denotes PbI_2 peak.