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**INTERFACE ENGINEERING FOR ORGANIC–INORGANIC
HYBRID PEROVSKITE SOLAR CELLS**

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**Interdisciplinary Graduate School
Energy Research Institute @ NTU**

2021

INTERFACE ENGINEERING FOR ORGANIC–INORGANIC HYBRID PEROVSKITE SOLAR CELLS

FOO SHINI

INTERDISCIPLINARY GRADUATE SCHOOL

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

2021

Statement of Originality

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

31 July 2021

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

31 July 2021

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Huang YiZhong

Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journals / from papers accepted at conferences in which I am listed as an author.

Chapter 4 is published as as M. Thambidurai, S. Foo, K. M. Salim, P.C. Harikesh, A. Bruno, N. F. Jamaludin, S. Lie, N. Mathews, C. Dang. Improved photovoltaic performance of triple-cation mixed-halide perovskite solar cells with binary trivalent metals incorporated into the titanium dioxide electron transport layer. *J. Mater. Chem. C*. **7**, 5028–5036 (2019). DOI: 10.1039/C9TC00555B.

The contributions of the co–authors are as follows:

- I co–designed the study and performed all the laboratory work at the Energy Research Institute @NTU (ERI@N) and School of Electrical and Electronic Engineering. I also analyzed the data
- Dr M. Thambidurai and Prof C. Dang provided the initial project direction and edited the manuscript drafts.
- Characterization techniques and corresponding data evaluation such as x–ray diffraction, J–V measurements, incident photon–to–current conversion analysis, UV–Vis, and photoluminescence spectroscopies were conducted by me and Dr M. Thambidurai.
- I prepared the manuscript drafts. The manuscript was revised by A/Prof N. Mathews, A/Prof Y. Huang, S. Lie, and Prof C. Dang.
- X–ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy analysis were conducted by the Facility for Analysis, Characterization, Testing and Simulation.
- P. C. Harikesh assisted in the collection and interpretation of the electrochemical impedance spectroscopy data, field emission scanning electron microscopy, UV–Vis, and photoluminescence spectroscopies.
- Time-Resolved Photoluminescence was conducted by A. Bruno, N. F. Jamaludin.

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- I provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by A/Prof N. Mathews, A/Prof Y. Huang, and Prof C. Dang.
- I co-designed the study and performed all the laboratory work at the Energy Research Institute @NTU (ERI@N) and School of Electrical and Electronic Engineering. I also analyzed the data.
- Characterization techniques and corresponding data evaluation such as x-ray diffraction, J–V measurements, incident photon-to-current conversion analysis, UV–Vis, and photoluminescence spectroscopies were conducted by myself and Dr M. Thambidurai.
- X-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy analysis were conducted by the Facility for Analysis, Characterization, Testing and Simulation.
- P. C. Harikesh assisted in the collection and interpretation of the electrochemical impedance spectroscopy data, field emission scanning electron microscopy, UV–Vis, and photoluminescence spectroscopies.

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The contributions of the co-authors are as follows:

- I provided the initial project direction.

Abstract

Laboratory efficiencies of current state of the art organic–inorganic hybrid perovskite (OIHP) solar cells are on par with the well–established crystalline silicon–based solar cells. Despite the ideal intrinsic optoelectronic properties as efficient and relatively economical light absorbing layers, commercialization of OIHP materials is greatly impeded by issues such as poor stability and reproducibility. Comprising of various functional layers stacked on top of one another, interfaces often serve as transport barriers since defects tend to aggregate between the layers, impeding the photovoltaic performance, stability, and reproducibility of solar cells. To address these challenges, intensive developments have been made recently to interfacial engineering so as to reduce the amount of undesirable trap states in OIHP solar cells. Although significant progress has been made to improve the device performance and stability of OIHP solar cells using interfacial engineering, preferable properties of passivation material utilized at various interfaces are often overlooked. Therefore, this thesis focuses on the importance of passivation materials at interfaces found in OIHP solar cells, whereby properties tailored and profitable for various interfaces are highlighted. Specifically, modifications were conducted to the electron transport layer (ETL), as well as the ETL/ OIHP and OIHP/ hole transport layer (HTL) interfaces. Hence, this thesis hopes to encourage commercialization of OIHP solar cells by using premediated passivation materials at various interfaces for the creation of highly efficient, reliable, and stable of OIHP solar cells.

Work I. Despite the wide range of possible electron transport materials, titanium dioxide (TiO_2) continues to be the most utilized semiconductor in OIHP solar cells due to its good repeatability. However, the intrinsic properties of TiO_2 are incompatible for efficient electron transport since compact- TiO_2 (c- TiO_2) ETL has relatively low electron mobility and poor electrical conductivity. Dopants are commonly used to tune the properties of semiconductors. Here, aluminium (Al) and indium (In) dopants are co-doped into the conventional c- TiO_2 to form the AlIn doped TiO_2 (AlTO) ETL. When used in the mesoporous structure, superior photovoltaic performance and stability were demonstrated in OIHP solar cells. Systematic characterization of the individual dopants revealed that the

improved short-circuit current (J_{SC}) in the devices employing the Al doped TiO_2 ETL was due to the reduced optical losses while the enhanced open-circuit voltage (V_{OC}) and fill factor (FF) of the devices utilizing the In doped TiO_2 ETL allowed better energy level alignment and conductivity. When used in the mesoporous structure, superior photovoltaic performance and stability were demonstrated. All in all, this study shows a facile yet effective co-doping method to improve several cell parameters at once, consequentially, result in high overall power conversion efficiency (PCE).

Work II. As seen in the previous work, the compact AlIn doped TiO_2 (AITO) ETL employed in the mesoporous structured led to improved stability and efficiency in OIHP solar cell. However, planar OIHP solar devices exhibit ease in scalability due to the simple processing procedures. Yet, certified PCEs of planar OIHP solar devices remain inferior to that of the mesoporous configuration. In this study, the previously optimized compact AITO layer was utilized together with the SnO_2 ETLs to form the heterogeneous ETL. It is revealed, through this paper, that the use of both AITO and SnO_2 ETLs in a single device provides synergistic benefits to the overall performance, long-term stability, and reproducibility of the planar OIHP solar devices. Specifically, the addition of SnO_2 at the AITO/OIHP interface provided reduced recombination occurrences due to the passivating nature of SnO_2 films, as well as enhanced electron transport due to its high electron mobility. On the other hand, the AITO ETL deposited below the SnO_2 layer prevented shunting pathways and encourage stability. Despite the improved reproducibility, stability, and efficiency, the overall performances of the as-prepared OIHP devices are still unsatisfactory compared to commercially available silicon solar cells and can be improved further.

Work III. As can be seen in the second work, passivation at the ETL/OIHP interface using the heterogeneous ETL showed significant improvement in device reproducibility although further enhancements in device stability and efficiency are desirable. Owing to ionic and soft bonding characteristic of OIHP materials, defects such as under-coordinated ions and dangling bonds tend to concentrate at the OIHP/HTL interface. In addition, the hydroscopic

HTL deposited adjacent to the OIHP layer could accelerate degradation, reducing the stability of the OIHP solar device. Here, modifications were made to the previous optimized heterogeneous ETL based device, whereby 2-hydroxybenzophenone (HBP) molecules are deposited on top of the annealed OIHP layer. It is hypothesized that the HBP molecules passivate the under-coordinated lead (Pb^{2+}) defects accumulated at the interface by promoting favourable Lewis acid-base adduct formation. Through this work, it is verified that the use of an optimized Lewis base passivation layer enhances the overall device performance and stability attributed to the efficient hole transport across the OIHP/HTL interface and reduced recombination tendencies in the HBP passivated solar device.

Therefore, this thesis demonstrates the effectiveness and simplicity of interfacial engineering to which synergistically improvement in device efficiency, reproducibility and stability of OIHP solar cells can be attained. The thesis further shows the importance of using well-designed passivation materials, tailored for various interfaces of OIHP solar cells.

Lay Summary

Amongst the varied renewable energy sources proposed to replace fossil fuels, solar energy is an ideal candidate due to its cleanliness, abundance, and non-toxicity. In particular, perovskites are excellent materials as light absorbers attributed to the excellent electronic and optical properties. Furthermore, perovskite solar cells have good solution processability which is compatible with most low-cost fabrication techniques. However, perovskite solar cells degrade under various atmospheric conditions, unlike that of the commercialized silicon solar cells which demonstrate good stability and reproducibility. Therefore, this thesis focuses on synthesizing highly efficient perovskite solar cells with enhanced stability and reproducibility capabilities through modifications at various interfaces.

Perovskite solar cells are multilayered structures, comprising of various materials and layers surrounding the perovskite absorber. The stacked device consists of several interfaces whereby the quality and nature of the interfaces, particularly the contacts adjacent to the perovskite film, greatly influence the overall performance of the perovskite solar cell. This is because the properties of the charge transport layers, and presence of defects located at the interfaces can greatly alter the device efficiency, stability, and reproducibility of the solar cell. Although recent devotion to interfacial engineering has resulted in rapid increments in the overall performance of perovskite solar cells, understanding and importance placed in the nature of the passivation suited for various interfaces are still lacking. Hence, tailored interfacial materials were utilized at various interfaces during this Ph.D. period to uncover the importance of interfacial engineering and the effects of specific properties displayed by the passivation material at various interfaces. In particular, interfacial engineering between the electron transport layer (ETL) and perovskite layer, as well as between the hole transport layer (HTL) and perovskite layer.

Through this thesis, it is verified that the use of two dopant elements is an effective method to improve the overall performance of perovskite solar cells, whereby each dopant can result in improvements of different properties of the ETL. Employment of compatible

heterogeneous ETL also ensures synergistic enhancements to device efficiency, stability, and reproducibility. Further improvements in device stability and efficiency are demonstrated by using Lewis base passivation layers between the perovskite layer and HTL. Effects of passivation using Lewis base passivation showed great effectiveness in improving the efficiency and stability of perovskite devices.

In essence, this thesis shows the importance of modifying various interfaces through the addition of constructive interfacial materials to acquire high photovoltaic performance, long-term stability, and device reproducibility. Hence, this thesis shows the use of facile passivation materials as a simple yet highly effective approach to advance commercialization of perovskite solar cells.

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Table of Contents

Abstract	i
Lay Summary	v
Acknowledgements	vii
Table of Contents	ix
Table Captions	xv
Figure Captions	xvii
Abbreviations	xxv
 Chapter 1 Introduction.....	 1
1.1 Hypothesis (science)/Problem Statement (engineering)	2
1.2 Objectives and Scope	6
1.3 Dissertation Overview	7
1.4 Findings and Outcomes/Originality	9
References.....	9
 Chapter 2 Literature Review	 13
2.1 Overview	14
2.1.1 Introduction to Photovoltaics	15
2.1.2 Brief History of Photovoltaics	16
2.1.3 Introduction of OIHP	18

2.1.3.1	Strengths of OIHP	19
2.1.4	Device Engineering of OIHP solar cells	22
2.1.5	Defects in OHIP solar cells	25
2.1.6	Role of interfaces in a OIHP device.....	27
2.1.6.1	Defect Passivation at the Electron Transport Layer	30
2.1.6.2	Defect Passivation at the OIHP/HTL interface	35
2.1.6	Device Engineering of OIHP solar cells	27
2.2	Questions to answer based on literature	38
2.3	Novelty of Research	40
	References	41
Chapter 3	Experimental Methodology	49
3.1	Rationale for selection	50
3.2	Synthesis.....	52
3.2.1	Spin Coating.....	52
3.2.2	Thermal Evaporation	53
3.3	Characterization	54
3.3.1	Steady-state Photoluminescence Spectroscopy	55
3.3.2	Field-emission Scanning Electron Microscopy	57
3.3.3	Contact Angle Analysis	58
3.3.4	X-ray Diffraction Analysis	59
3.3.5	X-ray Photoelectron Spectroscopy	61
3.3.6	Ultraviolet photoelectron spectroscopy	63
3.3.7	Ultraviolet-Visible spectroscopy	63
3.3.8	Fourier Transform Infra-Red spectrometry	65
3.4.9	Current-density against Voltage Characterization	66

3.3.10 Incident Photon to Current Efficiency Measurement	70
3.3.11 Electrochemical Impedance Spectroscopy	71
References	72
 Chapter 4 Effects of co-doping on compact TiO₂.....	77
4.1 Introduction	78
4.2 Experimental Methods	80
4.2.1 Materials	80
4.2.2 Device Fabrication	81
4.2.3 Characterization	82
4.3 Results and Discussion.....	83
4.3.1 Verification of Co-dopants in the c-TiO ₂ ETL	83
4.3.2 Energy Band Levels of various ETL	84
4.3.3 Effect of Co-doping on the Photovoltaic Performance and Stability.....	85
4.3.4 Effects of Co-doping to the ETL.....	90
4.3.5 Effects of Co-doping to the Properties of the OIHP film	91
4.4 Conclusions	93
References	94
 Chapter 5 Effects of ETL/OIHP interface engineering	97
5.1 Introduction	98
5.2 Experimental Methods	100
5.2.1 Materials	100
5.2.2 Device Fabrication	100
5.2.3 Characterization	101

5.3	Results and Discussion.....	102
5.3.1	Chemical Characterization of various ETLs.....	102
5.3.2	Energy Band Levels of various ETLs	103
5.3.3	Effectiveness of the Homogeneous ETL Based Devices	104
5.3.3.1	J–V Measurements	105
5.3.3.2	Optoelectronic and Recombination Properties	106
5.3.3.3	Long–Term Stability.....	107
5.3.3.4	Device Reproducibility	109
5.3.4	Effectiveness of the Heterogeneous ETL Based Devices	110
5.3.4.1	Morphological Studies	111
5.3.4.2	J–V Measurements	113
5.3.4.3	Long–Term Stability.....	115
5.3.4.4	Device Reproducibility	116
5.3.4.5	Optoelectronic and Recombination Properties	117
5.4	Conclusions	119
	References.....	119
Chapter 6	Effects of OIHP/spiro–OMeTAD interface passivation	123
6.1	Introduction	124
6.2	Experimental Methods	126
6.2.1	Materials	126
6.2.2	Device Fabrication	126
6.2.3	Characterization	127
6.3	Results and Discussion.....	127
6.3.1	Verification of HBP Passivation	127

6.3.2	Morphological Studies	131
6.3.3	Optical and Electronic Studies.....	133
6.3.4	Energy Band Level Alignment.....	134
6.3.5	Device Performance and Reproducibility	135
6.3.6	Long-Term Stability	139
6.4	Conclusions	142
	References.....	142
 Chapter 7 Discussion and Future Work		147
7.1	Conclusions	148
7.2	Significant Contributions	150
7.3	Reconnaissance Results and Future Works.....	150
7.3.1	Effects of Lewis acid Passivation and its Importance	150
7.3.2	Passivation at Grain Boundaries compared to Interfaces	155
	References.....	159

Table Captions

Table 2.1 List of various TiO_2 , SnO_2 , and novel ETL based OIHP solar cells. V_{OC} , FF, PCE, and architecture of devices are also provided [75,81,85,92–102].

Table 2.2 Summary of various passivation materials at the OIHP/HTL interface [115–124].

Table 4.1 Photovoltaic parameters of the OIHP solar cells with various compact ETLs.

Table 4.2 Hall effect parameters of the glass/ TiO_2 /Au and glass/AlTO/Au substrates.

Table 4.3 Analysis of the TRPL with two-exponential decay characteristics for OIHP,

Table 4.4 Fitted parameters acquired during EIS measurements under dark condition.

Table 5.1 Photovoltaic parameters of homogeneous ETL based devices.

Table 5.2 Fitted parameters for EIS measurements acquired under dark condition.

Table 5.3 Photovoltaic parameters of the heterogeneous ETL based devices.

Table 5.4 Fitted parameters for EIS measurements acquired under dark condition.

Table 6.1 Photovoltaic parameters of as-prepared OIHP devices.

Table 7.1 Photovoltaic parameters of the pristine and CBSC-IN OIHP devices.

Figure Captions

Figure 2.1 (a) Band structure of a typical semiconductor [13]. (b) SQ limit in various types of solar cells measured under AM 1.5G condition with a mirror attached to the back surface [11].

Figure 2.2 Advancement in photovoltaic technology with corresponding best research–cell efficiency [10].

Figure 2.3 (a) An ideal cubic and (b) an alternative representation of the perovskite structure. The green, blue, and red circles represent the A-site, B-site and X-site ions, respectively [22].

Figure 2.4 (a) Density of states (DOS) of the MAPbI₃ absorber with contributions of various ions [28]. (b) Schematic illustration of various optical absorptions by different photovoltaic materials [29]. (c) Measured absorption coefficient of MAPbI₃ at various wavelength. The absorption coefficient (α) is measured from $\alpha = \frac{1}{l} = \ln\left(\frac{I_0}{I}\right)$, where l is the thickness of the TiO₂ film, I_0 is the intensity of incident light while I represents the intensity of transmitted light [30]. Comparison between MAPbI₃ and GaAs in terms of (d) DOS, (e) joint DOS, and (f) Optical absorptions [31].

Figure 2.5 Architecture evolution of OIHP solar cells [34–40].

Figure 2.6 Typical energy level alignments of the n–i–p and p–i–n configurations.

Figure 2.7 Schematic illustration of the working principle in a MAPbI₃ solar cell.

Figure 2.8 Schematic illustration of (a) various defects, (b) transition energy levels, and (c) the related defect formation energy commonly found in a MAPbI₃ solar cell

[34,46,47,64].

Figure 2.9 Illustration of the degradation process at the $\text{TiO}_2/\text{MAPbI}_3$ interface upon UV exposure [72].

Figure 2.10 Examples of OIHP solar devices containing various ETLs under different device stresses [80–84].

Figure 2.11 (a) Deposition of MgO prevents shunt pathway commonly found in monolayer SnO_2 ETLs [91]. (b) Schematic illustration of enhanced electron generation and extraction in the GQDs modified OIHP solar cell, resulting in improved PCE [92].

Figure 2.12 Chemical structure of DAP along with the schematic illustration of defect passivation via passivation of under-coordinated Pb^{2+} ion and moisture protection [114].

Figure 3.1 Schematic illustration of the spin coating technique [18].

Figure 3.2 Schematic of a typical thermal evaporation system [21].

Figure 3.3 Illustration of the PL (a) setup and (b) mechanism [23,24].

Figure 3.4 Illustration of the (a) band-to-band radiative and (b) nonradiative recombination pathways [25].

Figure 3.5 Schematic illustration of the SEM instrument [28].

Figure 3.6 Schematic illustration of contact angle and various interfacial energies [30].

Figure 3.7 Schematic diagrams of the (a) x-ray diffractometer and (b) Bragg's law [32].

Figure 3.8 Basic schematic diagrams of the XPS (a) setup and (b) physics [34,35].

Figure 3.9 Schematic diagrams of (a) a typical UPS spectrum and (b) the mechanism [37,38].

Figure 3.10 Schematic diagrams of a (a) UV–vis spectroscopy set–up and (b) Tauc plot [39,40].

Figure 3.11 Illustrations of the (a) ATR mode and (b) a typical FTIR spectrum [42,43].

Figure 3.12 (a) A typical J–V curve of a solar device along with (b) various ideality factor and associated recombination [44,46].

Figure 3.13 Various spectral distribution for different air mass conditions [51].

Figure 3.14 IPCE spectrum and its integrated current density of a typical OIHP solar cell [53].

Figure 3.15 Schematic illustrations of the (a) correlation between circuit elements and Nyquist plots and (b) equivalent circuit model commonly used for OIHP solar cells [55,56].

Figure 4.1 (a) X–ray diffraction patterns of TiO₂ and AITO films. XPS spectra of TiO₂ and AITO films at the peaks of (b) Ti 2p, (c) O 1s, (d) Al 2p and (e) In 3d.

Figure 4.2 (a) UPS, (b) transmittance, and (c) $(\alpha h\nu)^2$ versus $h\nu$ spectra of various films.

Figure 4.3 (a) Schematic illustration, (b) cross–sectional FESEM image, and (c) Energy level diagram of the as–prepared AITO ETL based device. (d) J–V curves of the Al–TiO₂ and (e) In–TiO₂ ETL devices at various concentrations. (f) IPCE curves

of the 0.02 M Al-TiO₂ and 0.02 M In-TiO₂ ETL devices. (g) J-V, (h) steady state efficiency measured at maximum power output, and (i) IPCE curves of the pristine TiO₂ and AITO ETL devices.

Figure 4.4 Statistical distribution of the photovoltaic parameters for solar cells with the TiO₂ and AITO ETL, specifically (a) J_{SC}, (b) V_{OC}, (c) FF, and (d) PCE.

Figure 4.5 J-V curves of the TiO₂ and AITO ETL based devices stored in ambient conditions after 25 days

Figure 4.6 (a) Photoluminescence and (b) TRPL spectra of the OIHP films coated on bare glass, TiO₂ coated glass and AITO coated glass substrates. The TRPL data were fitted using the bi-exponential decay rate (white line). (c) Equivalent circuit used to fit the (c) Nyquist plots of the TiO₂ and AITO ETL based devices cells.

Figure 5.1 (a) XRD and XPS spectra, specifically the (b) Sn 3d and (c) O 1s peaks of the SnO₂ film [33].

Figure 5.2 (a) UPS spectra and (b) plots of $(\alpha h\nu)^2$ versus $h\nu$ for the SnO₂ film. (e) Corresponding energy level diagram of the OIHP solar devices [33].

Figure 5.3 (a) Schematic and (b) SEM cross-sectional image of a complete homogeneous solar device. (c) J-V curves of various champion homogeneous ETL based devices. To duplicate the thickness used for the heterogeneous ETL, the homogeneous ETL were spun twice.

Figure 5.4 (a) Transmittance spectra of various homogeneous ETLs. (b) Nyquist plots of various homogeneous ETL based devices and the equivalent circuit used for the EIS analysis.

Figure 5.5 Stability curves of various homogeneous ETL based devices without

encapsulation, categorized into various photovoltaic parameters of (a) J_{SC} , (b) V_{OC} , (c) FF, and (d) PCE. Statistical histogram of the homogeneous ETL based devices divided into various photovoltaics parameters, specifically (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) PCE.

Figure 5.6 Statistical histogram of the homogeneous ETL based devices divided into various photovoltaics parameters, specifically (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) PCE.

Figure 5.7 Top view and corresponding cross-sectional SEM images of various OIHP films deposited on FTO (a & d), FTO/ TiO_2 / SnO_2 (b & e), and FTO/AlTO/ SnO_2 (c & f) substrates.

Figure 5.8 XRD patterns of various OIHP films deposited on FTO, FTO/ TiO_2 / SnO_2 , and FTO/AlTO/ SnO_2 substrates. Note that • represents peaks belonging to cubic PbI_2 while the remaining peaks represent the OIHP film.

Figure 5.9 (a) Schematic and (b) cross-sectional SEM image of a complete heterogeneous ETL based device. (c) Reverse and forward J–V and (d) IPCE curves of the champion heterogeneous ETL based devices.

Figure 5.10 Long-term stability of various heterogeneous ETL based devices under for 25 days without encapsulation, specifically (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) PCE.

Figure 5.11 Statistical histogram of the heterogeneous ETL based devices divided into various photovoltaics parameters, specifically (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) PCE.

Figure 5.12 (a) Transmittance spectra of various heterogeneous ETLs. (b) Absorption and (c) PL spectra of the OIHP films deposited on various heterogeneous ETLs. (d) Nyquist plots of heterogeneous ETL based devices.

Figure 6.1 (a) Molecular structure of HBP [32]. XPS spectra of the O 1s peak found in

the (b) pristine and (c) HBP passivated OIHP films. (d) XPS spectra of the Pb 4f peaks. The (e) complete and (f) magnified FTIR spectra of the as-prepared films.

Figure 6.2 XRD spectra of the pristine and HBP passivated OIHP films at various concentrations. Note that • represents peaks belonging to cubic PbI_2 while the remaining peaks represent the OIHP film.

Figure 6.3 FESEM image and grain size distribution of the (a & b) pristine, (c & d) 5 mg/mL, (e & f) 10 mg/mL and (g & h) 20 mg/mL HBP passivated OIHP films.

Figure 6.4 (a) UV-vis absorbance and (b) PL spectra of the pristine and HBP passivated OIHP films at various concentrations.

Figure 6.5 Enlarged (a) cut-off and (b) onset energy regions of the UPS spectra. (c) $(\alpha h\nu)^2$ against $h\nu$ plots of the pristine and HBP passivated OIHP films. (d) Band diagram of the complete OIHP device.

Figure 6.6 (a) Device architecture and (b) cross-sectional SEM image of the HBP passivated OIHP device. (c) Champion J-V curves and (d) IPCE spectra of both pristine and 5 mg/mL HBP passivated OIHP devices. Stabilized photocurrent and power output as a function of time for the (e) 5 mg/mL HBP passivated and (f) pristine OIHP devices.

Figure 6.7 Statistical distribution of the photovoltaic parameters, specifically the (a) V_{OC} , (b) J_{SC} , (c) FF, and (d) PCE. Note that the empty square in each box plot represents the average value achieved.

Figure 6.8 Contact angle measurements for both pristine and HBP passivated OIHP films.

Figure 6.9 Stability histogram of pristine and 5 mg/mL HBP passivated OIHP devices

over 120 days, divided into their respective photovoltaic parameters of (a) J_{SC} , (b) V_{OC} , (c) FF, and (d) PCE. Note that the average (filled circle) and standard deviation (error bar) were calculated from 5 devices of each configuration.

Figure 7.1 (a) Chemical structure of a CBSC molecule. (b) J–V, (c) UV–vis absorbance, and (d) PL spectra of the pristine and CBSC–IN OIHP devices at various concentrations.

Figure 7.2 XPS spectra of the pristine and 5 mg/mL CBSC–IN OIHP devices, specifically (a) deconvoluted Cl 2p, (b) deconvoluted O 1s, (c) Pb 4f, and (d) I 3d elements.

Figure 7.3 FESEM images and respective histograms of the (a&c) 5 mg/mL CBSC–IN and (b&d) 5 mg/mL CBSC–GB OIHP films. Cross-sectional FESEM of the (e) 5 mg/mL CBSC–IN and (f) 5 mg/mL CBSC–GB OIHP devices.

Figure 7.4 (a) UV–vis absorbance, and (b) PL spectra of the CBSC–IN and CBSC–GB OIHP devices.

Figure 7.5 XPS spectra of the CBSC–IN and CBSC–GB OIHP films, specifically the (a) deconvoluted Cl 2p, (b) deconvoluted O 1s, (c) Pb 4f, and (d) I 3d peaks.

Abbreviations

OIHP	Organic–Inorganic Solar Cell
AITO	Aluminium Indium doped Titanium Dioxide
TiO ₂	Titanium Dioxide
ETL	Electron Transport Layer
HTL	Hole Transport Layer
GB	Grain Boundary
AM	Air Mass
NREL	National Renewable Energy Laboratory
J _{sc}	Short–Circuit Current Density
V _{oc}	Open–Circuit Voltage
FF	Fill Factor
PCE	Power Conversion Efficiency
IPCE	Incident Power Conversion Efficiency
XPS	X–ray photoelectron spectroscopy
PL	Photoluminescence
UV–Vis	Ultraviolet–Visible
SQ	Shockley–Queisser
Au	Gold
LCOE	Levelized Cost of Electricity
ATR	Attenuated Total Reflectance
BEI	Backscatter Electron Images
BSE	Backscattered Electron
EIS	Electrochemical Impedance Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
SEI	Secondary Electron Images
XRD	X–ray Diffraction

Chapter 1

Introduction

This chapter provides an overview of the dissertation. Beginning with the hypothesis, the dissertation explores the effects of charge transport and interfacial engineering on the photovoltaic performance, reproducibility, and device stability in OIHP solar cells. Based on the hypothesis, aims and sub-objectives relevant to the thesis are established. The outlines of each subsequent chapters are also discussed with the results based on the content of the dissertation briefly summarized.

1.1 Hypothesis/Problem Statement

The future for solar is bright. Acting as an inexhaustible source of energy, the theoretical solar potential striking Earth's surface is approximately 89,300 TW [1]. With global annual energy consumption reported at approximately 140,000 TWh in 2018, it takes around 90 minutes of solar radiation to satisfy the world's energy demand [2,3]. Despite the huge potential, the contribution of solar energy to energy consumption remains negligible compared to that of fossil fuel [4]. In order for increased reliance on solar power, reduction in cost is pivotal. When the conversion efficiency of the solar panel increases or/and the cost of material decreases, the price tag on solar power also decreases. Unlike traditional photovoltaic cells such as silicon solar cells, production of organic–inorganic hybrid perovskite (OIHP) solar cells allow simple solution–based processing techniques whereby high–cost machineries and facilities commonly associated with semiconductor processing are not required. In addition, power conversion efficiency (PCE) of OIHP solar devices have soared to an all–time high of 25.2 % without the use of strict growth processes, typically necessary for high performing cells in other photovoltaic technologies [5]. Attributed to excellent intrinsic properties such as remarkable defect tolerance, exceptional charge carrier mobilities, and high light absorption coefficient, OIHP solar devices display immense potential for low–cost terawatt–scale solar deployment.

In order for OIHP solar cells to be competitive, levelized cost of electricity (LCOE) for residential use has to be at 9.0 cents/kWh by 2020 and 5.0 cents/kWh by 2030 [6]. To attain LCOE of 9.0 cents/kWh by 2020, a 1 by 1 m² solar panel has to have an average PCE greater than 20 % and a lifespan surpassing that of 20 years, even if cost of raw materials is assumed at zero. However, the low LCOE is too demanding for OIHP solar cells. Though the rapid increase in efficiency of OIHP solar cells is remarkable, current best–research cell efficiency remains remote compared to the Shockley–Queisser (SQ) theoretical limit of 31.4 % for an absorber with a band gap of 1.55 eV [7]. In addition, poor stability and batch–to–batch inconsistency greatly hamper commercial endeavors of highly efficient OIHP solar devices. Current stability of OIHP solar devices are limited to months,

miniscule compared to the required lifespan of 20 years [8,9]. Hence, improved PCEs, long-term stability, and reproducibility in OIHP solar devices are necessary and urgent.

Typically, solar devices with large amount of defects have lower PCE, stability, and reproducibility. This is because occurrences of non-radiative recombination increases with increasing defect concentration while carrier lifetime reduces with increasing trapped states [10,11]. To reduce the amount of defect states in OIHP solar cells, three common passivation techniques have been utilized namely (i) compositional engineering of the OIHP absorber layer, (ii) reduction of defects in the adjacent charge transport layers using dopants, and (iii) interfacial engineering by introducing passivating interlayers at various interfaces [10,12]. For the past few decades, great effort has been placed in fine-tuning the optoelectronic properties via compositional engineering of the OIHP absorber layer [13]. Thus, advances in compositional engineering has led to tremendous improvements in device stability and efficiency as seen in multi-cation and/or multi-halide OIHP solar cells. To date, compositional engineering of the OIHP absorber has matured considerably, resulting in the shift in focus with increasing publications dedicated to interfacial engineering and optimization of charge transport layers [14–16]. With the transportation of photogenerated charged carriers in direct competition with the recombination process, it is vital to optimize the transport layers along with the interfaces present in OIHP solar cells. Presence of energy barriers, interfacial trap states, charge accumulation, and poor charge transport at various transport layers could adversely affect the charge collection efficiency at the electrodes which, in turn, undermines the overall performance of OIHP solar cells [10–12]. As such, this thesis focuses on charge transport optimization and interfacial engineering to improve issues regarding the efficiency, stability, and reproducibility of OIHP solar devices.

Hypothesis

Some of the highest efficiencies obtained in n-i-p OIHP solar devices employ titanium dioxide (TiO_2) as the electron transport layer (ETL). This is because TiO_2 ETLs offer diverse fabrication techniques, favourable energy levels with the adjacent OIHP absorber,

and good environmental stability [17,18]. However, compact-TiO₂ (c-TiO₂) films demonstrate poor electron mobility which greatly limits the charge separation at the c-TiO₂/OIHP interfaces [19,20]. Consequently, devices that use c-TiO₂ as its ETL often exhibit inferior PCE, stability, and reproducibility. To enhance the conductivity of c-TiO₂, addition of dopants is often conducted. By adding trivalent dopants with similar ionic radii such as Al³⁺ (approximate ionic radius of 0.054nm) in replacement of the larger oxidation state Ti⁴⁺ (approximate ionic radius of 0.061nm), substitutional defects such as oxygen vacancies are generated [21,22]. In turn, electrons are donated to maintain electrical neutrality, enhancing charge carrier concentration and mobility. It is often reported that the use of aluminium (Al) dopants generates oxygen vacancies in the lattice while improving the conductivity of the c-TiO₂ film [21–23]. Another effective dopant is indium (In) whereby the In doped TiO₂ ETL showed better work function with the adjacent OIHP layer [23–25]. However, it is often challenging to simultaneously enhance several photovoltaic parameters using the dopant technique. For example, the addition of In dopant could improve the fill factor (FF) of the OIHP device through the reduction in work function. However, addition of In might not enhance the short-circuit current density (J_{SC}) since J_{SC} is closely associated to the transmittance of devices. Based on the problem statement above, the first hypothesis is established:

- The dissertation tests the assumption of simultaneous improvement in several photovoltaic parameters using the co-doping approach in the c-TiO₂ ETL.

In recent years, tin oxide (SnO₂) has become an attractive ETL due to the low required annealing temperature and high electron mobility even at amorphous state. However, the low fabrication temperature often results in poor film morphology with high tendencies for pinhole formation. As such, most highly efficient SnO₂ ETL-based OIHP solar devices employ sophisticated fabrication techniques, inappropriate for low-cost production necessary for commercial endeavours of OIHP solar cells [26,27]. Furthermore, solution processed SnO₂ ETLs often suffer from poor consistency, with large variation in attained PCE ranging from shorting devices to PCEs exceeding 20 %. Since different ETLs possess varied electrical and chemical properties, the use of complimentary ETLs could exploit the

advantages unique to each ETL while concealing the potential weaknesses of each film. Based on the problem statement above, the second hypothesis is established:

- The dissertation tests the effectiveness of heterogeneous ETL in improving the efficiency, stability, and reproducibility of OIHP solar cells.

Comprising of an assortment of layers, interfaces between the OIHP and charge transport layers demonstrate utmost importance in governing the overall performance of the solar device. This is because interfaces are particularly prone to the accumulation of dangling bonds and under-coordinated ions. As such, interfaces are highly susceptible to nonradiative recombination [10–12]. The interface found at the OIHP/ hole transport layer (HTL) is particularly prone to defect generation owing to the rapid crystal growth of the OIHP film and the solution-processing deposition techniques employed [28–30]. As such, effectiveness of the charge transport process is often compromised. It is reported that under-coordinated lead ions (Pb^{2+}) are the main sources of recombination centers at the surface of the OIHP film [28,29]. This is because methylammonium and halide ions present in the OIHP film could be lost during the annealing process which, consequentially, give rise to defects such as under-coordinated Pb^{2+} . Since Pb^{2+} exhibit soft Lewis acid character, Lewis base passivation is often utilized to improve the overall photovoltaic performance OIHP devices. In addition, the OIHP layer is highly sensitive to several factors such as moisture, heat, oxygen, and continuous illumination. For these reasons, OIHP film are often termed as highly sensitive and prone to chemical decomposition. Thus, the use of interfacial materials at the OIHP/HTL interface not only acts as a protective shields for the underlying OIHP films, chemical interactions between the functional groups found in the interfacial material and the defects found at the interface could suppress charge recombination and extend device stability [10,12,30]. Based on the problem statement above, the third hypothesis is established:

- The dissertation tests the effects of interfacial engineering at the OIHP/HTL interface using a hydrophobic Lewis base passivation material to which significant improvement in ambient stability and PCE of the OIHP device is postulated due to the lowered charge recombination and protective nature of the interfacial material.

1.2 Objectives and Scope

The main objective of this thesis is to enhance the photovoltaic performance, reproducibility, and long-term stability of OIHP solar devices through the use of sensible charge transport and interfacial engineering. In addition, the thesis also hopes to investigate the properties important for passivation at various interfaces. Based on the hypotheses above, detailed sub-objectives of the dissertation are listed below:

1.2.1 Evaluate the significance of co-doping on conventional electron transport layer

In order to attain PCE close to that of the theoretical limit, most corresponding photovoltaic parameters of OIHP solar devices must be high. To illustrate, in order for an OIHP solar cell with a band gap of 1.6 eV to achieve efficiency of 30.5 %, open-circuit voltage (V_{OC}), J_{SC} , and FF have to be approximately 1.33 V, 25.4 mAcm^{-2} , and 0.91, respectively [31,32]. To push the efficiency of OIHP solar cells closer to that of the theoretical limit, it is essential to develop high-quality ETLs that allows increment of multiple photovoltaic parameters since all parameters play significant importance on the overall power conversion efficiency (PCE) attained. Excessive use of dopants could also deteriorate the device performance and stability such as increment in series resistance or poor surface morphology [33]. Hence, it is important to carry out systematic investigation to understand the effects of individual dopants. By using a variety of characterization tools such as current-density against voltage (J-V) results, field-emission scanning electron microscopy (FESEM), x-ray diffraction (XRD) analysis, x-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS), photoluminescence (PL) spectroscopy, ultraviolet-visible spectroscopy (UV-vis) spectroscopy, and ultraviolet photoelectron spectroscopy (UPS), the effects of the individual dopants, along with their synergistic effects, can be evaluated.

1.2.2 Investigate the effects of interfacial engineering on the photovoltaic parameters

Although the main source of nonradiative recombination remains highly debatable, it is generally believed that defects concentrate at the interfaces due to the change in chemical composition compared to the bulk composition. Recent literatures show significant evidence that most recombination losses occur at or across interfaces surrounding the OIHP layer amid operation [33–37]. Passivation, in the field of OIHP solar cells, is typically referred to the chemical passivation of defect states or the physical passivation of certain functional layer by acting as a physical barrier to isolate the underlying film [24,33,38]. By introducing interfacial materials at interfaces, improved charge transport can be attained via defect healing [38]. Hence, the use of suitable interfacial engineering should reduce the amount of defects and occurrences of nonradiative recombination, significantly increasing corresponding cell parameters such as V_{OC} and FF.

1.2.3 Investigate the effects of interfacial engineering on device stability

The OIHP film is extremely vulnerable to a variety of solvents and solutes, metals, and environmental conditions [39,40]. Therefore, it is vital to use interfacial materials not only tolerable to the sensitive absorber film, but also beneficial to the photovoltaic performance, reproducibility, and stability of OIHP solar devices. It is also important to uncover the properties vital to the enhancement in the overall performance of OIHP solar cells at various interfaces. By using suitable interfacial engineering to reduce the amount of defects and occurrences of nonradiative recombination, V_{OC} and FF should increase significantly. Stability and reproducibility of devices should also improve since defects act as degradation initiators [41,42]. Hence, this thesis hopes to increase the V_{OC} and FF of OIHP solar cells by using interfacial materials with passivating properties.

1.3 Dissertation Overview

The thesis addresses three key factors affecting the commercialization of OIHP solar devices namely, high efficiency, good device reproducibility, and respectable long-term stability. Specifically, the dissertation assesses the overall performance of OIHP solar

devices through modifications at the ETL, ETL/OIHP, and OIHP/HTL interfaces. Hence, this thesis provides simple yet powerful insights to generate highly stable, reproducible, yet efficient OIHP solar devices via rational interfacial engineering.

Chapter 1 provides an overview of the dissertation. Beginning with the problem statement, the chapter introduces the hypothesis and rationale for the research. In addition, the sub-objectives and contributions made to the scientific communities are also mentioned.

Chapter 2 reviews the literature concerning the evolution of photovoltaics with emphasis on OIHP solar devices. Excellent optoelectronic properties resulting in the rapid development of OIHP devices are also discussed. The chapter further evaluates the role of interfaces, interfacial materials, and their effectiveness in enhancing the overall performance of the solar device. Developments of various interfacial engineering and passivation strategies are also summarized. This chapter serves as a guide to the subsequent chapters and gaps in knowledge that the thesis will be addressing.

Chapter 3 discusses the principles underlying the synthesis and characterization techniques employed in the dissertation. The main deposition methods applied in the fabrication of the as-prepared films such as spin coating and evaporation are also discussed. Principles related to various characterization techniques are also explained.

Chapter 4 elaborates the first major set of results. Effectiveness of co-doping in the conventional compact ETL is evaluated. Systematic investigation is utilized to discern the contributions of respective dopants to various photovoltaic parameters. Effects to long term stability and reproducibility are also examined.

Chapter 5 elaborates the second major set of results. Effectiveness of compatible heterogeneous ETL in the planar OIHP solar devices is evaluated. Effects of interfacial engineering at the ETL/OIHP interface on the photovoltaic parameters, long term stability, and reproducibility are investigated.

Chapter 6 elaborates the third major set of results. This chapter evaluates the use of Lewis base at the OIHP/HTL interface whereby the effect of defect passivation on the recombination resistance and charge transport are assessed.

Chapter 7 presents the main conclusions of this dissertation and draws together the threads of this thesis. Objectives mentioned in Chapter 1 are achieved with main hypothesis of the thesis proven. The chapter further elaborates on the opportunities and strategies for future work. Reconnaissance studies that did not warrant a complete chapter are also included.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Established that co-doping of ETL allows systematic enhancement in several photovoltaic parameters.
2. Showed that the use of heterogeneous ETL as a straightforward yet powerful method to provide synergistic enhancements in various photovoltaic parameters, device stability, and also device reproducibility in OIHP devices.
3. Demonstrate the use of hydroscopic Lewis base passivation as an effective material to allow chemical and physical protection to the underlying OIHP film.
4. Reiterates the importance of tailored interfacial optimization in benefiting the overall performance of OIHP solar cells.

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Chapter 2

Literature Review

This chapter provides an overview of the fundamental concepts required to understand the contents of the subsequent chapters. Beginning with an introduction to solar energy, the development of photovoltaics is also mentioned, with special emphasis on organic–inorganic hybrid perovskite solar cells and their unique properties. The working principles and historic developments are also discussed with special mentions regarding the different advantages and challenges of various solar cell architectures. The importance of interfaces, along with current interfacial engineering strategies, are examined in detail. At the end of the chapter, research questions of the dissertation based on the literature review are presented.

2.1 Overview

Due to the scarcity and environmental burden derived from fossil fuel combustion, current approaches to generate electricity are unsustainable and inadequate to meet the soaring energy demand. Solar energy has been one of the most promising renewable energy alternative due to its massive potential and incredible technological advancement over the recent years. Yet, the contribution of photovoltaic power generation is miniscule whereby contribution to the global energy consumption is less than 2 % [1,2]. Ubiquitous implementation of renewable sources of energy is crippled by the steep pricing and intermittency of renewable sources of energy [1,3]. To date, most deployed photovoltaics are only made competitive to non-renewable sources through lavish government policies and hefty subsidies [4]. Thus far, majority of the installed photovoltaics are silicon solar cells. With increased installation and manufacturing experience, the price tag on silicon solar cells should decline [1,3]. However, the inherent properties of the silicon semiconductor as a photovoltaic material are lacking. For example, silicon is an indirect band gap material with limited maximum absorption capability [1,3,5,6]. To develop a silicon solar cell with respectable efficiency, the silicon material should also possess high purity which requires the use high temperature and costly manufacturing procedures. The bulkiness, rigidity, and high power-to-weight ratio further impedes the ease of transportation and installation of conventional silicon modules.

In order for photovoltaics to be prevalent and less dependent on government subsidies, it is important to develop cheaper solar alternatives with respectable efficiency and reliability. Given these points, organic-inorganic hybrid perovskite (OIHP) solar cell appears as the potentially transformative photovoltaic technology owing to its solution processibility and fitting intrinsic properties [2,7,8]. OIHP is a direct band gap material with high absorption coefficient, high defect tolerance, and long charge carrier mobility. In addition, the OIHP solar cell exhibits merits of several predecessor photovoltaic technologies [9]. Similar to inorganic thin-film photovoltaics such as gallium arsenide (GaAs) and copper indium gallium selenide (CIGS) solar cells, OIHP solar cells are also lightweight and flexible. The highly attractive band gap tunability and solution processibility found in dye-sensitized

solar cells (DSSCs) and organic solar cells are also present in OIHP solar cells. With power conversion efficiency (PCE) at a high of 25.2 %, OIHP solar cells demonstrate excellent viability as the alternative technology to provide the world with endless and cheap source of energy [10]. Nonetheless, concerns regarding poor reproducibility, device instability, and material degradation in ambient environments pose great hurdles for commercialization of OIHP solar cells. By understanding the intrinsic properties, operating mechanism, degradation pathways, and key developments of OIHP solar cells, insights necessary to improve the efficiency, reproducibility, and stability are examined.

2.1.1 Introduction to Photovoltaics

In 1905, Albert Einstein proposed the particle–wave duality of light in which light is sometimes regarded as waves and sometimes regraded as particles. This phenomenon can be explained using the photoelectric effect whereby electrons are emitted from a matter by an incident light. Instead of acting solely as a wave, Einstein explained that light sometimes behaves as particles of electromagnetic energy and is emitted as little packets of energy aka photon. Mathematically, light is defined by the Plank’s equation of $E=h\nu$, where E is the energy of photon measured in joules (J), h is the Plank’s constant at 6.626×10^{-34} Js, while ν is the frequency of light measured in hertz (Hz).

Solar cells, also known as photovoltaic cells, operate on the principle of photovoltaic effect. When incident light hits a suitable material in which energy from the photon is transferred to the electrons in the material, charge carriers are liberated, and electricity is produced. In general, semiconductors make up the light absorbers in solar cells. Possessing electronic properties between that of conductors and insulators, the application of suitable light empowers excitation and generation of usable current in semiconductors. Defined as the minimum amount of energy required to remove an electron from its valence band to its conduction band, the capability of a semiconductor to absorb incident light depends on its band gap (E_g). In the case of solar cells, energy required for electron excitation from the valence band to the conduction band is provided by photons, which are packets of electromagnetic radiation from the sun at varying wavelengths and energy. When a photon

with smaller energy strikes a solar cell with a larger band gap, the photon is absorbed in the form of thermal energy and no excitation occurs. As seen in Figure 2.1a, photons possessing energies greater or equals to the E_g of the material allow excitation of electrons from the valence band maximum (VBM) energy level to the conduction band minimum (CBM) energy level, generating photocurrent [11–13]. Note that a singular photon can only excite an electron from the valence to the conduction band. According to the Shockley–Queisser (SQ) limit, the maximum theoretical conversion efficiency of any single p–n junction solar cell under air mass (AM) 1.5G conditions with band gap of 1.34 eV is around 33.7 % [11,12]. In other words, when incident light of 1000 W/m^2 falls on an ideal solar cell, only 337 W/m^2 of incident power can be converted to electricity. As seen in Figure 2.1b, maximum efficiency is typically achieved by semiconductors with band gaps within the 1.3–1.4 eV [11]. Hence, small band gap materials such as germanium ($E_g = 0.67 \text{ eV}$) are usually used to absorb low energy photons while large band gap materials such as gallium phosphide ($E_g = 2.26 \text{ eV}$), largely transparent in the visible spectrum, are typically used for infrared absorption.

Figure 2.1 (a) Band structure of a typical semiconductor [13]. (b) Shockley Queisser (SQ) limit in various types of solar cells plotted against band gap of various solar cells, measured under AM 1.5G condition with a mirror attached to the back surface [11].

2.1.2 Brief History of Photovoltaics

In 1839, Edmond Becquerel discovered the direct conversion of sunlight into electricity when platinum electrodes coated with silver chloride and silver bromide were submerged

in an acidic solution [14]. Then, Chapin, Fuller, and Pearson from Bell Laboratories fabricated the first silicon-based semiconductor solar cell with a PCE of 6% [15–17]. Figure 2.2 illustrates the advancement in solar photovoltaics technology along with their respective champion certified efficiencies [15]. However, manufacturing of crystalline silicon solar cells was initially too expensive due to the requirement of high purity raw materials, high temperatures, and harsh environmental conditions. As such, initial deployments of solar cells in the early 1970s were greatly limited to space satellites [18]. With reduced cost of solar panel production and maturation of the silicon industry, crystalline solar cells dominate present commercial and private photovoltaic markets [16]. Yet, the indirect band gap found in the crystalline silicon material opposes its suitability as an effective light absorber material. To absorb considerable amount of light in an indirect band gap material, a relatively thick amount of semiconductor (typically 200 μm) is required. As such, commercial crystalline silicon solar cells are comparatively heavy and inappropriate for flexible application. In hopes to reduce the bulkiness of crystalline silicon solar cells, thin film photovoltaics were created.

Currently, most thin film photovoltaics employ direct band gap semiconductor materials such that minimal amount of material is required. In addition, promising PCEs were attained. To illustrate, efficiencies of 14.0, 22.1, 22.6, and 28.8 % were achieved in the amorphous silicon (a-Si), cadmium telluride (CdTe), CIGS, and GaAs-based solar cells, respectively [15]. However, these materials are expensive, toxic, and incur high manufacturing fees. To reduce material and production costs, numerous next-generation photovoltaic technologies were developed namely, organic photovoltaics (OPVs), DSSCs, and quantum-dot solar cells (QDSCs) [19–21]. Such technologies allow low-temperature processability and encourage large-scale production since solution printing technologies such as roll-to-roll printing can be employed.

Recently, OIHP solar cells demonstrate great potential as the up-and-coming thin film photovoltaic technology due to its competitive energy output against the total cost required. Levelized cost of electricity (LCOE) is an integral standard commonly used to analyze different photovoltaic technologies by both companies and customers. Unlike traditional

photovoltaic cells such as silicon solar cells which utilize high-cost facilities and techniques, the solution processability of OIHP solar cells allows facile solution deposition methods such as slot-die coating, spray coating, doctor blading, and continuous roll-to-roll processing, greatly reducing the cost of production. Furthermore, the cost incurred from raw materials is small due to the abundance of materials. The rapid increase in PCE further advances the commercialization of OIHP solar cells [15].

Figure 2.2 Advancement in photovoltaic technology with corresponding best research-cell efficiency [10].

2.1.3 Introduction of OIHP

To be exact, the true perovskite compound is a mineral called calcium titanate (CaTiO_3). As time progresses, the term perovskite is often used to classify any crystalline compound a similar crystal structure as CaTiO_3 , and has a generic chemical formula of ABX_3 . Figure 2.3 illustrates the chemical structure of an OIHP crystal by which the A-site ions are usually monovalent organic cations that occupy the corners of the lattice, divalent inorganic cation commonly used as the B-site ions occupy the center of the lattice, while the X-site ions are usually monovalent halides that completes the BX_6 octahedral [22]. Depending on the elemental combinations used, alteration in the tolerance factor occurs such that various crystal structures with unique properties are fabricated. The Goldschmidt tolerance factor

(t) can be calculated using the equation $t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)}$. The radii of the A-, B-, and X-site are represented by symbols R_A , R_B , and R_X , respectively. Although a tolerance factor of 1 would indicate a perfect cubic perovskite structure, OIHP materials typically have t values between 0.81–1.11 [23]. If $t > 1.1$ or $t < 0.8$, the cubic perovskite structure will not be generated [24]. Yet, the broad range of acceptable tolerance factors indicate a wide combination of possible atoms/molecules. By tuning the composition of the perovskite material, characteristic tweaking towards specific applications can be carried out [25].

Figure 2.3 (a) An ideal cubic and (b) an alternative representation of the perovskite structure. The green, blue, and red circles represent the A-site, B-site, and X-site ions, respectively [22].

2.1.3.1 Strengths of OIHP

OIHP is an intriguing material for photovoltaic application with immense photovoltaic potential due to its favourable optoelectronic properties [26,27]. Specifically, the OIHP material is a direct band gap absorber and shows unique ionic and covalent properties, high absorption coefficient, low binding energy, and long carrier diffusion lengths. Given the superior optoelectronics, it is understandable why efficiencies of OIHP solar cells saw rapid increment within a quarter of the timespan of traditional solar cells [10].

1. Unique electronic structure and high absorption coefficient

Figure 2.4a represents the density state of the methylammonium lead triiodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$ or MAPbI_3) structure to which the electronic characteristic is highly

dependent on the lead (Pb) and iodine (I) ions, while the A-site ions remain electronically inactive, contributing mostly to the structural integrity of the crystal structure instead [28]. Specifically, the VBM energy level display strong Pb 6s–I 5p antibonding character, while the CBM energy level exhibit strong Pb 6p–I 5p and Pb 6p–I 5s antibonding characters, providing unique ionic and covalent properties in OIHP materials.

Figure 2.4b shows the favourability of the OIHP material compared to other photovoltaic materials [29]. Since OIHP is a direct band gap material, absorption coefficient of OIHP is also higher than silicon. Defined as the effectiveness of light absorbance by a material, direct band gap semiconductors typically show higher absorption coefficient compared to indirect band gap materials as it does not require phonon-assisted transition. In contrast to the indirect band gap silicon material, OIHP is a direct band gap material with two orders of transition probability between the valence and conduction bands, thus allowing the use of much lesser absorber material. Figure 2.4c represents the absorption coefficient of the direct band gap MAPbI₃ material under various wavelengths [30]. At 550 nm, the absorption coefficient of MAPbI₃ is calculated to be $1.53 \times 10^4 \text{ cm}^{-1}$, indicating a penetration depth of approximately 0.66 μm . Likewise, absorption coefficient at 700 nm corresponds to $0.53 \times 10^4 \text{ cm}^{-1}$, indicating an increase in penetration depth to 2 μm . As such, OIHP is often characterized as having a broad light harvesting spectrum range, with absorbance capability of nearly the entire visible light spectrum despite the use of a thin MAPbI₃ film of less than 2 μm [16]. Although GaAs is also a direct band gap material, the electronic band structure vastly differs from that of the OIHP material. As seen in Figure 2.4d, the CBM of GaAs is dominated by the atomic s orbital while the VBM is dominated by the atomic p orbital [31]. Since the s orbital is more dispersed than the p orbital, the density of states at the conduction band of GaAs is significantly lower than that of OIHP, leading to a lower joint density of states as seen in Figure 2.4e. In addition, the energy levels of the bands in the MAPbI₃ material are contributed by a mixture of Pb and I ions, the intra-atomic transition probability is much higher in OIHP compared to GaAs, explaining the higher optical absorption in the visible spectrum, as seen in Figure 2.4f.

2. Low binding energy and long diffusion lengths

The binding energy of MAPbI₃ (around 25 meV at room temperature) is comparable to the thermal energy. Since the binding energy of excitons is defined as the measure of coulombic attraction found between an electron–hole pair, effectiveness of subsequent charge transport heavily relies on the fraction of dissociated excitons. With binding energies similar to that of thermal energy, spontaneous generation of free electrons and holes is expected in the OIHP material upon light absorption. As such, rapid dissociation of free charge carriers takes place without the need for addition energy. Furthermore, OIHP materials exhibit long balanced diffusion lengths. To illustrate, the diffusion lengths of electrons and holes in a MAPbI₃ thin film are estimated to be 130 and 100 nm, respectively. With slight increment in the MAPbI_{3-x}Cl_x film, diffusion lengths are estimated to be approximately 1 μ m for both charge carriers [32,33].

Figure 2.4 (a) Density of states (DOS) of the MAPbI₃ absorber with contributions of various ions

[28]. (b) Schematic illustration of various optical absorptions by different photovoltaic materials
 [29]. (c) Measured absorption coefficient of MAPbI₃ at various wavelength. The absorption coefficient (α) is measured from $\alpha = \frac{1}{\ell} \ln \left(\frac{I_0}{I} \right)$, where ℓ is the thickness of the TiO₂ film, I_0 is the intensity of incident light while I represents the intensity of transmitted light [30]. Comparison between MAPbI₃ and GaAs in terms of (d) DOS, (e) joint DOS, and (f) Optical absorptions [31].

2.1.4 Device Engineering of OIHP solar cells

Photovoltaic capabilities of OIHPs have been known since the 1800s, although most applications were highly restricted to transistors and light-emitting diodes (LEDs). Incorporation of OIHP for solar cell application was first demonstrated by Miyasaka et al. in 2006 to which, during spin coating, the OIHP material readily crystallized onto the surface of the thick nanocrystalline titanium dioxide (TiO₂) paste and showed potential as a facile sensitizer [34]. As seen in Figure 2.5, initial OIHP sensitized DSSCs showed low efficiencies with the MAPbBr₃ based DSSC achieving PCE of 2.2 % while the MAPbI₃ based DSSC attained higher PCE of 3.8 % [25,34]. Due to the corrosive nature of the iodide/triiodide (I⁻/I³⁻) liquid electrolyte commonly used as the redox couple in DSSC, initial liquid electrolyte based OIHP solar cell garnered little interest in the research field due to rapid degradation and poor stability. Enthusiasm only returned in 2012 when Gratzel et al. replaced the liquid electrolyte with a solid-state hole transport layer (HTL), known as the 2',7,7'-tetrakis-9,9'-spirobifluorene (spiro-OMeTAD) which achieved long-term stability greater than 500 h [35]. In the same year, Snaith et al. showed improved device stability using the MAPbI₂Cl absorber, with stable performance despite exposure to constant illumination for 1000 hours [36]. He also showed the possibility of omitting the electron transport layer (ETL) whereby the MAPbI₂Cl-based DSSC coupled with an insulating Al₂O₃ scaffold attained improved efficiency of 10.9 % as opposed to when the TiO₂ ETL was utilized. This suggested excellent charge transport properties in the OIHP films, indicating the negligibility of the mesoporous ETL. This discovery also led to the shift in the usual mesoporous architecture to the planar structured OIHP solar devices. Unlike the mesoporous structure, planar OIHP solar cells show greater suitability for

commercial production due to the straightforward fabrication procedure [36,37].

Snaith et al fabricated the first regular (n-i-p) planar device which, unfortunately, obtained lower efficiency compared to its mesoporous counterpart. Snaith et al. realized that the low efficiencies attained in the planar OIHP solar cells are due to the poor surface coverage of the OHIP film. After optimization of the OIHP deposition process, improved efficiency was observed to 11.4 % [38]. However, high temperatures ($> 450\text{ }^{\circ}\text{C}$) utilized in the TiO_2 ETL fabrication ($> 450\text{ }^{\circ}\text{C}$) restrict allowable substrate and increases the processing cost. You et al. adopted the inverted (p-i-n) structure instead which employed charge transport layers that requires fabrication temperatures under $120\text{ }^{\circ}\text{C}$ [39]. The p-i-n configuration resembles an organic photovoltaic cell where photogenerated holes flow towards the transparent electrode (anode) while electrons move towards the opaque electrode (cathode). Using multiple elements namely the $\text{Cs}_x(\text{MA}_{0.17}\text{FA}_{0.83})_{(100-x)}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ triple cation composition, superior efficiency and stability were demonstrated [40]. Gratzel et al. attained remarkable PCE and sustained efficiency at 18 % despite 50 hours of testing under operational conditions. Advancing at a startling pace, OIHPs thus became the front runners among emerging photovoltaic materials. To date, efficiencies of laboratory based photovoltaic cells have reached 25.2 %, comparable to crystalline silicon solar cells [10].

Figure 2.5 Architecture evolution of OIHP solar cells [34–40].

In general, a typical OIHP solar cell is made up of several layers stacked on top of one another, serving different purposes. For a regular OIHP solar cell, the device consists of a transparent conductive oxide such as the fluorine-doped tin oxide (FTO), an ETL such as a n-type metal oxide, the OIHP absorber, a HTL such as a p-type organic molecule, and the metal electrode. As seen in Figure 2.6, the charge transport layers provide smooth injection and transport of selective charge carriers. The presence of the ETL provides a staggered energy alignment such that electrons from the OIHP absorber are transported smoothly to the cathode with little charge accumulation [41]. Similarly, the HTL extracts positively charged holes from the OIHP film while ensuring transport of electrons to the anode does not occur. The use of charge transport layers promotes unipolar transference of charge carriers while reducing carrier recombination tendencies.

Figure 2.6 Typical energy level alignments of the n-i-p and p-i-n configurations.

2.1.5 Defects in OIHP solar cells

In an ideal solar cell, all absorbed photons are converted and transported to their respective electrodes, whereby the only recombination channel is radiative recombination of the free electrons and holes. The working mechanism of OIHP solar cells is shown in Figure 2.7. When incident photons with energy higher than the band gap ($h\nu > E_g$) strikes the OIHP absorber, electrons are excited from the valence to the conduction band (process 1), whereby the photogenerated electron-hole pairs are separated (process 2) by the built-in electric field and transported via diffusion to the charge transport layers (process 3). After multiple transportation and extraction processes, free electrons and holes are collected at the negative and positive electrodes, respectively (process 4). However, unlike the ideal state as described above, the OIHP solar cell also undergo various types of nonradiative recombination processes (process 5) including Auger, the Shockley-Read-Hall (SRH), surface, and interface recombination [42,43]. To understand the relationship between defects and recombination, effective carrier lifetime (τ_{eff}) is commonly characterized as follows:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{1}{\tau_{\text{surf}}} = \frac{1}{\tau_{\text{Aug}}} + \frac{1}{\tau_{\text{SRH}}} + \frac{1}{\tau_{\text{surf}}} = \frac{\Delta n}{U_{\text{eff}}}$$

, where τ represents the charge carrier lifetime, Δn is the excess-charge carrier concentration, and U_{eff} is the effective recombination rate [43–45]. τ_{bulk} represents the lifetime of associated with defects found in the bulk OIHP absorber and can be further

divided into the SRH recombination (τ_{SRH}) and Auger recombination (τ_{Aug}). Defects can also be found at the surface and interface, with its charge carrier lifetime represented by τ_{surf} .

Figure 2.7 Schematic illustration of the working principle in a MAPbI₃ solar cell.

Type and density of defects present in OIHP solar cells are highly dependent on the processing procedure and absorber composition. Also, defect generation occurs not only during synthesis of device but also during device operations. As seen in Figure 2.8a, there are various types of defects namely, 1) intrinsic 0D defects, including vacancy, interstitial, impurities, and antisite substitution, 2) 2D defects, like grain boundaries (GBs) and surface defects, and 3) 3D defects like lead clusters [34,46,47]. Annealing the OIHP film for an extended duration could result in evaporation of the organic and halide elements, leaving behind under-coordinated Pb²⁺ ions at interfaces or even encourage PbI₂ growth [48–50]. To improve the stability and efficiency of the MAPbI₃ absorber, a small percentage of MA⁺ (CH₃NH₃⁺) is often replaced with FA⁺ or Cs⁺, Pb²⁺ replaced with Sn²⁺, and I[−] with other halogens such as Br[−] or Cl[−] [24,51]. Thus, 0D point defects such as Pb²⁺ vacancies (V_{Pb}), I[−] vacancies (V_I), interstitial I₃[−], interstitial Pb²⁺, and PbI₃[−] antisite (Pb–I, Pb_I, I_{Pb}) are commonly found within the bulk OIHP material [32]. Defects in OIHP films can also be categorized into shallow- and deep-level defects, as illustrated in Figure 2.8b [47]. The difference is that shallow-level defects such as under-coordinated halides and Pb²⁺ form sub-energy levels near the conduction band minimum (CBM) and valence band maximum

(VBM) edges while deep-level defects such as PbI_3^- antisite generate transition levels in the middle of the band gap [47,64]. As such, shallow-level defects are regarded as benign to the device performance of OIHP solar cells whereas deep-level defects strongly impede the efficiency of solar cells. This is because charge carriers trapped in deep-level defects require high amounts of energy before jumping back into the conduction or valence band. As such, charge transport of photogenerated carriers decreases and nonradiative recombination increases [34,46,47,64]. Figure 2.8c shows that formation energies of deep-level defects are higher than that of shallow-level defects [64]. Hence, occurrence and density of shallow-level defects should be much higher compared to deep-level defects, explaining the high degree of defect tolerance commonly attributed to OIHP solar cells [47,64].

Figure 2.8 Schematic illustration of (a) various defects, (b) transition energy levels, and (c) the related defect formation energy commonly found in a MAPbI_3 solar cell [34,46,47,64].

2.1.6 Role of interfaces in a OIHP device

Despite favourable intrinsic properties reported in the bulk OIHP material, the overall optoelectronic characteristics of a OIHP solar cell is highly dependent on the processes occurring at the interfaces found between various layers and traits of the interfacial materials [52,53]. As mentioned in section 2.5, majority of high efficiency devices employ

a sandwich structure to which there are four predominant interfaces, specifically the cathode/ETL, ETL/OIHP, OIHP/HTL and HTL/anode interfaces. These interfaces, together with the interfacial materials, regulate the working principals of the OIHP device which, in turn, govern the overall OIHP solar cell performance and stability. With major influences on the OIHP film morphology, energy band alignment, density of trap sites and optoelectronics of the solar device, interfacial engineering plays a significant role in determining the effectiveness of charge generation, transport, collection, and recombination in a solar cell.

Although the origin of nonradiative recombination remains a highly datable subject, recent studies propose interfacial and GB recombination as a weightier influence than recombination within OIHP grains [54,55]. This is because abrupt discontinuities in the crystal structure found at GBs and interfaces produces large density of defects commonly termed as dangling bonds [56]. These dangling bonds found in the active material forms non-stoichiometric balance of charges, resulting in positive or/and negative charged trap sites such as under-coordinated halides ions (e.g. Γ^-), under-coordinated lead ions (Pb^{2+}), PbI_3^- antisite defects, and Pb clusters. These under-coordinated sites are highly susceptible to oxidation and reduction reactions, degrading the ideal OIHP lattice while generating detrimental species instead. To illustrate, reduction of the under-coordinated Pb^{2+} ion produces metallic Pb, usually found on the surface of the OIHP layer. Oxidation of under-coordinated Γ^- produces volatile I_2 which, when evaporated from the film, results in decomposition of the OIHP film. In addition, presence of the I_2 molecule within the OIHP film triggers a series of chemical chain reactions, further accelerating the rate of degradation in a OIHP solar cell.

Although shallow-level defects lead to little nonradiative recombination, V_{OC} is greatly affected by the presence of such defects. This is because the V_{OC} of a OIHP solar device is determined by the quasi-Fermi level splitting (QFLS) of electrons and holes levels of the OIHP film, as well as the adjacent charge transport layers under illumination [57–59]. If the OIHP film has high density of shallow-level defects located near the CBM energy level of the OIHP film, the QFL of the ETL layer will be pinned closer to near the defect state.

Similarly, if high density of shallow-level defects is situated near the VBM energy level of the OIHP film, QFL of the HTL will also be pinned to the energy level of the trapped states instead. As a result, the achievable V_{oc} of the device, which is governed by the difference in QFLS between the transport layers under illumination, will be reduced [57,58]. In addition, defects such as under-coordinated Pb^{2+} found on the OIHP layer act as nonradiative recombination centres, reducing charge carrier lifetime and overall device performance. To illustrate, Caprioglio et al. utilized QFLS measurements to decouple the contributions of bulk recombination currents and interfacial recombination currents [59]. When OIHP materials were deposited directly on the glass substrates, large QFLS values were observed. On the other hand, substantial reduction in QFLS values were observed in the ETL/OIHP, OIHP/HTL, followed by the ETL/OIHP/HTL glass substrates.

In recent years, general consensus agree that J–V hysteresis is closely related to ion migration in the OIHP film, though other plausible explanations include the ferroelectric effect, unbalanced charge carrier transport, and trap-assisted charge recombination [60,61]. Since the OIHP absorber is ionic, presence of intrinsic interstitial defects can easily drive ion and ion vacancy migration. Interfaces between the charge transport layers and OIHP play critical roles in the extent of device hysteresis since factors such as energy level alignment, density of recombination sites, and electron mobility of adjacent charge transport layers can easily influence the charge separation and accumulation at the ETL/OIHP and OIHP/HTL interfaces [62,63]. By modifying the internal electric field, effectiveness of charge extraction and occurrence of recombination are altered, justifying the contrasting photocurrents when different voltage scan directions are applied. To identify the type of ion migration responsible for hysteresis in OIHP solar cells, Eames et al. hypothesized that the activation energy required for ion or vacancy migration should align with the activation energy required for hysteresis [62]. Eames et al. discovered that migration of I^- and Pb^{2+} general occurs along the octahedron while MA^+ moves diagonally along the $\langle 110 \rangle$ direction. Activation energy of hysteresis was measured to be 0.60–0.68 eV, well corresponding to the activation energy to I^- vacancy of 0.58 eV. Hence, the authors believe that I^- vacancy dominate ion migration under operations compared to defects such as Pb^{2+} and MA^+ vacancies. I^- moves in opposite direction to the

photogenerated current, reducing internal electric field and adversely reducing the total collected charge carriers at the electrodes. Unlike charge accumulation caused by ion or vacancy migration, the charge trapping and detrapping of captured charge carriers at trap sites could also lead to hysteresis [60,61,64]. To illustrate, charged carries can be trapped at the recombination sites under forward bias and released under short-circuit condition, before being refilled again during operation. The relatively slow act of charge trapping and detrapping explains the delay in photocurrent and voltage.

2.1.6.1 Defect Passivation at the Electron Transport Layer

Endowed with properties such as low exciton binding energies, high charge mobilities, long carrier diffusion lengths, balanced and ambipolar charge transport properties, OIHP solar cells do not require any charge transport layer since, theoretically, the active OIHP absorber material permits direct transport of harvested charge carriers to their respective electrodes [65,66]. Unfortunately, PCEs of OIHP solar cells without charge transport layers remain inferior [66,67]. This is because the charge transport layers provide smooth injection and transport of selective charge carriers [66].

To attain high efficiency and stability, ETLs of OIHP solar cells should fulfil a list of criteria [68,69]. First, the ETL should have CBM energy level intermediate to the OIHP absorber and electrode, so as to ensure cascading energy levels [70,71]. Second, the ETL should possess deep valence energy level by acting as hole blocking layer such that only unipolar transference is allowed [72]. Third, the ETL should possess good electron mobility such that fast electron transportation within the electron transport material is promoted. The strong electron-accepting property further facilitates electron extraction which explains the frequent use of materials with high electron affinity and ion potential. Fourth, the surface profile of the ETL should also be smooth since the characteristics of the adjacent layer is highly affected by the morphology, roughness, and interfacial contact of the underlying film. Lastly, the ETL should promote favourable chemical interaction between the terminating groups of the electron transport and OIHP materials [73,74].

Although TiO_2 continues to be a popular ETL candidate, the TiO_2 material shows inferior electron mobility of $0.1\text{--}4.0\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ [65,66]. In addition, TiO_2 is unstable under UV illumination [72,75,76]. Acting as a photocatalytic material, TiO_2 contains large density of oxygen vacancies which serves as deep electron donating sites, encouraging oxygen absorption from the environment which then act as deep defects [77–78]. Ito et al. proposed the generation of holes within the TiO_2 ETL upon UV illumination. As seen in Figure 2.9, these holes promote electron extraction from I^- in the OIHP film, to which I_2 is generated while the OIHP crystal structure is destroyed. To overcome the low mobility and poor device stability of TiO_2 ETL based OIHP solar cells, three strategies are commonly utilized namely doping, the use alternative ETL material, or defect passivation at the ETL/OIHP interface. [72,75,76]. Table 1 shows a list of high performing OIHP solar cells with various ETLs while Figure 2.10 illustrates the use of various dopants and ETLs under different device stresses.

Figure 2.9 Illustration of the degradation process at the $\text{TiO}_2/\text{MAPbI}_3$ interface upon UV exposure [72].

Figure 2.10 Examples of OIHP solar devices containing various ETLs under different device stresses [80–84].

1. Dopant and various ETL materials

To improve conductivity and stability of the various ETLs, approaches such as doping and alternative ETL materials are often employed. Table 2.1 shows some examples of high performing OIHP solar devices with various ETLs. To illustrate, Yang et al. showed improved electron mobility from $9.92 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the pristine tin (IV) oxide (SnO₂) film to $2.27 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the ethylene diamine tetraacetic acid (EDTA)-doped SnO₂ film [85]. Manseki et al. added magnesium (Mg) into the TiO₂ ETL to which increased CBM energy level by 1 eV. This resulted in improved Voc from 587 to 802 meV [86]. When small amounts of yttrium (III) chloride (YCl₃) was added to the TiO₂ film, decreased series resistance and increased CBM energy level from -4.08 to -3.95 eV was observed. This allowed smooth electron transfer from the OIHP layer to the YCl₃ doped

ETL [87]. In 2017, Tan et al. utilized Cl doped TiO_2 colloidal nanocrystal film and retained 90 % of initial efficiency despite 500 h of continuous operation at maximum power point (MPP) under simulated illumination of 100 mW cm^{-2} [88]. The group attributed the superior stability to the decline in recombination occurrences and enhanced charge extraction at the doped-ETL/OIHP interface. Yang et al. also showed the significance of ETL engineering in improving the morphology of the adjacent OIHP film [89]. When the 3-aminopropyltriethoxysilane (APTES) SAM modified SnO_2 ETL was employed, improved surface uniformity and grain size of the OIHP film were observed. With increasing APTES treatment, contact angle of the ETL reduced from 71° in the pristine SnO_2 to a contact angle of 39° . As such, the increased wetting encouraged larger OIHP grain formation with smaller nuclei density. As expected, devices containing the APTES modified SnO_2 ETL showed superior PCE of 17.03 % compared to the pristine device of 14.69 %. To overcome the shortcomings of the TiO_2 ETL, several research groups employ ETLs with higher electron mobility and lower bulk defect density instead. For example, SnO_2 and zinc oxide (ZnO) display higher mobilities of 240 and $205\text{--}300 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively [69]. Anaraki et al. achieved a remarkable PCE of 21 % using the solution processed planar SnO_2 ETL solar cell [90].

Table 2.1 List of various TiO_2 , SnO_2 , and novel ETL based OIHP solar cells. V_{OC} , FF, PCE, and architecture of devices are also provided [75,81,85,92–102].

ETL Type	ETL Composition	Device Architecture	VOC (V)	FF	PCE (%)	Ref
TiO_2 based ETL	c- TiO_2 /meso- TiO_2	FTO/c- TiO_2 /meso- TiO_2 /CsFAMAPbI _{3-x} Br _x /Spiro-OMeTAD/Au	1.14	77.5	20.8	[88]
	c- TiO_2	FTO/c- TiO_2 /CsFAMAPbI _{3-x} Br _x /Spiro-OMeTAD/Au	11.2	79.9	20.9	[88]
	Niobium doped TiO_2 (Nb- TiO_2)	FTO/Nb- TiO_2 /FA _{0.79} MA _{0.16} Cs _{0.05} Pb(Br _x I _{1-x}) ₃ /Spiro-OMeTAD/Au	1.09	78.0	21.3	[89]
	Chlorine doped TiO_2 (Cl- TiO_2)	ITO/Cl- TiO_2 /FA _{0.85} MA _{0.15} PbI _{2.55} Br _{0.45} /Spiro-OMeTAD/Au	1.20	76.4	21.4	[90]

SnO ₂ based ETL	Fluorine doped SnO ₂ (F-SnO ₂)	FTO/F-TiO ₂ /(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} /Spiro-OMeTAD/Au	1.13	78.1	20.2	[91]
	Graphene quantum dots doped SnO ₂ (GQD-SnO ₂)	ITO/GQD-SnO ₂ /MAPbI ₃ /Spiro-OMeTAD/Au	1.13	77.8	20.3	[87]
	SnO ₂	ITO/SnO ₂ /Cs _{0.05} (FA _{0.83} MA _{0.17}) _{0.95} PbI _{2.55} Br _{0.5} /Spiro-OMeTAD/Au	1.12	83.0	20.3	[92]
	SnO ₂ /Yttrium doped SnO ₂ (Y-SnO ₂)	FTO/SnO ₂ /Y-SnO ₂ /Cs _{0.05} (FA _{0.83} MA _{0.17}) _{0.95} PbI _{2.55} Br _{0.5} /Spiro-OMeTAD/Au	1.12	78.2	20.6	[93]
	Chlorine-containing imidazole ionic liquid 4-imidazoleacetic acid hydrochloride doped SnO ₂ (ImAcHCl-SnO ₂)	FTO/ImAcHCl-SnO ₂ /(FAPbI ₃) _{0.95} (MAPbBr ₃) _{0.05} /Spiro-OMeTAD/Au	1.15	79.0	21.0	[94]
	SnO ₂	ITO/SnO ₂ /(FAPbI ₃) _{1-x} (MAPbBr ₃) _x /Spiro-OMeTAD/Au	1.13	80.6	21.5	[95]
	Ethylene diamine tetraacetic acid doped SnO ₂ (EDTA-SnO ₂)	ITO/EDTA-SnO ₂ /FA _{0.95} Cs _{0.05} PbI ₃ /PCBM/Al	1.11	79.2	21.6	[80]
Novel ETL	c-TiO ₂ /WO ₃	FTO/c-TiO ₂ /WO ₃ /MAPbI ₃ /Spiro-OMeTAD/Au	1.09	78.6	20.1	[96]
	SnS	ITO/SnS/FA _{0.75} MA _{0.15} Cs _{0.1} PbI _{2.65} Br _{0.3} /Spiro-OMeTAD/Au	1.16	73.0	20.1	[97]
	Choline chloride/C60/BCP	ITO/PTAA/CsFAMAPbI _{3-x} Br _x /Choline chloride/C60/BCP/Cu	1.14	78.0	21.0	[69]
	c-TiO ₂ /Lanthanum doped BaSnO ₃ (La-BaSnO ₃)	FTO/c-TiO ₂ /La-BaSnO ₃ /MAPbI ₃ /PTAA/Au	1.12	81.3	21.3	[76]

2. Defect passivation at the ETL/OIHP interface

Another approach commonly used to improve the device performance and stability of OIHP solar cells is to insert a favourable passivation layer at the ETL/OIHP interface. As seen in Figure 2.11a, Ma et al. simply added a MgO layer at the FTO/SnO₂ interface and observed significant improvement from 16.43 to 18.23 % in the MgO-modified OIHP solar device. The authors attributed the enhancement to the reduction in charge recombination since the MgO interfacial layer prevented direct contact of OIHP layer with the FTO substrate. Interfacial materials with high electron mobility are also commonly used to encourage efficient charge transport through improved conductivity across the ETL/OIHP interface and reduced trap states. For example, graphene quantum dots (GQDs) was employed as an electron bridge to facilitate electron injection between the OIHP and TiO₂ ETL, as seen in Figure 2.11b [92]. With the GQD modified ETL, transient absorption

measurements revealed enhanced electron extraction from 280 picoseconds (ps) in the pristine sample to 90 ps.

Figure 2.11 (a) Deposition of MgO prevents shunt pathway commonly found in monolayer SnO₂ ETLs [91]. (b) Schematic illustration of enhanced electron generation and extraction in the GQDs modified OIHP solar cell, resulting in improved PCE [92].

2.1.6.2 Defect Passivation at the OIHP/HTL interface

Spiro-OMeTAD is often used as the HTL in the n-i-p structured OIHP solar cell. Pristine spiro-OMeTAD, however, is hardly utilized for OIHP solar cell application due to its high series resistance and low conductivity. Consequently, hole accumulation at the OIHP/spiro-OMeTAD interface results in recombination losses and poor photovoltaic performance [103,104]. To improve its conductivity, p-dopants such as lithium bis(trifluoromethanesulfonyl)imide salt (LiTFSI), 4-tert-butylpyridine (tBP), cobalt (III) complexes, and exposure to oxygen are often performed. Unfortunately, the doped spiro-OMeTAD HTL is highly susceptible to moisture adsorption due to the hydroscopic

nature of the Li-TFSI dopant [104,105]. To make matters worse, evaporation of tBP and hydration of Li-TFSI often lead to pinhole formation in the spiro-OMeTAD film [106,107]. Replacement or removal of dopants in the spiro-OMeTAD film are plausible strategies to improve the stability of the OHIP device. Yet, the PCE of such devices are often inferior to that of doped counterparts [108–110]. Moreover, synthesis of the OIHP film requires thermal annealing at approximately 100 °C to promote growth of OIHP crystals and evaporation of residual solvents. However, during thermal annealing of OIHP films, halide and/or MA ions are often lost, creating under-coordinated ions as well as antisites [111]. These defects act as electronic trap which further escalate OIHP degradation since trap charges act as weakness points to moisture, oxygen, and light attacks.

Optimally, interfacial engineering at the OIHP/HTL interface should lead to both chemical and physical passivation. Apart from reduction in defect trap states and improved charge transfer owing to favourable chemical passivation at the OIHP/HTL interface, the passivation film should also act as a physical protective layer to isolate the underlying absorber OIHP layer from undesirable external conditions [112,113]. For example, Wu et al. employed 1,3-diaminopropane (DAP) as its passivation material as seen in Figure 2.12 [114]. The hydrophilic $-NH_2$ functional group in the DAP molecule encouraged effective coordination with the under-coordinated Pb^{2+} and/or A-site vacancies, boosting both V_{oc} and PCE. As a consequence of the coordinate bond formation, the hydrophobic alkyl functional group found in the alkylamine molecule was directed towards the HTL, acting as a moisture barrier. Consequentially, enhanced device stability was observed whereby the pristine MAPbI₃ solar device degraded to 50 % of its initial PCE after 500 hours while the DAP passivated MAPbI₃ device retained more than 90 % of original PCE despite storage for 1000 h. To date, many publications focus on Lewis base passivation which targets interactions with under-coordinated Pb^{2+} . On the other hand, Lewis acid passivation on negatively charged PbI_3^- or under-coordinated halides is still scarce. Table 2.2. shows the list of passivation materials and their corresponding photovoltaic parameters [115–124].

Figure 2.12 Chemical structure of DAP along with the schematic illustration of defect passivation via passivation of under-coordinated Pb^{2+} ion and moisture protection [114].

Table 2.2 Summary of various passivation materials at the OIHP/HTL interface [115–124].

Passivation material	Targeted defect	Under standard AM 1.5 G illumination (100 mW cm^{-2})			Long-term stability (% of initial PCE retained) (C/P)	Ref
		V_{OC} (V) (C/P)	FF (C/P)	PCE (%) (C/P)		
Iodopentafluorobenzene	Undercoordinated I^-	1.02/1.06	0.57/0.67	13.0/15.7	NA	[115]
Thiophene	Undercoordinated Pb^{2+}	0.95/1.02	0.68/0.68	12.1/14.3	NA	[116]
Pyridine	Undercoordinated Pb^{2+}	0.95/1.05	0.68/0.72	12.1/15.5	NA	[116]

Graphene oxide	Undercoordinated Pb ²⁺	0.93/1.04	0.64/0.73	10.0/15.1	NA	[117]
4-Mercaptobenzoic	Undercoordinated Pb ²⁺	1.00/1.02	0.66/0.66	13.2/14.1	20/80 after 10 days	[118]
Benzylamine	Undercoordinated Pb ²⁺ and FA vacancies	0.96/1.12	0.65/0.73	14.2/19.2	NA	[119]
N-Doped reduced graphene oxide	Undercoordinated Pb ²⁺	1.12/1.15	0.73/0.74	17.3/18.7	NA	[120]
Poly(4-vinylpyridine)	Undercoordinated Pb ²⁺	1.09/1.15	0.75/0.81	18.1/20.2	85/59 after 104 days	[121]
n-hexyl trimethyl ammonium bromide	Van der waals forces between the wide band gap material and HTL	0.92/1.14	0.69/0.80	15.8/22.8	20/95 after 130 h under continuous 1-Sun illumination	[122]
Lewis acid dopant poly(triaryl amine)	Undercoordinated I ⁻	0.99/1.05	0.65/0.81	12.7/19.0	0.32/78% of its initial efficiency after 70 days exposure to air	[123]
2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane	Undercoordinated I ⁻	1.07/1.07	72.7/78.1	15.3/18.1	46.4/74.5 stored for 40 days in ambient air	[124]

2.2 Research Gap Identified from Literature Review

Despite its relatively high efficiency, commercial endeavours of OIHP solar cells remain distant due to issues regarding poor long-term stability and device reproducibility. Unlike

many other photovoltaic techniques collated in the ‘Best Research–Cell Efficiency Chart’ by NREL, certified PCEs obtained for OIHP solar cells are often regarded as unreliable or unstable. This is because, despite its relatively high certified efficiency, OIHP solar cells possess poor batch-to-batch reproducibility and stability. With intentions to march closer to commercialization of OIHP solar cells, improvements in device stability and reproducibility are critical, keeping in mind that efficiency of the solar cell should also not be compromised. To better aid commercialization of OIHP solar cells, beneath are some questions that should be answered:

First, adjacent layers within the stack also play decisive roles in the stability and overall PCE of the device. Conventional devices use a TiO_2 electron transporting layer (ETL) which is relatively poor in conductivity. This could greatly deteriorate the performance of OIHP devices due to charge accumulation, increased recombination, and poor charge transport from the OIHP layer to the electrode. Also, it is often difficult to improve multiple photovoltaic parameters using dopants. As such, co-doping is explored in the c- TiO_2 layer in hopes of improving several cell parameters through enhanced conductivity and reduced optical losses.

Second, several studies have shown possibility of achieving high stability and efficiency in planar n-i-p OIHP solar cells. However, these studies often require the employment sophisticated techniques such as radio frequency sputter deposition, atomic layer deposition (ALD), or the use of complicated colloidal nanocrystal fabrication procedures. Yet, such techniques reduce the attractiveness of OIHP solar cells such as ease in fabrication, scalability, and cost. The use of facile solution-processible ETLs often compromise the stability, reproductivity and efficiency of the OIHP solar cells due to increased susceptibility to pinhole formation and charge leakage. Furthermore, the small surface area in a compact film compared to the mesoporous structure impairs the effectiveness of charge collection at the ETL/OIHP interface. Hence, it is vital to explore highly efficient, stable, and consistent solution processed ETLs and ETL/OIHP interfacial materials.

Third, OIHP absorber films have high inclination to defect formation at its surface due to its soft ionic and polycrystalline nature. Defects such as under-coordinated ions and dangling bonds compromise device performance due to high charge recombination and poor charge transport between the OIHP and HTL layers. Furthermore, the lithium containing doped spiro-OMeTAD film is highly hygroscopic, increasing the instability of the underlying sensitive OIHP film. Several studies utilized Lewis base passivation at the OIHP/spiro-OMeTAD interface and showed enhanced stability and efficiency. However, most studies report continuous illumination stability or long-term stability of weeks. Hence, OIHP/HTL interface research showcasing high efficiency, reproducibility and extended long-term stability is vital in the commercialization of OIHP solar cells.

2.3 Novelty of Research

This thesis addresses the aforementioned research gaps regarding simultaneous attainment of high efficiency, stability, and reproducibility. By improving charge mobility while reducing recombination centers found throughout OIHP solar cells, this dissertation explores the effectiveness of doping and interface engineering at the ETL/OIHP and OIHP/HTL interfaces. My contributions are described below:

First, systematic investigations of the effects of Al and In dopants on the solution processed c-TiO₂ ETL were explored. Through the addition of Al, transmittance was enhanced resulting in increased absorbance and improved J_{sc}, while the addition of In showed improved charge conductivity and hence enhanced FF. When co-doping was utilized, a paramount PCE of 19 % was attained compared to the pristine TiO₂ devices of 16.67 %. In addition, AlIn-TiO₂ based device with anti-reflection film exhibited PCE of 19.31 %. As such, this study shows a facile yet effective co-doping method to improve several cell parameters at once, which, consequentially, resulted in the high overall PCE.

Second, a thin solution processed SnO₂ layer was deposited on the previously optimized AlIn-TiO₂ film, whereby the heterogeneous film showed paramount efficiency of 18.9 %, high reproducibility with average PCE of 18.4 % attained from 30 devices, and remarkable

long-term stability with 90 % PCE retainment despite the absence of encapsulation after 25 days, stored in 40 % relative humidity, air and dark conditions. These enhancements were attributed to the high charge mobility and passivating characteristics found in the SnO₂ film. It was verified, through this study, that the use heterogeneous ETL conceals the weaknesses of individual ETLs while promoting the strengths of the complimentary layers. Our work demonstrates a straightforward method to acquire prolonged stability and improved device reproducibility without compromising on efficiency, which will be of great interest to broad readers.

Last but not least, a thin layer of 2-hydroxybenzophenone (HBP) was deposited at the OIHP/spiro-OMeTAD interface in the fully planar configuration via simple solution-based processing. HBP was dissolved in the commonly utilized chlorobenzene solvent which did not damage the underlying OIHP film. Instead, the HBP film showed effective passivation of the under-coordinated Pb²⁺ trap states of the OIHP film through the donation of electron lone pairs found in the ketone and phenol functional groups of the HBP interlayer. It was verified, through this study, that the HBP passivated OIHP device achieved superior V_{OC} of 1.11 V, nonpareil PCE of 19.26 % and outstanding long-term stability whereby 93 % of initial PCE was retained despite the absence of encapsulation after 120 days in 40 % relative humidity, air, and dark conditions. Hence, this study demonstrates the importance of using a premeditatedly designed surface passivation material to acquire high photovoltaic performance, long-term stability, and device reproducibility.

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Chapter 3

Experimental Methodology

This chapter discusses the rationale behind material synthesis and procedure used to prepare various layers required in OIHP solar device. Techniques and roles behind each characterization method are also discussed. The chapter begins with the reasonings behind the selection of materials. Subsequently, principles governing various deposition techniques employed such as spin coating and vacuum thermal evaporation methods are mentioned. Detailed explanation comprising of the operations and significance behind respective characterization techniques used in chapters 4–7 are discussed, with aims to better optimize the device performance and stability of OIHP solar devices.

3.1 Rationale for selection

The printability of materials has been the motivation behind thin-film solar cell technologies. Especially so for OIHP solar cells, solution processability of materials promises a wide array of economically practical applications since solution processing is often described as both scalable and cost-effective. To select the most suitable and economical fabrication technique for OIHP solar cell fabrication, the following attributes should be considered:

1. Solution processible
2. Allows fabrication of films in controlled environment without the need for sophisticated set-ups
3. Relatively short duration required for synthesis
4. Easy control over thickness of film
5. Produces homogeneous thin films

In this thesis, all OIHP films and charge transport layers are synthesized from solution precursors using the spin coating technique. However, spin coating is not scalable for large area fabrication with large amount precursor solution wastage [1]. As such, alternative solution-processing approaches such as spray coating, roll-to-roll printing or doctor blade coating could be better suited for large scale production instead. That being said, the spin coating technique continues to be the main technique used to construct laboratory-scale and small-scale OIHP solar cells. This is because spin coating fulfills all the basic attributes mentioned above. The portable spin coater can be easily transported into existing controlled environments such as a glovebox without needing additional and sophisticated set-ups. In addition, spin coating is a rapid solution processing technique whereby production of homogeneous thin film can be quickly synthesized. By manipulating a few parameters such as spin speed, spin duration, and spin rate, thickness of resultant thin film can easily be engineered. Also, most highly efficiency OIHP solar cells mentioned in the NREL efficiency chart uses the spin coating technique. By using the commonly employed fabrication technique, easy comparison of performances can also be conducted [2].

The gold (Au) electrodes are thermally evaporated onto the HTL. Thermal evaporation was chosen due to the ability to deposit highly pure Au materials at relatively low temperatures ($< 100\text{ }^{\circ}\text{C}$) since high temperatures could degrade the underlying OIHP and spiro-OMeTAD layers. In addition, thicknesses of electrodes can be easily controlled via simple manipulation of applied current. Desired areas and shapes of electrodes can also be fabricated by attaching desired masks.

As mentioned in chapter 1, the main objective of this thesis is to enhance the photovoltaic performance, reproducibility, and long-term stability of OIHP solar cells through interfacial engineering at the ETL/OIHP and OIHP/HTL interfaces. Ensuring that all interfacial modifications remain solution processible, solutes and solvents involved in synthesizing the interfacial layer are carefully chosen to ensure improved performance with little disruption to the adjacent layers. All interfacial modifications were carried out through alterations in the solute-solvent mixture to which the films are spin coated onto the substrates.

The dissertation begins with c-TiO₂ ETL optimization using Al and In dopants. It is often reported that the quality of the OIHP absorber depends significantly on the quality of the underlying layer since the quality of the OIHP absorber is at mercy of the physical and chemical properties of the underlying layer [2]. TiO₂ was selected due to its good consistency, chemical stability, and non-toxicity [3,4]. Furthermore, the conduction and valence band energy levels of TiO₂ favour efficient electron transport and hole blocking capability, respectively. However, TiO₂ films have relatively poor electron mobility with reportedly high densities of defect sites. To overcome these shortcomings, two approaches were utilized in this thesis namely, (i) co-doping of TiO₂ with Al and In and (ii) SnO₂ passivation at the ETL/OIHP interface. Trivalent Al and In metal dopants were selected due to the extensive affirmations in conductivity enhancements when employed [4–12]. Moreover, these dopants do not form aggregates when added to the TiO₂ precursor mixture. Instead, the dopants dissolve easily in the mixture comprising of titanium (IV) butoxide, 2-methoxyethanol, and acetylacetone, to form a clear and homogeneous solution. SnO₂

was chosen as the passivation material at the TiO_2/OIHP interface due to its superior electrical and optical properties. In particular, amorphous SnO_2 films exhibit high optical transparency and superior carrier mobility. The SnO_2 ETL also impede hole migration across the ETL/OIHP interface owing to its highly negative valence band. As such, improved recombination resistance is often reported with the use of SnO_2 films due to their passivating properties [4,13–15]. A low annealing temperature of 200 °C utilized in the fabrication of the SnO_2 films further complements commercial endeavours [15].

Unlike interfacial modification at the ETL/OIHP interface, modifications at the OIHP/HTL interface are more delicate due to the sensitivity of adjacent OIHP layer. To ensure minimal disturbance to the sensitive OIHP absorber film, interfacial material chosen should show good solubility in anti-solvents commonly used during the deposition of OIHP. 2-hydroxybenzophenone (HBP) and 4-chlorobenzene sulfonyl chloride (CBSC) were selected as the interfacial materials due to its Lewis base and acid characteristics, respectively. In addition, both interfacial materials readily dissolve in chlorobenzene which is an anti-solvent commonly employed to aid in the nucleation of OIHP crystals. Hence, the use of HBP and CBSC passivation ensures little disruption to the electro-optical properties of the active OIHP absorber layer while promoting photovoltaic performance and stability of the OIHP solar cell.

3.2 Techniques

3.2.1 Spin Coating

The primary fabrication technique used in the thesis is spin coating. Complete n-i-p OIHP solar devices studied in the thesis are multilayered stacks. All layers were fabricated using the spin coating technique apart from the Au electrodes which were thermally evaporated onto the surface of the HTL. Devices fabricated have a general configuration of fluorine-doped tin oxide (FTO)/ ETL/ OIHP/ HTL/ gold (Au). Figure 3.1 illustrates the spin coating procedure consisting of four major steps: (i) dropping, (ii) spin-up, (iii) spin-off, and (iv) evaporation [16]. In the sol-gel procedure, nanoparticles dissolved in a

solvent are dropped onto the substrate surface and spun up to high speeds between 2000–6000 rotations per minute (rpm), followed by rapid spin-off and evaporation. It is important to note that evaporation occurs throughout the entire spin coating procedure. The precursor solution is deposited throughout the surface via centrifugal force to which the usage of high spin speeds flings majority of the solution away from the surface, reducing the thickness of the resultant film. Uniform thickness is attainable due to the rapid rotation and evaporation of solvents. Typically, highly volatile components are removed during spinning whereas less volatile components of the solution remain on the surface of the substrate until heat treatment or after a prolonged period of time [16,17]. By optimizing factors such as surface tension, spin speed, spin rate, viscosity, and concentration of the precursor solution, thickness of the resultant film can be controlled [17,18]. After spinning, the residual precursor solution forms a gelatinous network on the substrate. Elevated temperatures further evaporate any remaining solvent while solidifying the gel to form a thin solid layer.

Figure 3.1 Schematic illustration of the spin coating technique [18].

3.2.2 Thermal Evaporation

Thermal evaporation is a straightforward physical vapour deposition technique whereby emitted material from a heated source travels to the substrate and condenses on the surface to form a thin film. Advantages of such a technique includes large-area deposition and high tolerance to a wide range of materials such as metals, semiconductors, and composite materials [19]. However, deposition rate is typically slow at deposition rates of 10–100 nm/min. In order to ensure high purity and quality of the evaporated film, the chamber should be in high vacuum of approximately 10^{-6} Torr. High pressure also ensures that oxidation of the source is avoided [20]. Resistive heating is most commonly employed for

thin film deposition. The heated filament or boat is typically made of refractory metals such as tungsten (W) or molybdenum (Mo), while the crucible is typically quartz, alumina, or boron–nitride. Figure 3.2 illustrates a typical thermal evaporation system. To begin, the material in the crucible is heated using electrical current. The high temperature causes sublimation of materials to which vapour particles travel directly to the substrate and condenses to form a thin solid film [19,20]. To attain film with high quality, low deposition rates of approximately 10 nm/min are often employed. The evaporation rate of the material can be controlled by altering the vapour pressure of the source material via heating [20]. In this thesis, gold electrodes used for OIHP solar cells were thermally evaporated onto the surface of the spiro–OMeTAD layer under high vacuum condition to which the active area of each OIHP solar device is approximately 0.096 cm².

Figure 3.2 Schematic of a typical thermal evaporation system [21].

3.3 Characterization Techniques

To investigate the optoelectronic properties of the as-prepared films, various characterization techniques such as photoluminescence (PL) and electrochemical impedance spectroscopies (EIS) are utilized. Changes to the surface and cross-sectional morphologies of the films and devices are also investigated using the electron microscopies while the wetting properties studied using the sessile drop contact

angle measurements. Elemental studies were conducted using the x-ray diffraction (XRD) analysis, x-ray photoelectron spectroscopy (XPS), and fourier transform infra-red (FTIR) spectrometry. Finally, photovoltaic parameters and stability of the devices are characterized using J-V characterization and incident photon-to-current conversion (IPCE) analysis. Subsequent sections of the chapter evaluate the working principles behind various characterization tools in great detail.

3.3.1 Steady-state Photoluminescence Spectroscopy

PL spectroscopy is a non-intrusive technique commonly used to determine the electro-optical and defect properties of materials. In general, PL spectroscopy is a procedure involving the absorption and re-radiation of photons by a material. Figure 3.3a illustrates the PL setup whereby the excited monochromator picks a wavelength while the emission monochromator and records the luminescence, one wavelength at a time [22,23]. Figure 3.3b shows the Jablonski diagram of the PL procedure. In essence, light of a specified wavelength is directed onto the sample to which light is absorbed by the sample. This process is also termed as photoexcitation. During photoexcitation, electrons in the valence band of the semiconductor are promoted across the band gap and into the conduction band, leaving behind holes in the valence band. Due to the excess amount of energy provided, excited electrons enter permissible excited states. Within picoseconds, the excited electrons relax to the conduction band edge via inter- or intra- sub-band scattering [22]. To return back to their equilibrium states, excess energy must be released which could happen radiatively or nonradiatively. When excess energy is released radiatively, the process is often termed as radiative recombination which involves the emission of photons as the electrons fall from the conduction band to the valence band. This process of emitting photons is also termed as photoluminescence. The emitted photon usually possesses similar energy to the material's band gap energy. Mathematically, the frequency (ν) of the emitted photon can be derived from the equation $h\nu = E_g$, where h is Planck's constant and E_g is the band gap energy of material. The emitted photon is then directed to the optical fiber and spectrometer. Inside the spectrometer, a diffraction grating diffracts various wavelengths towards an array of photodetector where the intensity of each

wavelength is measured. The digital information is then interpreted by the computer to produce a PL spectrum reflective of the sample's composition [23,24].

Figure 3.3 Illustration of the PL (a) setup and (b) mechanism [23,24].

Steady-state PL spectroscopy is a commonly employed characterization technique for OIHP materials. This is because results obtained from the PL spectrum provide direct information regarding the charge transference, as well as radiative and nonradiative recombination properties of the sample. The peak observed in a PL spectrum also provides information regarding the electronic energy level of the material. For a typical methylammonium lead iodide (MAPbI_3) film, peak is usually observed at a wavelength of 532 nm, corresponding to the photon energy and band gap of 1.6 eV. Variation in the peak intensity, on the other hand, is often used to understand the effectiveness of charge extraction of ETLs. It is generally accepted that a highly quenched PL peak indicate better electron extraction of the ETL compared to an ETL with a higher peak intensity. Also, peak intensity obtained from steady-state PL spectroscopy is often used in passivation studies. Providing a relative measure of defects present in the material, PL spectroscopy does not measure the absolute defect density within a film. As such, intensity of PL peak is often used for qualitative study to which higher PL intensity often indicate lower nonradiative recombination due to the reduction in nonradiative traps. As seen in Figure 3.4, the presence of defects or dangling bonds tend to facilitate non-radiative recombination by providing mid-gap states, resulting in electrons being emitted as phonons instead of contributing to the PL signal [25]. In this thesis, PL spectra of the films were recorded

using a spectrofluorophotometer (Shimadzu, RF-5301PC) measured at excitation of 600 nm in ambient conditions.

Figure 3.4 Illustration of the (a) band-to-band radiative and (b) nonradiative recombination pathways [25].

3.3.2 Field-emission Scanning Electron Microscopy

Field-emission scanning electron microscopy (FESEM) delivers elemental evidences and morphologies at magnification range of 10–300,000 times. Unlike the conventional thermionic emitter, a field emission gun produces a smaller electron beam which is more coherent and higher in current density [26,27]. Hence, FESEM is able to examine particles as small as 1 nm at very high resolution. Since OIHP grains are usually in the nanometer scale, the use of FESEM allows sharper SEM images, useful for surface topography and cross-sectional morphology understanding. Figure 3.5 shows the FESEM setup. To begin, the gun head, column, and sample must be in high vacuum. Electrons are generated from a field-emission cathode where the primary electrons accelerate through the column and multi-hole aperture. After passing through the stigmator and alignment coils, the narrow electron beam is focused onto the surface of the sample using the objective lenses. As a result, primary electrons bombard the sample whereby interactions between the electrons and atoms in the sample produce various signals namely, inelastic and elastic scatterings. Depending on the interactions between the primary electrons and atoms at various depths within the sample, various types of signals such as secondary electrons, backscattered electron (BSE), characteristic x-rays are produced.

Since secondary electrons have low energies in the order of 50 eV, only electrons located at the top few nanometers of the surface of the sample escape. A secondary detector then receives the secondary electrons and convert them into electronic signals which are amplified and transformed into a digital image displayed on a monitor [27]. All samples characterized using FESEM are first coated with a thin layer of platinum to improve the conductivity of samples while reducing possible surface charging. Measurements are usually conducted at high vacuum with working distance of 8 cm and accelerating voltage at 15 kV.

Figure 3.5 Schematic illustration of the SEM instrument [28].

3.3.3 Contact Angle Analysis

Sessile drop contact angle measurement is often conducted to estimate the wettability of a surface. Wetting refers to the degree of spreading observed by a droplet on a substrate. As seen in Figure 3.6, forces acting on the droplet include the solid–vapour interfacial energy (γ_{SG}), solid–liquid interfacial energy (γ_{SL}), and liquid–vapour interfacial energy (γ_{LV}) at a

certain contact angle (θ_C). To quantify the wettability of a material, the Young's equation of $\gamma_{SG} - \gamma_{SL} - \gamma_{LV} \cos \theta_C = 0$ is employed with the assumption that gravitational forces applied on the droplet are negligible. When the system is at equilibrium, total tangential forces acting on the droplet equates to zero [29]. When complete wetting is observed, the resultant θ_C corresponds to zero (superhydrophilic). When θ_C is 180° , the droplet forms a sphere where the droplet only touches the solid surface at a single point (superhydrophobic). If θ_C lies between $0-90^\circ$, the film is wettable (hydrophilic) while values between $90-180^\circ$ indicate that the film is non-wettable (hydrophobic). Depending on the application, a large or small contact angle may be preferred. In the case of passivation on top of the OIHP film, hydrophobic interfacial materials are often preferred due to the ability to act as a waterproof layer. By shielding the underlying OIHP film from water molecules, moisture stability of the OIHP solar devices are expected [17]. For the thesis, contact angle measurements are conducted using the Dataphysics OCA-15 Pro. Attained contact angles are recorded 1 s after dispersal. The dispense unit contains $0.06 \mu\text{L}$ drop of deionized water.

Figure 3.6 Schematic illustration of contact angle and various interfacial energies [30].

3.3.4 X-ray Diffraction Analysis

X-ray Diffraction Analysis (XRD) is a non-destructive analytical technique that provides phase identification, preferred crystal orientation, structure, strain, crystallinity, and unit cell dimension of a crystalline material [31]. In 1912, Max Von Laue identified that passing a beam of x-ray through a crystalline material results in the diffraction of x-rays within the crystals. Since a crystalline material is made up of parallel rows of atoms separated by a unique distance known as d-spacing, the diffraction pattern attained during XRD analysis reflects the periodic arrangement of the atoms in a crystal. Depending on the orientation of

the crystal lattice with the incident radiation, the direction and intensity of the diffraction peaks will differ. Phase identification is usually carried out by cross referencing attained pattern with the standard crystallographic database [32]. Figure 3.7a shows the basic setup of the XRD system. X-ray diffractometers consists of 3 basic elements namely, a cathode ray tube, a sample holder, and an x-ray detector. To begin, x-rays are generated within the cathode ray tube by heating a filament which produces electrons. These electrons are accelerated towards a target by applying a voltage to which accelerated electrons with sufficient energy dislodge inner shell electrons of the target material, producing a characteristic x-ray spectrum. Some common target materials include copper (Cu), iron (Fe), molybdenum (Mo), and chromium (Cr). A copper target material produces a monochromatic Cu K_α radiation with wavelength of approximately 1.5418 Å. These x-rays are collimated and directed onto the sample [32]. As the incident beam bombards the sample, interactions between the monochromatic x-ray and electrons within the core atoms of the sample produces elastic scattering. When the geometry of incident x-rays impinging the sample satisfies the Bragg equation, constructive interference occurs and x-ray signals are produced. Subsequently, a detector records these signals and convert them to count rates which are then reflected on a computer monitor. As seen in Figure 3.7b, Bragg's Law is defined by the equation $2d \sin\theta = n\lambda$, where d is the lattice d-spacing between each lattice plane, θ is the angle of incidence, n is an integer which represents the diffraction order, and λ is the wavelength of incident x-ray [31].

For this thesis, the crystal structures and phases present in the OIHPs and ETLs were investigated using the XRD patterns. Using the Bruker D8 Advance with Cu K_α radiation, scans were collected under ambient condition with scan angles (2 theta) ranging from 20 to 70° at corresponding step size and rate of 0.05° and 1 s/step.

Figure 3.7 Schematic diagrams of the (a) x-ray diffractometer and (b) Braggs' law [32].

3.3.5 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is a remarkable technique for elemental surface studies of thin films. Typically, XPS is conducted under ultra-high vacuum ($< 10^{-8}$ Torr) since chamber pressure of approximately 10^{-6} mbar could promote unwanted reactions between background gas constituents (O_2 , H_2O , etc.) and sample. Traditionally, XPS is sub-divided into two categories based on the source of radiation utilized. When soft x-ray radiation (200–2000 eV) is used, surface profile of core levels (inner-shell electrons) is revealed. On the other hand, when vacuum UV radiation (VUV; 10–45 eV) is utilized, surface profile of the valence levels (outer-shell electrons) is revealed. The latter technique is often used for ultraviolet photoelectron spectroscopy (UPS) which will be discussed in greater detail later. Figure 3.8a shows the basic XPS setup. To begin, the sample is irradiated with x-rays to which these photons are capable of penetrating the sample to depths on the order of micrometer. Typically, the sample is excited with monochromatic aluminium (Al) or magnesium (Mg) $K\alpha$ radiations with respective photon energies of 1486.6 and 1253.6 eV [33]. When sufficient energy is absorbed by the core electrons of the sample, these electrons break free from the inner core electrons with certain kinetic energy and collected by an electron analyzer. As seen in Figure 3.8b, the emitted electron is also known as a photoelectron. Energy spectrum of intensity (number of photo-ejected electrons versus time) is then plotted against binding energy. Theoretically, the core electrons of an atom located at the surface of the sample possess characteristic binding energy equal to that of the ionization energy of the electron. Binding energy (E_b) of the core electron is given by the relationship of $E_b = h\nu - E_k - \phi$, where $h\nu$ is the x-ray photon energy, E_k is the kinetic energy of photoelectron which can be measured by the energy analyzer, and ϕ is the work function. Electrons found further away from the nucleus requires less energy to be ejected. As such, binding energies of electrons in subshells (s, p, d, f, etc.) further away from the nucleus have lower energies. Core electrons found in an element has unique binding energies. Apart from helium and hydrogen, all elements found

in the periodic table can be identified through the characteristic binding energy. The binding energy of a core electron is also dependent on the chemical environment of the element. Binding to a different species could alter the binding energy of the core electron, resulting in the shift in peak on the XPS spectrum. Chemical shift in binding energy is often used for chemical analysis as it reveals the chemical status of a particular element. Also, the number of photoelectrons is dependent on the atomic concentration of an element in the sample. As such, an XPS spectrum acts as a unique element identifier whereby the position and intensity of energy peaks provides both qualitative and quantitative elemental information [36]. XPS spectra in this thesis are measured using the AXIS Ultra DLD.

Figure 3.8 Basic schematic diagrams of the XPS (a) setup and (b) physics [34,35].

3.3.6 Ultraviolet photoelectron spectroscopy

As mentioned previously, UPS uses the same principles as XPS except that lower UV radiation with energies of 10–45 eV probes the valence energy levels (outer-shell electrons) instead of the core energy levels. By measuring the kinetic energy of the emitted photoelectrons from the sample using photoelectric effect, molecular orbital energies in the valence region of the electron can be determined. UV photons are commonly produced via a helium gas discharge lamp whereby the emitted photoelectrons have energies of 21.2 (He I) and 40.8 eV (He II). UPS is typically utilized for valence band maximum energy level

(E_{VBM}) and electronic workfunction acquisition [37]. As seen in Figure 3.9, the UPS spectrum provides information regarding the valence band. E_{VBM} can be determined by subtracting the cutoff energy level and Fermi energy level (E_f) from the incident radiation ($h\nu$) using the equation of $E_{\text{VBM}} = h\nu - (\text{cutoff} - E_f)$. Depending on the composition and structure of material, attained E_{VBM} will differ greatly [38]. UPS measurements are conducted with the AXIS Ultra DLD (KRATOS Inc.) instrument using a monochromatic He I (21.22 eV) light source.

Figure 3.9 Schematic diagrams of (a) a typical UPS spectrum and (b) the mechanism [37,38].

3.3.7 Ultraviolet–Visible spectroscopy

Ultraviolet–Visible (UV–Vis) spectroscopy can be referred as the absorption or transmittance spectroscopy conducted within the ultraviolet and visible wavelengths. UV–Vis spectroscopy is a fast analytical method commonly used to quantify various analytes such as transition metal ions to biological molecules [39]. Figure. 3.10a shows the typical mechanism used by the UV–Vis spectrophotometer. The Beer–Lambert law shows the direct relationship between absorbance (A) of a sample to the pathlength (l), concentration (c), and molar absorptivity of the analyte [39,40]. The Beer–Lambert law is defined by the mathematical equation of $A = \log_{10} \frac{I_0}{I} = \epsilon lc$, where I_0 is the intensity of incident, I represents the intensity of transmitted light, and ϵ is the molar absorptivity. Molar absorptivity is an intrinsic property which measures how strongly a chemical species

attenuates light at a given wavelength. Hence, when a beam with wavelength between 180–1100 nm strikes a sample, the sample absorbs certain wavelength of the spectral region while transmitting the rest, allowing simple calculation of the absorbance and concentration of the analyte. UV–Vis spectroscopy can also be used to calculate the band gap of a material. Using Tauc equation of $(\alpha h\nu) = A(h\nu - E_g)^{0.5}$, where α is the absorption coefficient, h is the Plank's constant, ν is the radiation frequency, and A is a constant, the band gap (E_g) of the material can be determined [40]. Figure 3.10b represents the Tauc plot where the interception between the extrapolated curve and energy axis represents the E_g of the material. To calculate the conduction band minimum (E_{CBM}) energy levels of a material, E_{VBM} derived from the UPS spectrum must be added to the E_g value derived from UV–Vis spectroscopy. In this thesis, UV–Vis spectra are obtained with the Shimadzu UV–1800 UV–vis spectrophotometer.

Figure 3.10 Schematic diagrams of a (a) UV–vis spectroscopy set-up and (b) Tauc plot [39,40].

3.3.8 Fourier Transform Infra-Red spectrometry

Fourier Transform Infra-Red (FTIR) is a useful qualitative technique commonly used to characterize organic molecules since each molecule has a unique characteristic absorption under infrared radiation, allowing the structural interpretation of the molecule. When a molecule is exposed to infrared radiation, the molecule selectively absorbs specific wavelengths of incident light, causing the dipole moment of a molecule to change. Consequently, vibrational energy levels at excited states are transferred back to ground state whereby the vibrational energy gap determines the frequency of the absorption peak

[41]. In ATR mode, the ATR crystal is exposed to infrared radiation such that the incident light passes through the crystal and reflects off the interface in contact with the sample multiple times [42]. As seen in Figure 3.11a, these reflections produce evanescent waves which extends into the sample with a penetration range of 0.5–2 μm . The penetration depth depends on the wavelength of incident radiation, angle of incidence, and indices of refraction. Some of the energy of the evanescent wave is absorbed by the sample, while the rest returns to the crystal and directed to the detector. The detector then converts the attenuated infrared radiation to produce a infrared spectrum as seen in Figure 3.11b. In this thesis, the Shimadzu RAffinity-1S FTIR spectrophotometer with frequency range of 4000–400 cm^{-1} at resolution of 2 cm^{-1} was utilized.

Figure 3.11 Illustrations of the (a) ATR mode and (b) a typical FTIR spectrum [42,43].

3.3.9 Current–density against Voltage Characterization

As seen in Figure 3.12a, current density against voltage (J–V) characterization is often used to quantify the performance of an OIHP solar cell, and remains one of the most important characterization techniques in photovoltaic application [44]. Main photovoltaic parameters used to quantify the effectiveness of a solar cell include the short–circuit current

density (J_{SC}), open-circuit voltage (V_{OC}), and fill factor (FF), power conversion efficiency (PCE) [44,45] Other parameters such as maximum power point (MPP), space charge limited current (SCLC), series resistance (R_s), shunt resistance (R_{SH}) and Ideality factor can also be derived from the J-V results.

The short-circuit current (I_{SC}) of a solar cell depends on the spectrum of the incident light, optical properties of the solar cell such as absorption of the active absorber film and reflection of the device. I_{SC} is also heavily dependent on the area of the solar device. To omit the effects of surface area, achieved current is often divided over the area of cell and represented as current density (J) instead. As such, J-V curves are often plotted in substitution of the I-V curve, whereby J_{SC} represents the largest possible current density drawn from a solar cell which occurs when no voltage is applied to the solar device. In an ideal solar cell with no resistive losses, I_{SC} equates to light-generated current (I_L) whereby the solar cell acts like an ideal diode with uniform generation of charge carriers and no losses from recombination. Depending on the material type which dictates the generation rate (G), electron diffusion length (L_n), and hole diffusion lengths (L_p), I_{SC} is greatly altered based on the equation of $I_{SC} = G(L_n + L_p)$ [46,47].

V_{OC} is the maximum voltage attainable by the solar cell when current flow is zero. V_{OC} depends heavily on the photo-generated current density (J_{ph}) saturation current density (J_0) according the equation of $V_{OC} = \frac{k_B T}{q} \ln \left(\frac{J_{ph}}{J_0} + 1 \right) = \frac{k_B T}{q} \ln \left(\frac{J_{ph}}{J_0} + 1 \right)$, where q is the electronic charge of 1.602×10^{-19} eV, k is the Boltzmann constant of 8.6173×10^{-5} eV K⁻¹, and T is temperature in Kelvin. Since J_0 depends on the recombination in the solar cell, changes in V_{OC} could reflect the degree of recombination in a device. Despite V_{OC} and I_{SC} representing the largest attainable voltage and current respectively, power of solar cell is zero under both conditions. FF, in conjunction with V_{OC} and I_{SC} , determines the maximum power (P_{max}) of a cell using the equation of $FF = \frac{P_{MAX}}{I_{SC} \times V_{VOC}}$. As seen in Figure 3.13, FF is defined as the ‘squareness’ of the J-V curve. The maximum FF achievable for a solar can be calculated by the equation of $\frac{V_{OC} - \ln(V_{OC} + 0.72)}{V_{OC} + 1}$. This equation suggests increase in FF

when V_{OC} increases. However, experimentally, difference in V_{OC} between various types of materials are approximately 120 mV which equates to a small theoretical discrepancy in FF by 0.02 between different materials. Such is not reflected in the experimental results whereby variation in FF can be significantly different for various solar cells. This observation can be explained by the ideality factor. Figure 2.12b shows the relationship between the ideality factor and type of recombination [46]. In an ideal diode, where ideality factor (n) is 1, all recombination occurs through band-to-band recombination or recombination at trap sites with the bulk absorber. In practice, n values of solar cells deviate from 1 since presence of parasitic resistive losses are unavoidable. When recombination is large, the n value might be closer to 2 whereby the high ideality factor greatly reduces the attained FF value which probably also results in a lower V_{OC} achieved.

PCE is a commonly employed photovoltaic parameter used to compare the effectiveness of various solar cells. Determined by the fraction of incident power converted to electricity, PCE can be calculated using several equations of $PCE = \frac{P_{MAX}}{P_{in}} = \frac{I_{MPP} \times V_{MPP}}{P_{in}} = \frac{I_{SCP} \times V_{OC} \times FF}{P_{in}}$. As such, PCE depends on multiple factors such as incident light spectrum, orientation of cell, resulting operating temperature of cell, applied electrical load, wavelengths of incident light, orientation of sample, and temperature.

Figure 3.12 (a) A typical J–V curve of a solar device along with (b) various ideality factor and associated recombination [44,46].

The primary source of energy on Earth is radiant energy from the Sun. Acting as a natural nuclear fusion reactor, the Sun emits a relatively constant radiation of the black body with

temperature of 5800 K with wavelengths mainly in the range of 0.2–2.6 μm [48,49]. However, as solar radiation travel away from the sun's surface onto that of the Earth's, radiation is attenuated, absorbed, and scattered. As solar radiation travels through the atmosphere, chemicals such as water vapour, oxygen, nitrogen, and carbon dioxide molecules interact with the sun's rays. By the time the solar radiation reaches the Earth's surface, a considerable amount of solar radiation has already been absorbed and scattered, resulting in a vastly different solar irradiance in which the spectrum is strongly confined to the near ultraviolet (UV) to far-infrared wavelengths. Defined as the pathlength through which solar radiation must pass through, Air Mass (AM) can be represented by the equation $AM = \frac{1}{\cos\theta}$, where θ is the angle between incident solar radiation relative to the normal of Earth's surface (zenith angle in degrees). As seen in Figure 3.13, AM 0 represents the uniform spectral distribution of sunlight in the absence of Earth's atmospheric interference. Approximated to the 5800 K blackbody, AM 0 is often used for characterization of space power applications such as communication satellites. On the other hand, AM 1 ($\theta = 0$) is used to describe the position of the sun when it is directly overhead whereby the solar radiation is presumed to have travelled through '1 atmosphere' to reach the sea level. Solar cells located at the equatorial and tropical regions could use AM 1 for a more accurate performance deduction. However, in most regions of the world such as Europe, China, and many more, the sun is at an angle to the zenith such that light has to travel through a thicker atmosphere. For this reason, AM 1.5 is typically used instead, corresponding to an atmosphere thickness of 1.5 and zenith angle of 48.12°. As a matter of fact, AM 1.5G is often used as the standardized spectrum to describe solar irradiance received on Earth's surface. The 'G' found in AM 1.5G stands for global which includes both direct (D) and diffuse radiation. AM 1.5D, which is commonly used for concentrator solar cells and only includes direct radiation with approximated intensity of radiation 28 % less than that of the AM 0 solar spectrum. AM 1.5G, however, has 10 % higher spectral power density compared to the AM 1.5D solar spectrum. With AM 0 having a total power density of approximated to 1367 kW/m^2 (also known as solar constant), the power density of AM 1.5G can be estimated to be 970 W/m^2 [50]. To allow easy comparison between various papers, the standard test conditions (STC) were employed for this thesis of Air Mass 1.5 global (AM 1.5G). The Keithley 2612A source meter was utilized with solar illumination

at 100 mW/cm² [51]. This spectrum was chosen as it matches the mid-latitudes of the Earth's surface. Devices are also measured at 25 °C. To ensure that the solar simulator J–V has a constant intensity of 1000 W/m², a calibrated reference cell is used to monitor the total irradiance of the solar simulator during testing. A common reference cell is the Si cell packaged based on the World Photovoltaic Scale (WPVS) design.

Figure 3.13 Various spectral distribution for different air mass conditions [51].

3.3.10 Incident Photon to Current Efficiency Measurement

Incident photon to current efficiency (IPCE) measures the ratio of photogenerated carriers (current) collected by the solar cell to the incident photons as a function of wavelength or energy. Mathematically, IPCE can be calculated using the equation of $IPCE = \frac{\text{Electrons out } (\lambda)}{\text{Incident photons } (\lambda)} = \frac{J_{sc}(\lambda)}{q\phi(\lambda)} = \frac{hc}{q} \times \frac{J_{sc}(\lambda)}{\lambda P_{in}(\lambda)} = 1240 \times \frac{J_{sc}(\lambda)}{\lambda P_{in}(\lambda)}$, where Φ is the incident photon flux, P_{in} is the light intensity at a certain wavelength (λ), q is the elementary charge, and h and c are the Planck's constant and speed of light, respectively [52,53]. By integrating the IPCE spectra using the equation, one can derive the integrated J_{sc} . Generally, IPCE uses a xenon or halogen lamp coupled to a monochromator. Photon flux of incident light is usually measured using a calibrated photodiode at wavelength range of 400 to 800 nm. It is important to ensure sufficient measurement duration at each

wavelength so as to achieve a stable current output. The magnitude of the IPCE spectrum depends on the amount of incident light absorbed and, subsequently, converted to electrons whereby values attained indicate effectiveness of photon absorption, charge transport, charge excitation and separation within the complete solar cell. Figure 3.14 shows a typical IPCE curve and integrated J_{SC} of a OIHP solar cell. An ideal IPCE curve of 100 % is square shaped [53]. Such an IPCE curve indicates successful conversion of all incident photons to charge carriers. However, this is rare since recombination processes present in the solar cell greatly impedes achievable IPCE.

Figure 3.14 IPCE spectrum and its integrated current density of a typical OIHP solar cell [53].

3.3.11 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) uses impedance characteristics of an electrochemical system over a range of frequencies via the association of theoretical circuit elements to the electrochemical process in a material. An EIS spectrum is obtained by applying a small alternating current (AC) signal over a steady direct current (DC) bias on the sample and measuring the resultant AC current obtained over a frequency range. Data closest to the origin is termed as the higher frequency spectrum while data further away is termed as the lower frequency spectrum. Impedance results are then presented as a Nyquist plot where the AC signal is divided into two components with the real component (Z') on the horizontal axis (x-axis) and the imaginary component (Z'') on the vertical axis (y-axis) [54]. As seen in Figure 3.15a, fitting an equivalent circuit model to the Nyquist plot

provides parameters related to the device property. The shape of the Nyquist plot also provides clues to the possible physical processes present. For example, a plot parallel to the y-axis indicates the presence of a capacitor in series with a resistor to which the resistance value corresponds to the x-axis intercept. If, however, the Nyquist plot is a semicircle that intercepts the origin, the equivalent circuit probably contains a capacitor in parallel with the resistor [54,55]. Nyquist plots of OIHP solar cells often contain two features. The first feature is a high-frequency semicircle while the other is usually a low-frequency semicircle or linear graph. At high frequencies where electronic process typically dominate, the device can be modelled using a simple resistance-capacitance circuit [55]. At lower frequencies the ionic transport dominates and often modelled as a Randles circuit model. Yet, in middle frequency ranges, both ionic and electrical influences are strong, making it difficult to formulate the equivalent circuit model. Figure 3.15b shows the typical equivalent circuit model used for OIHP solar devices. Values of various circuit elements obtained upon fitting provides both qualitative and quantitative representation of effective various processes present in the device. All EIS measurements in this research were conducted in ambient conditions with the Autolab PGSTAT302N using applied perturbation of 20 mV. Frequencies vary from 10 Hz to 1 MHz at a DC voltage of 800 mV under dark condition.

Figure 3.15 Schematic illustrations of the (a) correlation between circuit elements and Nyquist plots and (b) equivalent circuit model commonly used for OIHP solar cells [55,56].

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Chapter 4

Effects of co-doping on compact TiO₂

Among the next-generation photovoltaic technologies, OIHP solar devices continue to attract significant interest. Apart from the OIHP absorber component, adjacent layers within the stack play decisive roles in the stability and overall power conversion efficiency (PCE) of a device. Here, we demonstrated the use of aluminium indium titanium oxide (AITO) as a highly effective compact electron transport layer (ETL) to achieve outstanding performance of OIHP solar cells. Incorporation of AlIn into the TiO₂ layer allowed better energy band alignment of the ETL-OIHP interface, improved the transparency, and enhanced the conductivity as compared to the case of pristine TiO₂. Via co-doping these trivalent metals, an enhancement in voltage, current density, and even fill factor was observed in OIHP solar cells. In addition, the results obtained from electrochemical impedance spectroscopy revealed that the AITO ETL based device exhibited larger recombination resistance, which significantly benefited the performance of the devices. As a result, the optimized AITO ETL device attained the surpassing PCE of 19 % as compared to the pristine TiO₂ solar device having the PCE of 16.67 %.

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4.1 Introduction

In recent years, organic–inorganic halide perovskite (OIHP) materials have been extensively studied owing to their potential applications in solar cells, light-emitting diodes, sensors, photodetectors, field effect transistors, lasers, etc [1–6]. Displaying excellent optical and electronic properties, OIHP materials are known for their high carrier mobility, tunable band gap, high absorption coefficient, low trap density, and significant electron/hole diffusion length, which are crucial to achieve high-performance photovoltaic devices [7–11]. Moreover, in just a few years, a significant increment in the power conversion efficiency (PCE) has been achieved [12–15]. Generally, the conventional configuration of a OIHP solar cell includes an electron transporting layer (ETL), followed by the OIHP absorber layer, and a hole transporting layer (HTL) [16]. In OIHP solar cells, the ETLs play critical roles in both the collection and transportation of photogenerated electrons as well as the suppression of the electron–hole recombination. Theoretically, an ideal ETL should possess the following qualities: good optical transparency, high efficiency in transporting the electrons and blocking holes, good electrical conductivity, and well-matched energy levels with the perovskite materials [17–19]. To achieve a highly effective ETL, various wide band gap semiconducting materials, such as zinc oxide (ZnO), tin oxide (SnO₂), and titanium oxide (TiO₂), have been introduced as the ETLs in the hope of enhancing the overall photovoltaic performance of the device. Among the various materials, TiO₂ has emerged as a promising ETL candidate due to its good transparency, chemical inertness, air stability, low cost, and non-toxicity [20,21]. Compared to the ZnO and SnO₂ ETLs, the TiO₂ ETLs have relatively low electron mobility and poor electrical conductivity. As a result, metal doping is commonly employed to improve the electrical properties of the TiO₂ compact layer as well as tailor the energy bands structure for easy transportation of electrons from the OIHP layer to the transparent electrode [22–26].

Several studies have shown that the introduction of suitable n-type dopants into TiO₂ can alter the material properties (grain size, orientation, conductivity, and optical properties) of pure TiO₂, such that the rate of recombination is reduced, whereas the electron transport/injection properties are improved [27–30]. For example, Zhang et al. reported

that a solution-processed Mg-doped TiO₂ compact layer enhanced the electron injection/transport properties through reduction in resistivity [31]. Li et al., on the other hand, fabricated OIHP solar cells using a spray-coated La-doped TiO₂ compact layer and achieved the efficiency of 17.2 % [32]. Similarly, Lv et al. showed the effective use of Zn-doped TiO₂ as an efficient ETL with the fabricated cell having relatively good efficiency of 15.25 % with enhanced device stability [33]. Aluminium has been proven to be a promising dopant, especially when used in the TiO₂ lattice. Apart from its relative abundance and low cost, the addition of aluminium has been reported to significantly improve the relatively poor conductivity of TiO₂ [34]. When Ti⁴⁺ is replaced with a smaller oxidation state ion such as Al³⁺, substitutional point defects, such as oxygen vacancies, are introduced. Thus, theoretically, the addition of aluminium should enhance the charge carrier concentration as well as the electrical conductivity of the poorly conductive TiO₂ electron transporting film [35]. For example, Roose et al. reported that Al-doped TiO₂ films exhibited excellent optical transparency and low resistivity [36]. Moreover, in good agreement with this, Yun et al. reported the use of Al-doped TiO₂-based OIHP solar cells having the efficiency of 14.7 % [30]. On the other hand, the addition of the indium (In) metal is reported to reduce the work function of most of the oxide films due to the generation of large amount of free electrons [37]. In particular, Peng et al. have shown an improved band alignment of indium-doped TiO₂ ETL as compared to that of pristine TiO₂ ETL, whereby the work function of In-TiO₂ is closer to the CBM energy level of the OIHP material [38]. This being said, it is often hard to improve several cell parameters using simple ETL modification. For example, it is difficult to boost both fill factor (FF) through reduction in work function and/or enhanced conductivity whilst also improving the short-circuit current density (J_{sc}) via improved transparency of device. Therefore, there remain a large deficiency in the usage of simple ETL modification to enhance several cell parameters such as improved FF, J_{sc}, and energy alignment, simultaneously.

In this study, we introduced the trivalent dopants aluminium and indium into the conventional TiO₂ ETL layer to form an AITO ETL via simple solution-based processing. By adding Al and In at stoichiometric amounts into the conventional TiO₂ precursor solution, superior performance was achieved with the champion cell showing the enhanced

efficiency of 19 % while the conventional devices attained inferior PCE of 16.67 %. This is due to enhancement in the transparency and conductivity, as observed via the improved Jsc and FF, respectively, when Al and In are introduced into the TiO₂ ETL. Furthermore, AITO ETL based device showed higher Voc as compared to the pristine devices due to the reduced work function and better energy level alignment. We further explored the usage of individual dopants and discovered that the addition of aluminium significantly altered the transparency and optical quality of the perovskite device through the improved Jsc values. On the other hand, the addition of indium leads to better energy level alignment and conductivity, as demonstrated by the enhanced Voc and FF, respectively. Thus, our study demonstrates a simple yet versatile co-doping method to utilize the advantages of both dopants and simultaneously improve several cell parameters, and the employment of AITO leads to an upward shift in the conduction level, improved light transmittance, and enhanced electrical conductivity.

4.2 Experimental Methods

4.2.1 Materials

Most chemicals were purchased from Sigma Aldrich. These include titanium (IV) butoxide (97 %), indium (III) nitrate hydrate (99.99 %), aluminum nitrate nonahydrate (99.997 %), 2-methoxyethanol (99.8 %), acetylacetone (≥ 99.8 %), Tin (II) chloride (SnCl₂, 99.99 %), cesium iodide (CsI, 99.999%), absolute ethanol, N,N-dimethylformamide (DMF, 99.8 %), dimethyl sulfoxide (DMSO, 99.99 %), spiro-OMeTAD (> 99%), bis(trifluoromethylsulfonyl)amine lithium salt ($\geq 99\%$), 4-tert-butylpyridine (98 %), acetonitrile (99.8 %), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) tri[bis(trifluoromethane)sulfonimide] (FK209 Co (III) TFSI salt, 98 %), and chlorobenzene (99.8 %). Chemicals purchased from Tokyo Chemical Industry (TCI) include lead (II) iodide (PbI₂, 99.99 %), and lead (II) bromide (PbBr₂, 99.99 %). TiO₂ paste (30NRD), Formamidinium iodide (FAI, >99.5 %), methylammonium bromide (MABr, >99.5 %) were purchased from Dyesol. All chemicals were used as purchased.

4.2.2 Device Fabrication

The AITO compact layer was prepared via a simple sol-gel method using stoichiometric amounts of titanium (IV) butoxide (0.45 M), aluminum nitrate nonahydrate (0.01 M), and indium (III) nitrate hydrate (0.01 M) dissolved in 2-methoxyethanol and acetylacetone. After 3 hours of stirring at room temperature, a clear and homogeneous light-yellowish solution was attained. To prepare thin films of the AITO ETL, the as-prepared sol was spin coated on the FTO surface and annealed at 500 °C for 1 hour.

For OIHP solar cell fabrication, we followed the standard device configuration. The fluorine-doped tin oxide (FTO) glass substrates were patterned using Zn powder and diluted hydrochloric acid (HCl). The etched FTO glass substrates were sequentially cleansed through sonication in detergent, deionized water, and a variety of alcohols, followed by UV treatment for 20 min. The AITO compact layer was then deposited on the FTO surface at the spin rate of 3000 rpm (at the acceleration of 500 rpm) for 40 s. Later, the AITO coated FTO substrates were annealed at 500 °C for 1 h in air and cooled down to room temperature. Mesoporous TiO₂ (meso-TiO₂) was prepared by dissolving the TiO₂ (30-NRD) paste in absolute ethanol. The as-prepared meso-TiO₂ solution was then spun on the substrate at 5000 rpm for 30 s and annealed at 500 °C for 15 min. Subsequently, the samples were subjected to UV ozone treatment before perovskite spin coating. To prepare the OIHP precursor solution, 507 mg of PbI₂ (1.1 M), 172 mg of FAI (1.0 M), 81 mg of PbBr₂ (0.22 M), and 22.3 mg of MABr (0.2 M) were added to 1 mL of a mixture consisting of 800 mL of anhydrous DMF with 200 mL of anhydrous DMSO. Then, 42 mL of the stock solution of CsI (1.5 M) was added to the abovementioned mixed solution. The solution was stirred for 3 hours at room temperature. The triple cation perovskite solution was deposited through a two-step spin coating program: 1) 2000 rpm for 10 s and 2) 6000 rpm for 30 s. 15 s into the second step of the dynamic spin-coating, 100 mL of chlorobenzene was drop casted followed by an hour of annealing at 100 °C. Dissolved in 1 mL of chlorobenzene, 70 mg spiro-OmeTAD, 28 mL 4-tert-butylpyridine, 16.94 mL bis(trifluoromethylsulfonyl)amine lithium salt, and 35 mL FK209 Co(III) TFSI salt (18.8 mg/50 mL in acetonitrile) were used to prepare the spiro-OMeTAD solution. After this, the

solution was spun at 4000 rpm for 30 s to form a thin spiro-OMeTAD above the perovskite layer. The perovskite and spiro-OMeTAD depositions were carried out in an argon-filled glove box. Finally, thermal evaporation was employed to deposit 80 nm of gold as the last layer of the complete device.

4.2.3 Characterization

X-ray diffraction (XRD) studies were carried out using a X-ray diffractometer (D8 Advance). X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements were conducted using the AXIS His photoelectron spectrometer and AXIS Ultra DLD (KRATOS Inc.), consisting of a monochromatic HeI (21.22 eV) light source. Field emission scanning electron microscopy (FESEM, JEOL JSM-7600F) was employed to investigate the morphologies of the devices. For current density-voltage (J-V) characterization, a source meter (Keithley 2612A) was used in standard conditions of simulated Air Mass 1.5 global (AM 1.5G). The light intensity of the solar simulator was calibrated to 100 mW cm⁻² using a standard silicon device. Incident photon-to-current conversion (IPCE) spectra were obtained using the dual xenon/quartz halogen light PVE300 (Bentham) source without light bias. Absorption spectra were obtained by a UV-Vis spectrophotometer (Shimadzu, UV-1800). Photoluminescence (PL) spectra of the films were obtained using a spectrofluorophotometer (Shimadzu, RF-5301PC). The effective area of the solar cell was 0.096 cm². Electrical properties of the films were determined by the Hall-effect measurements (MMR Technologies, H-50) using the Van der Pauw method. Time-resolved photoluminescence (TRPL) measurements were conducted using a time-correlated single photon counting (TCSPC) system (PicoQuant, PicoHarp 300). A picosecond-pulsed laser diode ($\lambda = 405$ nm, $f = 40$ MHz) (Picoquant P-C-405B) was used to excite the sample. Impedance spectroscopy measurements were conducted inside an argon-filled glove box with Autolab PGSTAT 302N by applying a 20 mV perturbation with the frequencies varying from 10 Hz to 1 MHz at the DC voltage of 800 mV under dark condition.

4.3 Results and Discussion

4.3.1 Verification of Co-dopants in the c-TiO₂ ETL

The structural properties of the films were first characterized. Figure 4.1a shows the XRD patterns of the pristine TiO₂ and AITO films. The diffraction patterns indicate the adoption of an anatase structure, corresponding to the (101) plane for both film samples. The intensity of diffraction peaks decreased after the incorporation of Al and In, implying the loss of crystallinity. Also, no other impurity phase was detected, indicating the absence of secondary phases in the as-prepared AITO film. This could be attributed to the small doping concentration used and/or the homogeneous distribution of Al and In in TiO₂. XPS was utilized to unravel the chemical composition of the fabricated films. The XPS spectra of the TiO₂ and AITO films are shown in Figure 4.1b–e. In good agreement with other studies, herein, peaks are observed at the binding energies of 458.25 and 464.06 eV representing the presence of Ti 2p_{3/2} and Ti 2p_{1/2} in the pristine TiO₂ films, respectively [39]. As seen in Figure 4.1b, the Ti 2p_{3/2} and Ti 2p_{1/2} peaks of the AITO film are shifted by a small degree towards the higher binding energies of 458.42 and 464.29 eV, respectively. Since Ti, Al, and In have the electronegativity values of 1.54, 1.61, and 1.78, respectively, a negative charge transfer towards the less electronegative aluminium and indium in the Ti–O–In–Al bond should occur [38,40]. As such, the shifting could be reasoned using the Pauling electronegativity theory by which a shift in Ti 2p core binding energy towards that of higher levels was observed. Furthermore, the shift in O 1s peak position is observed in the AITO film, as shown in Figure 4.1c. In Figure 4.1d, the In 3d_{5/2} and In 3d_{3/2} peaks are represented by the binding energies of 444.21 and 451.78 eV, respectively [41]. The binding energy of Al 2p, as shown in Figure 4.1e, is located at 74.19 eV [42]. During the fabrication of the proposed AITO film, 0.01 M of Al and 0.01 M of In were added to the dopant precursor solution. According to the XPS results, the atomic concentrations of Ti, O, Al and In in the 0.01 M Al and 0.01 M In doped TiO₂ film are 26.95%, 70.98%, 1.35% and 0.72%, respectively. Basically, the XPS results suggest the successful incorporation of both the aluminium and the indium elements into the TiO₂ lattice.

Figure 4.1 (a) XRD and XPS spectra of the pristine and AITO films, specifically the XPS peaks of the (b) Ti 2p, (c) O 1s, (d) Al 2p and (e) In 3d elements.

4.3.2 Energy Band Level of various ETL

To examine the energy levels of the as fabricated films, UPS and UV–visible transmittance spectroscopy measurements were utilized. As shown in Figure 4.2a, the valence band maximum (E_{VBM}) energy levels of the TiO₂ and AITO films are -7.45 and -7.24 eV, respectively, calculated from the equation $E_{\text{VBM}} = [21.22 - (E_{\text{cutoff}} - E_{\text{onset}})]$, where E_{cutoff} is the higher binding energy cutoff and E_{onset} is the onset energy in the valence band region. Furthermore, the conduction band minimum (E_{CBM}) energy levels were estimated using the corresponding optical band gap and E_{VBM} levels [5,7]. As seen in Figure 4.2b, the AITO film displays better optical transmittance as compared to the pristine TiO₂ film at the wavelength between 400 and 900 nm. The higher transmittance consequently contributes towards the improved photocurrent. To calculate the band gap of the as-prepared films, we employed the Tauc equation of $\alpha h\nu = A(h\nu - E_g)^{0.5}$, with α being the absorption coefficient, h the Planck's constant, A is a constant, and E_g and ν representing the band gap and the corresponding frequency of radiation, respectively. Figure 4.2c shows the plot of $(\alpha h\nu)^2$ against $h\nu$ for both the TiO₂ and AITO films. Using the abovementioned formula,

band gaps of the TiO₂ and AITO films were estimated via extrapolation of a straight linear fit over the energy axis in the Tauc plots. The band gap of the AITO film was found to be 3.31 eV, higher than that of the TiO₂ film (3.20 eV). The difference in calculated E_{CBM} levels of the TiO₂ (−4.25 eV) and AITO (−3.93 eV) films is relatively small at 320 meV.

Figure 4.2 (a) UPS, (b) transmittance, and (c) $(\alpha h\nu)^2$ versus $h\nu$ spectra of various films.

4.3.3 Effect of Co-doping on the Photovoltaic Performance and Stability

Figure 4.3a shows the schematic of the fabricated mesoporous OIHP device consisting of the following layers: the FTO-coated glass substrate as the transparent electrode, TiO₂ or AITO as the compact ETL, meso-TiO₂, Cs_x(MA_{0.17}FA_{0.83})_(100-x)Pb(I_{0.83}Br_{0.17})₃ OIHP layer, spiro-OMeTAD layer, and the gold (Au) layer as the back-contact. The exact cross-sectional morphology of the complete solar device is shown in Figure 4.3b, with the equivalent thickness of the compact AITO, meso-TiO₂, OIHP, spiro-OMeTAD, and Au films being 60, 200, 390, 180, and 80 nm, respectively. The energy level diagrams, including the characterized energy levels of TiO₂ and AITO, of the materials are shown in Figure 4.3c. The E_{VBM} and E_{CBM} values of meso-TiO₂ and OIHP were obtained from literature [43,44]. The highest occupied molecular orbital (HOMO) for the spiro-OMeTAD was reported as 5.20 eV, whereas the lowest unoccupied molecular orbital (LUMO) was 2.50 eV [45]. Since the E_{CBM} level of AITO (3.93 eV) is closer to that of the OIHP than that of TiO₂ (4.25 eV), transportation of electrons towards the FTO electrode should occur with less potential losses in the AITO device. Moreover, the E_{CBM} levels of both AITO (7.24 eV) and TiO₂ (7.45 eV) are much lower than that of the OIHP (5.40 eV)

and spiro-OmeTAD (5.20 eV) layers, ensuring effective hole blocking as well as efficient hole transport from spiro-OmeTAD to the Au electrode.

The TiO₂, Al-TiO₂, In-TiO₂, and AITO layers were deposited on the FTO substrates by spin coating. Optimization of the Al-TiO₂ and In-TiO₂ compact layers were conducted using different precursor concentrations (0.02, 0.04, and 0.06 M) which were obtained using simple sol-gel method containing different amounts of aluminum nitrate nonahydrate and indium (III) nitrate hydrate added to a fixed volume of solvent of 2-methoxyethanol (5 mL) and acetylacetone (230 mL). The OIHP devices with varied ETL materials, namely the TiO₂, Al-TiO₂, In-TiO₂, and AITO, were fabricated and studied. The device performances presented in Table 4.1 show good contrast between the devices fabricated with various ETL. As seen in Figure 4.3d, the solar cell with the 0.02 M Al-TiO₂ ETL achieved PCE of 17.98 % with respective open-circuit voltage (V_{OC}) at 1.05 V, short-circuit current density (J_{SC}) at 22.07 mAcm⁻², and fill factor (FF) at 77.18. Further addition of aluminium doping, however, deteriorated the performances of the devices with corresponding PCE of 17.43 and 17.15 % for the 0.04 M and 0.06 M Al-TiO₂ ETL based devices, respectively. Similarly, Figure 4.3e shows that the 0.02 M In-TiO₂ ETL based device exhibit the highest PCE of 18.04 % with V_{OC} of 1.05 V, J_{SC} of 21.75 mAcm⁻², and FF of 78.67. Variation in indium concentration also resulted in a similar trend with increasing concentration decreasing photovoltaic performances. As such, total precursor concentration of 0.02 M was determined as the optimal concentration for superior photovoltaic performance. In good agreement with the attained J_{SC} values, Figure 4.3f shows the incident photon-to-current conversion efficiency (IPCE) spectra of the 0.02 M Al-TiO₂ and 0.02 M In-TiO₂ ETL based device.

Displaying relatively poorer performance, the control device consisting of the TiO₂ ETL achieved the PCE of 16.67 %. Conversely, Figure 4.3g shows that the device co-doped with 0.01 M of Al and 0.01 M of In led to paramount performance with the V_{OC} of 1.07 V, J_{SC} of 22.30 mAcm⁻², FF of 79.50, and PCE of 19 % in the AITO ETL based device. Steady-state efficiencies were also studied for both the TiO₂ and AITO ETL based devices. As seen in Figure 4.3h, the AITO ETL based device display corresponding J_{SC} of 20.04

mAcm⁻² and PCE of 18.06 % at applied voltage bias of 0.90 V. On the contrary, the pristine TiO₂ ETL based device demonstrated poorer J_{SC} of 18.64 mA cm⁻² and PCE of 15.60 % at applied voltage bias of 0.83 V. Figure 4.3i shows higher IPCE in the AITO ETL device compared to the pristine TiO₂ ETL device. It is evident that the AITO ETL based device exhibits higher IPCE intensity over the entire wavelength range from 300 to 780 nm as compared to the pristine TiO₂, Al-TiO₂, and In-TiO₂ ETL based devices.

Table 4.1 Photovoltaic parameters of the OIHP solar cells with various compact ETLs.

ETLs	Voc (V)	Jsc (mAcm ⁻²)	FF	PCE (%)
0.02 M Al-TiO ₂	1.05	22.07	77.18	17.98
0.04 M Al-TiO ₂	1.05	22.04	75.26	17.43
0.06 M Al-TiO ₂	1.04	22.02	74.93	17.15
0.02 M In-TiO ₂	1.05	21.75	78.67	18.04
0.04 M In-TiO ₂	1.05	21.94	75.89	17.57
0.06 M In-TiO ₂	1.05	22.04	75.26	17.43
c-TiO ₂	1.04	21.17	75.43	16.67
AITO	1.07	22.30	79.50	19.00

Figure 4.3 (a) Schematic illustration, (b) cross-sectional FESEM image, and (c) Energy level diagram of the as-prepared AITO ETL based device. (d) J-V curves of the Al- TiO_2 and (e) In- TiO_2 ETL devices at various concentrations. (f) IPCE curves of the 0.02 M Al- TiO_2 and 0.02 M In- TiO_2 ETL devices. (g) J-V, (h) steady state efficiency measured at maximum power output, and (i) IPCE curves of the pristine TiO_2 and AITO ETL devices.

To verify the reproducibility of the as-prepared devices, 20 devices of each configuration are fabricated. Box plots of the TiO₂ and AITO ETL based devices are represented by Figure 4.4a–d. Box plots representing the V_{OC} and FF of the AITO ETL based devices show superior consistency compared to the TiO₂ ETL based devices, explaining the smaller deviation in the PCE of the AITO ETL based devices. The average PCE of the TiO₂ and AITO ETL based devices of 16.0 % and 18.20 %, respectively.

Figure 4.4 Statistical distribution of the photovoltaic parameters for solar cells with the TiO₂ and AITO ETL, specifically (a) J_{SC} , (b) V_{OC} , (c) FF, and (d) PCE.

In the absence of encapsulation, long-term stability of the TiO₂ and AITO ETL based devices were also investigated. Figure 4.5 shows that the pristine TiO₂ ETL based device retained 80 % of the initial PCE with corresponding V_{OC} , J_{SC} , FF, and PCE of 1.04 V, 19.85 mA cm^{-2} , 65.26, and 13.47 %. On the other hand, the AITO ETL based device retained 89 %

of the initial PCE with corresponding V_{OC} , J_{SC} , FF, and PCE of 1.09 V, 20.87 mA cm⁻², 74.27, and 16.90 % despite 25 days storage in ambient conditions.

Figure 4.5 J–V curves of the TiO₂ and AITO ETL based devices stored in ambient conditions after 25 days.

4.3.4 Effects of Co-doping to the Properties of the ETL

Conductivity, Hall mobility, and carrier density were measured using the Hall-effect measurements. As presented in Table 4.2, the conductivity of the AITO film is superior compared to the pristine TiO₂ film. This could be caused by the increased Hall mobility and carrier density, thus reducing the series resistance in the AITO ETL based device. Co-dopant effects on the optical properties of the pristine TiO₂ ETL were also investigated. As seen in Figure 4.2b & c, the AITO ETL has higher optical transmission and a wider energy band gap, accounting for the higher J_{sc} value observed in the AITO ETL based devices.

Table 4.2 Hall effect parameters of the glass/TiO₂/Au and glass/AITO/Au substrates.

ETLs	Type	Hall mobility (cm V ⁻¹ S ⁻¹)	Carrier density (1/cm ³)	Resistivity (Ohm*cm)	Conductivity (S cm ⁻¹)
TiO ₂	N	1.03	2.14×10^{14}	28310	3.53×10^{-5}
AITO	N	1.15	2.85×10^{14}	18926	5.28×10^{-5}

4.3.5 Effects of Co-doping to the Properties of the OIHP film

To investigate the charge recombination behaviour, photoluminescence (PL) spectra of the samples were obtained using excitation at 600 nm, as shown in Figure 4.6a. The peak observed at approximately 775 nm corresponds to the excited states (bound excitons) in OIHP film. A sharp PL peak with high intensity was observed in the OIHP film deposited on bare glass, suggesting high quality of the as-prepared OIHP film. However, PL intensity reduces in the OIHP film deposited on the TiO₂ and AITO coated glass substrates. The largest PL intensity reduction was observed for the sample containing the AITO film. A similar quenching trend was observed for the PL decay lifetimes, as seen in Figure 4.6b. As seen in Table 4.3 which shows the results obtained from the time-resolved photoluminescence (TRPL) measurements, OIHP deposited directly on the glass substrate exhibit the longest average fluorescence lifetime of $t = 233.9$ ns. When OIHP was deposited on the TiO₂ coated glass substrate, a significant reduction in lifetime to $t = 208.5$ ns was observed. Further reduction in lifetime was sighted when in the OIHP glass substrate containing the AITO ETL of $t = 150.1$ ns. The large PL quenching observed imply superior charge separation of excitons when co-doping of Al and In is conducted to the TiO₂ ETL. EIS measurements were also conducted for the TiO₂ and AITO ETL based devices. An equivalent circuit, as seen in Figure 4.6c, was used to fit the data in the Nyquist plots, and the corresponding values representing the recombination (R_{rec}) and series (R_{S}) resistances are shown in Table 4.4 [46]. Figure 4.6d represents the Nyquist plots under dark conditions with the applied forward bias of 800 mV. The first arc located in the high-frequency region of the Nyquist plot is related to the contact resistance of the interface, while the second arc located at lower frequencies corresponds to the recombination resistance and chemical capacitance of the device. An equivalent circuit, as seen in Figure 4.6c, was used to fit the data in the Nyquist plots, and the corresponding values representing the recombination (R_{rec}) and series (R_{S}) resistances are shown in Table 4.3 [46]. As seen, the recombination resistance obtained in the TiO₂ and AITO ETL based devices samples are 5.40 and 56.9 k Ω , respectively. Through the larger recombination resistance and smaller recombination rate displayed in the AITO ETL based device, it is evident that the charge transport of carriers is greatly promoted using the co-doped ETL, accounting for the marked increase

in J_{sc} as compared to that of the pristine TiO₂ sample. Therefore, the superior V_{oc} and J_{sc} exhibited by the AlIn-doped TiO₂ device can be correlated to the highly efficient electron extraction/transportation and lowered recombination rate.

Figure 4.6 (a) Photoluminescence and (b) TRPL spectra of the OIHP films coated on bare, TiO₂ coated and AITO coated glass substrates. The TRPL data were fitted using the bi-exponential decay rate (white line). (c) Equivalent circuit used to fit the (c) Nyquist plots of the TiO₂ and AITO ETL based devices cells.

Table 4.3 Analysis of the TRPL with two-exponential decay characteristics for OIHP, OIHP/TiO₂ and OIHP/AlTO coated glass substrates.

Samples	A ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	τ _{average} (ns)
OIHP	0.25	8.47	0.75	309.1	233.9
OIHP/TiO ₂	0.20	9.10	0.80	258.4	208.5
OIHP/AlTO	0.32	10.6	0.68	215.7	150.1

Table 4.4 Fitted parameters acquired during EIS measurements under dark condition.

ETLs	R _s (Ω)	R _{rec} (KΩ)
TiO ₂	19.5	5.40
AlTO	18.7	56.9

4. Conclusion

To summarize, this study demonstrates a facial approach to boost several cell parameters via simple ETL modification. The addition of both trivalent Al and In into TiO₂ is believed to significantly enhance the overall photovoltaic efficiency via three factors. Firstly, the conductivity of AlTO ETL based devices were tremendously improved as seen from the increased average FF. Secondly, better band alignment in the modified ETL layer whereby an upward shift in conduction band resulted in reduced work function. As such, enhanced average V_{OC} of the device was observed. Finally, the AlTO ETL based devices also displayed an enhanced optical quality and transmittance, as seen in the improved average J_{SC} value. Through these simultaneous improvements in various photovoltaic cell parameters, paramount efficiency of 19 % was attained using co-dopants in the conventional TiO₂ ETL.

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Chapter 5

Effects of ETL/OIHP interface engineering

Commercialization of OIHP solar cells remains distant because of various problems such as inconsistency, poor environmental stability, and small-scale production. In this study, we present the use of complimentary electron transporting layers (ETLs) as a highly effective approach to cover the weaknesses of individual ETLs while boosting the strengths of various ETL compositions. The heterogeneous ETL based device comprising of the aluminium and indium doped TiO_2 (AITO) and tin oxide (SnO_2) layers demonstrate paramount efficiency of 18.90 % and exhibit superior stability maintaining 93 % of its initial efficiency after 25 days. In essence, our results suggest the use of compatible heterogeneous ETLs as an appealing method to provide synergistic enhancements of the planar OIHP devices in various photovoltaic parameters, device stability, and device reproducibility.

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5.1 Introduction

Capturing and converting solar energy into electricity using organic–inorganic hybrid perovskite (OIHP) continue to appeal to many research groups [1–3]. Though the power conversion efficiencies (PCEs) of OIHP solar cells approach that of commercialized silicon solar cells, commercialization remains as a distant aspiration. This is because OIHP solar cells suffer from multiple issues regarding stability, scalability, cost–effectiveness, reproducibility, and hysteresis [4,5]. Using the standard mesoporous configuration, many groups have shown possibility of attaining excellent solar performances [3]. Yet, the planar OIHP solar cells demonstrate greater cost effectiveness and scalability via their simple processing procedures along with smaller hysteresis compared to mesoporous OIHP solar cells [6]. Furthermore, the planar configuration shows close to 100 % internal quantum efficiency, making it extremely promising and desirable [7,8]. As such, several researchers believe that commercialization of OIHP solar cells might be made more promising via the optimization of planar OIHP devices. However, the increased surface area derived from the mesoporous electron transport layer (ETL) structure promotes electron transport between the OIHP layer and ETL, advantageous to the photovoltaic performance of OIHP solar cells.

In pursuit of higher performance in planar OIHP solar cells, several approaches have been investigated such as surface passivation, additive engineering of the OIHP composition, interfacial engineering, and ETL compositional modification [8,9]. Titanium oxide (TiO_2) remains as the more commonly employed ETL material in OIHP solar cells. With conduction band energy level between -4.3 to -4.0 eV, the TiO_2 ETL provides favourable electron transference between the OIHP absorber layer and the FTO substrate [10]. Its deep valence band also ensures good hole blocking properties. Furthermore, fabrication of compact- TiO_2 (c- TiO_2) films is highly reproducible, stable, and simple [11,12]. However, TiO_2 films possess relatively poor electron mobility and large amount of defect sites [13]. These traits often account for the high probability of charge recombination as well as poor charge transportation at the c- TiO_2 /OIHP interface [10,14]. To mitigate these issues, doping is commonly utilized to allow better band alignment and charge mobility [15–17].

Aluminium (Al) is a promising dopant especially when employed in the TiO_2 lattice. Apart from its relative abundance and low cost, the addition of aluminium has been reported to significantly improve the relatively poor conductivity of TiO_2 [18]. When Ti^{4+} is replaced with a smaller oxidation state ion such as Al^{3+} , substitution defects such as oxygen vacancies are introduced. As such, the addition of Al should, theoretically, enhance the charge carrier concentration along with the electrical conductivity of the poorly conductive TiO_2 electron transporting film [19]. On the other hand, the addition of indium (In) is reported to reduce the work function of most oxide films due to the generation of large amount of free electrons. In particular, the In- TiO_2 film showed better energy level alignment with the OIHP film compared to the pristine TiO_2 ETL [20,21].

Similar to TiO_2 , tin oxide (SnO_2) is a n-type semiconductor with a wide band gap between 3.6 and 4.1 eV [24]. In addition, SnO_2 films possess good transmittance, high electron conductivity, and good band alignment with the OIHP layer [23–26]. In addition, SnO_2 display passivating properties whereby significant reduction in charge recombination tendencies were reported with high hole blocking capabilities [23,25]. Despite the various advantages, performances of solution processed planar SnO_2 based OIHP solar devices often display poor reproducibility and stability due to their susceptibility to pinhole formation [19,27]. For this reason, several research groups deposit SnO_2 on top of a TiO_2 layer, or vice versa, so as to enjoy the advantageous of the SnO_2 material while enhancing the reproducibility of planar SnO_2 devices via the use of a highly reproducible c- TiO_2 layer [28–32]. Yet, these high efficiencies usually require the use of sophisticated equipment or still rely on mesoporous materials, impeding the commercialization process.

In this chapter, we examined the performance of the homogeneous ETL based OIHP solar cells. Specifically, the photovoltaic parameters, stability, and reproducibility of the previously optimized aluminium and indium doped TiO_2 (AITO) ETL were compared against the pristine TiO_2 and pristine SnO_2 ETL based OIHP devices [33]. With intentions to prevent current leakage, attain superior performance, improve device stability, and demonstrate high device reproducibility, we further explored the use of heterogeneous ETLs for efficient OIHP solar cell application, whereby a thin SnO_2 film was spun on top

of the underlying AITO ETL to provide synergistic combination between the different yet complimentary compositions. By stacking a SnO₂ film on the AITO ETL, high electron mobility and reduction in recombination sites were provided by the SnO₂ layer, while prevention of shunting pathways and improved reproducibility were contributed by the AITO layer. With paramount PCE of 18.9 %, the AITO/SnO₂ ETL based device further demonstrated enhancements in device stability and device reproducibility. Henceforth, our results illustrate the potential of heterogeneous ETL, which builds on the strengths of individual layers, as an effective approach to provide benefits beyond that of homogeneous ETLs standing alone.

5.2 Experimentals

5.2.1 Materials

Most chemicals used in this research were obtained from Sigma Aldrich such as titanium (IV) butoxide (97 %), indium (III) nitrate hydrate (99.99 %), aluminum nitrate nonahydrate (99.997 %), 2-methoxyethanol (99.8 %), acetylacetone (≥ 99.8 %), Tin (II) chloride (SnCl₂, 99.99 %), cesium iodide (CsI, 99.999%), absolute ethanol, N,N-dimethylformamide (DMF, 99.8 %), dimethyl sulfoxide (DMSO, 99.99 %), spiro-OMeTAD (> 99%), bis(trifluoromethylsulfonyl)amine lithium salt ($\geq 99\%$), 4-tert-butylpyridine (98 %), acetonitrile (99.8 %), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) tri[bis(trifluoromethane)sulfonimide] (FK209 Co (III) TFSI salt, 98 %), and chlorobenzene (99.8 %). Chemicals from Tokyo Chemical Industry (TCI) include lead (II) iodide (PbI₂, 99.99 %), and lead (II) bromide (PbBr₂, 99.99 %). Formamidinium iodide (FAI, >99.5 %), methylammonium bromide (MABr, >99.5 %) were purchased from Dyesol. Chemicals were used as purchased.

5.2.2 Device Fabrication

Fluorine-doped tin oxide (FTO, Nippon sheet glass Co., Ltd., Japan) coated glass substrates were cleansed with detergent and a series of sonication in various solvents. The

dried substrates were then treated with oxygen plasma for 10 min. The compact AITO layer was spun onto the FTO surface at 3000 rpm for 40 s and heated to 500 °C for 1 h. Preparation of the AITO layer solution involves the addition of stoichiometric amounts of aluminum nitrate nonahydrate (0.01 M) and indium (III) nitrate hydrate (0.01M) dissolved in 2-methoxyethanol, titanium (IV) butoxide, and acetylacetone. The substrate is then UV treated again before spinning the SnO₂ layer comprised of tin (II) chloride dissolved in ethanol at 3000rpm for 40s and heated at 200°C for 1h. The OIHP solution was prepared using 1.1 M PbI₂, 1.0 M FAI, 0.22 M PbBr₂, and 0.2 M MABr dissolved in 1 mL of anhydrous DMF: DMSO (4:1 volume ratio). 42 µL of CsI (1.5 M) stock solution was also added to the as-prepared solution and dissolved well. Spin coating of the perovskite solution involved two separate spin coating steps: 1) 2000 rpm for 10 s and 2) 6000 rpm for 30 s. With 15 s left in the second step, 100 µL of chlorobenzene was drop casted onto the spinning substrate before annealing at 100 °C for 1 h. A thin layer of spiro-OMeTAD was spun at 5000 rpm for 30 s using a mixture consisting of 70 mg spiro-OMeTAD, 28 µL 4-tert-butylpyridine, 16.94 µL bis(trifluoromethylsulfonyl) amine lithium salt (520 mg/mL in acetonitrile), and 35 µL FK209 Co(III) TFSI Salt (18.8 mg/50 µL in acetonitrile) dissolved in 1 mL of chlorobenzene. Last but not least, 80nm of gold electrodes were thermally evaporated directly on the spiro-OMeTAD layer.

5.2.3 Characterization

Surface morphologies of the samples were analyzed using field emission scanning electron microscope (FESEM; JEJOL JSM-7600F), while structural and chemical characteristics of samples were investigated using x-ray diffraction (XRD; Bruker D8 Advance XRD) and x-ray photoelectron spectroscopy (XPS; Kratos AXIS Supra XPS). Ultraviolet photoelectron spectroscopy (UPS) measurements were conducted with Kratos AXIS Supra. Current density against voltage (J-V) plots were recorded under one-sun AM 1.5G (100 mW/cm²) using the Keithley 2612A source meter with measured active area of 0.096 cm². The light intensity was calibrated against the traditional silicon solar cell. UV-vis spectrophotometer (Shimadzu, UV-1800) and spectrofluorophotometer (Shimadzu, RF-5301PC) were employed to record the absorbance and photoluminescence (PL) spectra,

respectively. Incident photon-to-current conversion (IPCE) was measured using PVE300 (Bentham). Impedance spectroscopy (Autolab PGSTAT302N) was conducted under dark condition by applying a perturbation of frequencies varying from 10 Hz to 1 MHz at a DC voltage of 800 mV.

5.3 Results and Discussion

5.3.1 Chemical Characterization of various ETLs

In our recent work, successful fabrication of both pristine c-TiO₂ and AITO films were verified using both X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). As mentioned in section 4.3.1, the as-fabricated c-TiO₂ and AITO films coincide with the (101) plane and anatase structure. XPS results further revealed that the addition of Al and In into TiO₂ resulted in shifts in peak positions toward that of higher binding energy levels as illustrated in chapter 4 [28,33,34]. In essence, the XPS results suggest successful incorporation of both Al and In dopants into the TiO₂ lattice. As seen in Figure 5.1a, no diffraction peaks were observed due to the amorphous nature of the SnO₂ film. To verify the successful fabrication of the as-prepared SnO₂ film at low temperature, chemical analysis of sample surface was also carried out using XPS. As seen in Figure 5.1b, the XPS spectrum exhibits two distinct peaks at 495.8 and 487.3 eV which are commonly associated with the presence of Sn⁴⁺ ions. In addition, the asymmetrical O 1s peak in Figure 5.1c can be deconvoluted by the presence of two peaks fitted at binding energies of 530.8 and 532.4 eV representing the Sn–O bond and existence of impurities such as water molecules or OH ligands, respectively.

Figure 5.1 (a) XRD pattern of the SnO₂ film. XPS spectra of the (b) Sn 3d and (c) O 1s peaks of the SnO₂ film [33].

5.3.2 Energy Band Levels of various ETLs

Ultraviolet photoelectron spectroscopy (UPS) and UV-visible transmittance spectroscopy were utilized to examine the energy levels of the SnO₂ film. As seen in the UPS spectrum labelled as Figure 5.2a, the valence band maximum (E_{VBM}) energy level is calculated using the equation $E_{VBM} = -[21.22 - (E_{cutoff} - E_{onset})]$, where E_{onset} represents the low binding energy while E_{cutoff} represents high binding energy cutoff [33]. As such, the as-fabricated SnO₂ film has an estimated calculated E_{VBM} of -8.06 eV which is much deeper than the pristine TiO₂ and AITO energy levels [33,35]. Its lower E_{VBM} promotes effective passivation of hole transportation to the ETL [35]. Using the valence band maximum and corresponding energy band gap (E_g) of 3.87 eV as seen in Figure 5.2b, the conduction band minimum (E_{CBM}) energy level is calculated to be -4.19 eV. As seen in Fig. 1d the conduction band minimum (E_{CBM}) energy level of the SnO₂ layer is lower than that of the AITO layer (-3.9 eV), acting as an effective hole blocking layer [36]. However As such, the AITO film possesses a higher E_{CBM} energy level compared to SnO₂ as illustrated in the band alignment schematic reflected in Figure 5.2c. This creates an energy level mismatch between the adjacent SnO₂ and AITO layer. Yet, this energy mismatch is compensated by the positive effects attributed from the heterogeneous ETL in which the photovoltaic performance gains large enhancement as presented in the later part of the report.

Figure 5.2 (a) UPS spectra and (b) plots of $(\alpha h\nu)^2$ versus $h\nu$ for the SnO₂ film. (c) Corresponding energy level diagram of the OIHP solar devices [33].

5.3.3 Effectiveness of the Homogeneous ETL Based Devices

Figure 5.3a shows the schematic illustration of the fully planar OIHP photovoltaic device utilized in this study: FTO substrate as the anode, solution processed ETL as the efficient electron transport layer, OIHP absorber as the active layer, spiro-OMETAD as the hole transporting layer (HTL), and Au as the cathode. With a general device architecture of FTO/ETL/OIHP/HTL/Au, each layer has a corresponding thickness of approximately 80, 480, 230, and 80 nm derived from the cross-sectional scanning electron microscopy (SEM) image (Figure 5.2b).

5.3.3.1 J-V Measurements

In order to understand the effectiveness and suitability of each composition in the fully planar device configuration, we first analyzed the device performance of the homogeneous ETLs. Specifically, the photovoltaic performance of pristine TiO_2 , AITO, and SnO_2 ETL based devices were manifested and evaluated via the current density–voltage (J–V) properties measured under AM1.5G illumination at light intensity of 100 mW cm^{-2} in ambient air. As illustrated in both Table 1 and Figure 5.3c, the pristine TiO_2 ETL device display much poorer power conversion efficiency (PCE) of 16.1 % compared to other homogeneous ETL counterparts. In good agreement with our previous work, the addition of Al and In into the TiO_2 ETL improved both short-circuit current density (J_{sc}) and fill factor (FF) indicating the simultaneous enhancement in optical transmittance and charge extraction, respectively [33]. The similar open-circuit voltage (V_{oc}) observed in the TiO_2 and SnO_2 ETL based devices could be attributed to the similar E_{CBM} energy levels [19]. Among the homogenous ETL devices, SnO_2 ETL based device showed superior PCE of 17.5%. This could be accredited to the higher transmittance and electron extraction commonly assigned to SnO_2 films unlike the slower charge separation often associated with the titanium based and perovskite interface, as verified in section 4.3.4 [30,37,38].

Figure 5.3 (a) Schematic and (b) SEM cross-sectional image of a complete homogeneous solar device. (c) J–V curves of various champion homogeneous ETL based devices. To duplicate the thickness used for the heterogeneous ETL, the homogeneous ETL were spun twice.

Table 5.1 Photovoltaic parameters of homogeneous ETL based devices.

Device ETL	Voc (V)	Jsc (mAcm ⁻²)	FF	η (%)	IQR (%)
TiO ₂	1.03	20.8	74.6	16.1	0.45
AlTO	1.05	21.3	76.5	17.2	0.42
SnO ₂	1.05	21.8	76.7	17.5	0.95

5.3.3.2 Optoelectronic and Recombination Properties

Optical transmittance characterization was carried out to gain better insights regarding the optical properties of the homogeneous ETLs. Similar to our earlier work conducted using the mesoporous configuration, addition of Al and In dopants into the pristine TiO₂ film allowed slight enhancement in transmittance [33]. Corresponding well with the heightened J_{SC} value of SnO₂ ETL device, Figure 5.4a shows the highest transmittance in the SnO₂ film followed by the AlTO film, with the greatest optical loss found in the pristine TiO₂ film. Henceforth, SnO₂ film appears as superior ETL candidate. The slightly higher PCE observed in the SnO₂ ETL based device compared to the AlTO counterpart can also be explained by the surpassing transmittance resulting in the heightened J_{SC}.

To investigate the charge transport behaviours in the homogeneous ETL based devices, EIS was employed. All EIS measurements were carried out under dark condition with an applied forward bias of 800 mV. Figure 5.4b shows the Nyquist plots of the homogeneous ETL based devices containing the experimental and fitted data. By using the equivalent circuit model represented by Figure 5.4c, the internal series resistance (R_s) and recombination resistance (R_{rec}) were obtained and recorded in Table 5.2. As indicated by the bigger semicircle displayed in Figure 5.4b which shows the tendency of hole carriers recombining with electrons from the conduction band, it is apparent that recombination resistance is much larger in the SnO₂ ETL based device compared to AlTO, followed by TiO₂ ETL based devices. This can be explained by the superior passivation of trapped sites at the SnO₂/OIHP interface commonly associated with the passivating role of SnO₂ films [21,27,35]. As such, the SnO₂ film could act as an ETL as well as an interfacial material,

encouraging electron transport while passivating defects found between the ETL and OIHP layer.

Figure 5.4 (a) Transmittance spectra of various homogeneous ETLs. (b) Nyquist plots of various homogeneous ETL based devices and the equivalent circuit used for the EIS analysis.

Table 5.2 Fitted parameters for EIS measurements acquired under dark condition.

ETL	R _s (Ω)	R _{rec} (kΩ)
TiO ₂	20.4	1.8
AITO	20.1	5.4
SnO ₂	20.7	18.1

5.3.3.3 Long-Term Stability

Long-term stability of the homogeneous ETL based devices stored under 40 % relative humidity and dark conditions for 25 days were examined. Figure 5.5a–d presents the long-term stability of the devices categorized according to the different photovoltaic parameters. Retaining only 63 % of its initial PCE, accelerated degradation was observed in the pristine TiO₂ ETL based device as opposed to the AITO ETL based device whose PCE retained 81% after 25 days. In other words, the addition of Al and In dopants not only enhanced device performance but also significantly improved device stability. The improved stability in the AITO ETL based device compared to the TiO₂ ETL based device is postulated to be due to the much lower amount of recombination sites as seen in its higher recombination resistance, which further facilitates better charge transfer between ETL and perovskite.

Unlike the titanium based ETLs, the SnO_2 ETL based device demonstrated superior long-term stability in which 86 % of its initial PCE was retained. In addition, relatively small decrease in FF was observed in the SnO_2 ETL based device unlike its counterparts which saw larger decrease in FF values. This can be explained by the significantly higher recombination resistance (Table 5.2), showcasing considerable reduction in defects and potential as an effective passivating interfacial material.

Figure 5.5 Stability curves of various homogeneous ETL based devices without encapsulation, categorized into various photovoltaic parameters of (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) PCE.

5.3.3.4 Device Reproducibility

In good agreement with other reports, the SnO₂ ETL based devices exhibited preferable device performance and stability but poorer reproducibility compared to both AITO and TiO₂ ETL based devices [19,27,31,32]. With each boxplot comprising of 20 independent OIHP devices, Figure 5.6a–d shows the statistical distribution of the homogeneous ETL based devices and their corresponding photovoltaic parameters. SnO₂ ETL based devices demonstrate poorer reproducibility with large variation in photovoltaic parameters represented by the wider data distribution. To quantify the performance variability of the as-fabricated homogeneous ETL based devices, we utilized the box plot of each ETL configuration and calculated their corresponding interquartile range (IQR). IQR measures the statistical dispersion between the 75th and 25th percentiles, omitting data that differs from the majority. The IQR, represented by the length of the boxplot, can thus be calculated using the equation of $IQR = Q_3 - Q_1$, where Q_3 and Q_1 represents the 3rd (upper) and 1st (lower) quartile of the boxplot. As seen in Table 4.1, the IQR of the SnO₂ ETL based devices is much larger compared to that of both AITO and TiO₂ ETL based devices. This corresponds to a wider spread in PCE values, indicating poorer consistency and reproducibility.

Figure 5.6 Statistical histogram of the homogeneous ETL based devices divided into various photovoltaics parameters, specifically (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) PCE.

5.3.4 Effectiveness of the Heterogeneous ETL Based Devices

To impede the possibility of charge leakage complications commonly found in planar devices and enhance device consistency, we deposited a highly reproducible AITO film before the thin SnO_2 transporting layer renowned for its pinhole formation [32,33]. In addition, it was observed, through the later section of the research, that the use of heterogeneous ($\text{TiO}_2/\text{SnO}_2$, AITO/ SnO_2) ETL showed synergistic enhancement in overall device performance and long-term stability.

5.3.4.1 Morphological Studies

To investigate the influence of various heterogeneous ETLs on the adjacent OIHP film formation, SEM was employed to study the surface and cross-sectional morphologies of the as-prepared films. Figure 5.7a–c shows the top-view morphologies of the OIHP films deposited on bare FTO, FTO/TiO₂/SnO₂, and FTO/AlTO/SnO₂ substrates. Figure 5.7d–f shows the cross-sectional morphologies of the FTO/OIHP, FTO/TiO₂/SnO₂/OIHP, and FTO/AlTO/SnO₂/OIHP substrates. It is evident that the average grain size and thickness of the OIHP film is significantly smaller when OIHP was deposited directly on the bare FTO substrate of approximately 320 and 400 nm, respectively. This could be due to the rougher FTO surface, resulting in much faster nucleation and smaller growth of perovskite crystals [39]. The SEM images show no sizable difference in grain size or thickness of the OIHP film when deposited on the heterogeneous TiO₂/SnO₂ or AlTO/SnO₂ ETL. OIHP films deposited on heterogeneous ETLs display good compactness, uniformity, and minimal pinholes with similar average grain size of approximately 430 nm and thickness range of 480–485 nm. Therefore, variation in the underlying heterogeneous ETLs fabricated in this study has very little effect on the nucleation and growth of the adjacent OIHP absorber layer. In addition, the uniformity in sizes and thicknesses observed in the SEM results allows us to believe that differences revealed in the photovoltaic performances are predominantly ascribed to the characteristics of the ETL compositions. This postulation is further supported by the similar XRD patterns obtained. Represented by Figure 5.8, all patterns well correspond to the OIHP film with small traces of residual PbI₂, indicating that the underlying heterogeneous ETLs have negligible effect on adjacent OIHP composition.

Figure 5.7 Top view and corresponding cross-sectional FESEM images of various OIHP films deposited on FTO (a & d), FTO/TiO₂/SnO₂ (b & e), and FTO/AlTO/SnO₂ (c & f) substrates.

Figure 5.8 XRD patterns of various OIHP films. Note that • represents peaks belonging to cubic PbI₂ while the remaining peaks represent the OIHP film.

5.3.4.2 J–V Measurements

Given the energy level mismatch between the AITO and SnO₂ layers as indicated in Figure 5.2e, effectiveness of electron charge transference could be significantly hindered. As such, device performances of the heterogeneous ETL based devices were tested. Figure 5.9a shows the schematic of the heterogeneous ETL based device. As seen in Figure 5.9b, the as-fabricated heterogeneous ETL based devices possess general configuration of FTO/ (TiO₂ or AITO)/ SnO₂/ OIHP/ spiro-OMeTAD/ Au with thickness of ETL similar to that of homogeneous ETL based devices (Figure 5.3e). Figure 5.9c shows the J–V curves of the champion devices measured under AM 1.5G simulated irradiation with 100 mW cm⁻² illumination. As summarized in Table 5.3, all heterogeneous ETL based devices demonstrate superior photovoltaic parameters compared to the homogeneous ETL counterparts. Through the simple insertion of a SnO₂ layer between the AITO/perovskite interface, V_{OC} and FF of the AITO/SnO₂ ETL based device significantly improved from 1.05 to 1.10 V and 76.5 to 79.8 compared to the AITO ETL based device, respectively. Large increases to the V_{OC} and FF values suggest preferable characteristics of the heterogeneous system compared to the homogeneous counterpart by which enhanced charge extraction capability are promoted despite the non-cascading energy levels [36,39,40]. Aligned with the trend observed in the homogeneous ETL based devices, unrivalled PCE was observed in the AITO/SnO₂ ETL based device of 18.90 % while the TiO₂/SnO₂ ETL based device remained inferior with attained PCE of 17.90 %. As seen in Figure 5.9d, the IPCE spectra further supports the higher J_{SC} observed in the AITO/SnO₂ ETL based device with integrated J_{SC} values of 20.1 mAcm⁻² unlike the TiO₂/SnO₂ counterpart with integrated current at 19.6 mAcm⁻². As seen in Figure 5.9c, hysteresis exist in our both heterogeneous ETL compositions. However, the AITO/SnO₂ ETL based device display notably smaller degree of hysteresis compared to the TiO₂/SnO₂ ETL based device. Using the equation of hysteresis index (HI) = $\frac{\text{PCE (reverse)} - \text{PCE (forward)}}{\text{PCE (reverse)}}$, HI obtained from the AITO/SnO₂ ETL based device is approximately 0.105 while HI of the TiO₂/SnO₂ ETL based device is larger of 0.162 [41,42]. This signifies that the degree of hysteresis is less severe in the AITO/SnO₂ ETL based device, although still present. This could be due to

the lower charge mobility of the TiO_2 ETL and less negative conduction band, resulting in greater electron accumulation in the $\text{TiO}_2/\text{SnO}_2$ ETL based device [43].

Figure 5.9 (a) Schematic and (b) cross-sectional SEM image of a complete heterogeneous ETL based device. (c) Reverse and forward J–V and (d) IPCE curves of the champion heterogeneous ETL based devices.

Table 5.3 Photovoltaic parameters of the heterogeneous ETL based devices.

ETL	Voc (V)	Jsc (mAcm^{-2})	FF	PCE (%)	IQR (%)
$\text{TiO}_2/\text{SnO}_2$	1.08	20.9	79.3	17.9	0.19
ATO/ SnO_2	1.10	21.5	79.8	18.9	0.34

5.3.4.3 Long-Term Stability

Long-term stability of the unencapsulated heterogeneous ETL based devices stored in 40 % relative humidity and dark conditions for 25 days were also examined. Figure 5.10 shows the changes in various photovoltaic parameters, specifically J_{SC} , V_{OC} , FF, and PCE. Similar to the results obtained in the homogeneous ETL based devices, the doped TiO_2 film displayed superior performance over the undoped film whereby the AITO/ SnO_2 ETL based device retained 93 % of its initial PCE while the TiO_2 / SnO_2 ETL based device saw 90 % retention of its initial PCE. In addition, the heterogeneous ETL based devices displayed remarkable stability in comparison to the homogeneous counterparts (Figure 5.5). This can be understood by the passivating effect of the SnO_2 layer whereby superior interfacial contact between the SnO_2 /OIHP is often reported [40]. The better stability demonstrated can be associated with the good passivating characteristic of the SnO_2 layer, in which the heterogeneous ETL based devices exhibit higher degree of defect tolerance compared to the homogeneous ETL based device despite all ETL thicknesses being kept relatively constant.

Figure 5.10 Long-term stability of various heterogeneous ETL based devices under for 25 days without encapsulation, specifically (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) PCE.

5.3.4.4 Device Reproducibility

Figure 5.11 shows the statistical distribution of the heterogeneous ETL based devices and their corresponding photovoltaic parameters, in which 20 of each ETL device were fabricated and tested. In good agreement with the champion devices, the as-prepared AITO/ SnO_2 ETL based devices showed superior average PCE of 18.4 % compared to that of the $\text{TiO}_2/\text{SnO}_2$ ETL based devices of 17.5 %. To verify the superior consistency of the heterogeneous ETL based devices, IQR of their corresponding PCE boxplot was calculated. As seen in Table 5.3, IQR of the AITO/ SnO_2 ETL based devices is 2.8 times smaller than that of the SnO_2 ETL based devices. This signifies that the addition of an AITO layer beneath the pinhole prone SnO_2 ETL greatly promotes the reproducibility and consistency of the device. Therefore, usage of heterogeneous ETL in planer OIHP devices not only enhances the overall performance by significantly improving PCE of devices, but also promotes long-term stability and device consistency tremendously.

Figure 5.11 Statistical histogram of the heterogeneous ETL based devices divided into various photovoltaics parameters, specifically (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) PCE.

5.3.4.5 Optoelectronic and Recombination Properties

UV–Vis absorption characterization was carried out to gain better insights regarding the optical properties of the heterogeneous films. Following the same trend as earlier results (Figure 5.4a), Figure 5.12a shows that higher transmittance in the glass/AlTO/SnO₂ film. In addition, UV–Vis absorption characterization was conducted on the glass/OIHP, TiO₂/SnO₂/OIHP, and AlTO/SnO₂/OIHP substrates. As seen in Figure 5.12b, superior light absorption in the wavelength range of 500–750 nm is observed in the AlTO/SnO₂/OIHP substrate while absorbance decreases when TiO₂/SnO₂ ETL was used. The lower optical losses found in the ETL, together with higher absorption in the OIHP layer, explain the enhanced performance of AlTO/SnO₂ ETL based device.

To evaluate the impact of the SnO₂ layer on the charge transport and charge recombination properties of the devices, steady–state photoluminescence (PL) characterization and EIS were conducted. Figure 5.12c shows the PL spectra obtained for the OIHP films deposited on three different substrates: glass alone, glass/TiO₂/SnO₂, and glass/AlTO/SnO₂. Excited at 580 nm, the characteristic peak observed at approximately 763 nm corresponds to the exciton emission in the OIHP films. Unlike the sharp and elevated peak observed for the glass substrate, significant reduction in PL intensity was observed for the OIHP films deposited on both heterogeneous ETLs. The significantly quenched PL intensity observed in the AlTO/SnO₂/OIHP substrate is an indication of superior electron transportation across the OIHP/AlTO/SnO₂ layers, compared to the OIHP/TiO₂/SnO₂ counterpart. Figure 4.12d shows the Nyquist plots of the heterogeneous ETL containing the experimental and fitted data. Table 5.4 summarizes the EIS results for the heterogeneous ETL based devices. Although variation in ETL composition has little effect on the R_s of the as–fabricated heterogeneous based ETL devices, significant difference in recombination density was observed. To illustrate, larger R_{rec} value of 28.9 k Ω was obtained for the AlTO/SnO₂ ETL

based device unlike the $\text{TiO}_2/\text{SnO}_2$ counterpart of 22.2 $\text{k}\Omega$. Hence, it is evident that the simple addition of a thin SnO_2 layer can significantly decrease the density of recombination sites. This further supports the enhanced stability, device reproducibility, and overall superior performance observed in the heterogeneous ETL based devices compared to the homogeneous counterparts.

Figure 5.12 (a) Transmittance spectra of various heterogeneous ETLs. (b) Absorption and (c) PL spectra of the OIHP films deposited on various heterogeneous ETLs. (d) Nyquist plots of heterogeneous ETL based devices.

Table 5.4 Fitted parameters for EIS measurements acquired under dark condition.

ETL	R_s (Ω)	R_{rec} ($\text{k}\Omega$)
$\text{TiO}_2/\text{SnO}_2$	20.7	22.2
AlTO/SnO_2	20.7	28.9

5. Conclusion

In summary, our study demonstrates the use of two compatible ETLs as a straightforward approach to acquire high photovoltaic performance, device reproducibility, and extended device stability in the fully planar OIHP configuration. In the beginning of the chapter, homogeneous ETLs were investigated in which the device performance and long-term stability revealed superiority in the SnO₂ ETL based device. However, the poor device reproducibility observed in the SnO₂ film prompted the use of the heterogeneous ETL. By depositing AITO before the SnO₂ ETL, enhanced consistency in photovoltaic parameters were observed in the heterogeneous ETL based devices. Furthermore, the addition of a thin SnO₂ layer between the AITO/ or TiO₂/OIHP interface confirmed significant reduction of trap density. The heterogeneous AITO/SnO₂ ETL based devices exhibited nonpareil PCE of 18.9 %. Notable long-term stability was also observed in which 93 % of its initial PCE was retained after 25 days despite the absence of encapsulation. Device reproducibility also saw significant improvement with IQR of the PCE boxplot reduced by 2.8 times in the AITO/SnO₂ ETL based devices compared to the SnO₂ ETL based devices. Henceforth, we believe if conscientious selection of transporting layers is applied in which corresponding strengths and weaknesses of various materials are manifested and masked, synergistic enhancement in various photovoltaic parameters, device stability and consistency can be achieved.

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Chapter 6

Effects of OIHP/spiro-OMeTAD Interface Passivation

Defects found on the surfaces of OIHP films greatly impede device performance. Herein, 2-hydroxybenzophenone (HBP) is introduced to the OIHP/spiro-OMeTAD interface in which the optimized device shows superior power conversion efficiency of 19.28 % and long-term stability in which 93 % of initial efficiency is retained, despite having been stored for 120 days. Improvements are attributed to the reduction in surface defects and strengthened charge transport properties, which are supported by the enhanced open-circuit voltage and fill factor, respectively. Acting as a Lewis base molecule, effective interactions between the HBP molecules and under-coordinated lead ions passivate the surface defects found on the OIHP film, allowing increase in both device efficiency and durability. The increased hydrophobicity further improves the stability of the device. Hence, this work provides a facile yet highly effective approach for achieving high efficiency, reproducibility, and stability in planar OIHP solar devices.

*This section published/submitted substantially as Interfacial 2-hydroxybenzophenone passivation for highly efficient and stable perovskite solar cells.

6.1 Introduction

Excellent inherent properties such as strong absorption coefficient, tuneable band gap, and ambipolar carrier characteristic have enabled current certified power conversion efficiency (PCE) of organic–inorganic hybrid perovskite (OIHP) solar cells to soar to efficiencies close to that of traditional silicon solar cells [1–3]. In spite of efficiencies close to that of commercial silicon solar cells, current PCEs are inferior to the thermodynamic PCE limit for methylammonium lead iodide (MAPbI₃)–based solar cells of 31 % [2,4,5]. Unlike the well-regulated properties in crystalline silicon solar devices, performances of the solution based OIHP solar devices are highly varied. The great variation is often attributed to the high tendencies for OIHP films to form imperfections [6–8]. Owing to their soft nature, low required defect formation energy, and solution-based fabrication procedure, polycrystalline OIHP films generally possess high defect densities of 10^{17} – 10^{18} cm⁻² [9,10]. In addition, the lack of stoichiometric composition and sublimation of organic molecules during thermal annealing of the OIHP film often leave behind dangling bonds and uncoordinated ions on the surfaces of the OIHP crystals. These defects not only exacerbate non-radiative recombination tendencies and reduced effective charge transport but also increase ion migration and hysteresis [10,11]. Apart from the deterioration in optoelectronic properties, presence of surface defects also greatly impedes the stability and reproducibility of OIHP solar devices. This is because the hygroscopic and low formation energy of OIHP absorber films increase decomposition susceptibility under moisture, oxygen, thermal stresses, and electric field, further hampering the performance, reproducibility, and device stability [6,7].

Recent progress on stabilization of OIHP devices largely involves defect management and optimization of the light-absorber composition. By adding small quantities of varied elements and molecules to the OIHP precursor solution, high-quality OIHP films are often achieved through beneficial chemical interactions between the OIHP material and specific functional groups found in the additive [12–14]. However, several reports have demonstrated micrometre diffusion lengths of photo-generated charge carriers in the OIHP material under illumination [15,16]. Thus, transport losses within the OIHP light absorber

are considered trivial compared to the losses at the interfaces between the electron transport layer (ETL) and the hole transport layer (HTL) [2,16]. In addition, photo-degradation is commonly associated with the deprotonation of MA⁺ cations in which thermal annealing of the OIHP film might result in sublimation of highly volatile organic molecules, promoting the formation of uncoordinated lead (Pb) atoms and vacancies [17–19]. Furthermore, the OIHP layer is exceptionally vulnerable to degradation when spiro-OMeTAD is utilized as the HTL since the commonly employed lithium doped spiro-OMeTAD is highly hygroscopic [20]. As such, interfacial engineering using an effective passivation material at the OIHP/ HTL interface is often employed [6,21,22]. Owing to the charged nature of the defects, it has been reported that the use of Lewis acid could provide effective passivation via coordination or electrostatic interactions to the undesirable negatively charged under-coordinated halides, whereas the use of Lewis base molecules passivate the positively charged under-coordinated Pb ions by donating a pair of lone pairs [6,10,14]. Hence, the employment of an effective OIHP/HTL passivation interlayer could significantly reduce the amount of trap sites and under-coordinated ions found on the surface of the OIHP film [14,23,24]. By using a suitable material at the OIHP/spiro-OMeTAD interface, the interlayer could also act as a physical shield to protect the underlying OIHP film from unfavourable atmospheric environments such as moisture protection [25].

Here, a thin layer of 2-hydroxybenzophenone (HBP) was deposited at the OIHP/HTL interface in the fully planar configuration via simple solution based processing. HBP passivates the under-coordinated Pb²⁺ trap states of the OIHP film by simple donation of electron lone pairs found in the ketone and phenol functional groups of the HBP molecules. It was verified in this chapter that the passivation layer enhances the overall performance, long-term stability and reproducibility of the planar devices. Specifically, efficient hole transportation and suppression of charge recombination were demonstrated with the addition of the HBP interlayer. Champion PCE of 19.28% was achieved in the 5 mg/mL HBP passivated solar device along with long-term stability in which the unencapsulated 5 mg/mL HBP passivated device whereby 93% of its initial PCE was retained after 120 days. In essence, this work reiterates the importance of intentional surface passivation between

the OIHP and HTL films. The simple employment of an optimized interlayer can greatly boost the photovoltaic performance and stability of OIHP solar cells.

6.2 Experiments

6.2.1 Materials

2-hydroxybenzophenone (99%) used in this research was purchased from Sigma Aldrich. The rest of the chemicals utilized in this study are reported in section 4.2.1. Chemicals were used as purchased.

6.2.2 Device Fabrication

Synthesis of compact TiO_2 (c- TiO_2), SnO_2 , OIHP, and spiro-OMeTAD precursor solutions are as recorded in section 4.2.2. Used as received, 2-hydroxybenzophenone (HBP, Sigma Aldrich, 99%) was dissolved in 1 mL of chlorobenzene (Sigma Aldrich, 99.8%) at various concentrations of 5, 10, and 20 mg/mL HBP.

Fluorine-doped tin oxide (FTO) substrates (Nippon sheet glass Co., Ltd., Japan) were cleansed and treated with oxygen plasma for 20 min to remove residual elements found on the surface. The compact TiO_2 layer was then spun onto the surface at 3000 rpm for 40 s and annealed at 500 °C for 1 h. A thin layer of SnO_2 was then deposited at 3000 rpm for 30 s before annealing at 200 °C for 1 h. Conducted in the glovebox, the perovskite film was prepared using two separate steps of 2000 rpm for 10 s and 6000 rpm for 30 s in which 100 μL of chlorobenzene was drop cast at the last 15 s of the second step. The as-prepared substrates were then held at 100 °C for 1 h. The HBP passivation layer was spun on top of the perovskite surface at 4000 rpm for 30 before further heating at 100 °C for another 10 min. The spiro-OMeTAD layer was spun at 5000 rpm for 30 s before the gold electrodes were thermally evaporated under high vacuum. TiO_2 ETL instead of AITO ETL was selected for this study to allow clear understanding regarding the effects of HBP, without doping effect.

6.2.3 Characterization

X-ray diffraction (XRD) analysis was conducted to investigate the crystal structure and phases present in the OIHP films using a D8 Advance x-ray diffractometer with Cu K α radiation. Cross-sectional and surface morphologies of the samples were investigated using a JEOL JSM-7600F field emission scanning electron microscope (FESEM). Chemical and elemental analysis of both HBP and OIHP films were investigated using a Shimadzu RAffinity-1S for Fourier transform infra-red spectrometry (FTIR) and AXIS Ultra DLD for x-ray photoelectron spectroscopy (XPS). To understand the effects of the HBP passivation layer on the optical properties of the underlying OIHP absorber, absorption and photoluminescence (PL) spectra of the OIHP films deposited on glass substrates were measured using the Shimadzu UV-1800 UV-Visible spectrophotometer and Shimadzu RF-5301PC spectrofluorophotometer, respectively. Current density-voltage (J-V) characterizations were measured in air using a Keithley 2612A source meter under 100 mW/cm² solar illumination and simulated Air Mass 1.5 global (AM 1.5G). Light intensity of the solar simulator was calibrated against a standard silicon device. Incident photon-to-current conversion (IPCE) was conducted using the Bentham PVE300 photovoltaic external quantum efficiency (EQE) tester with a dual xenon/quartz halogen light source in the absence of light bias. Contact angle analysis of the films was conducted using the Dataphysics OCA-15 Pro with dispense unit of 0.06 μ L drop of deionized water. Contact angle measurements were obtained 1 s after dispensing.

6.3 Results and Discussion

6.3.1 Verification of HBP Passivation

Passivation at the OIHP/HTL interface is tricky due to the sensitivity of the OIHP film. When exposed to hydrogen-bonded polar protic solvents, organic cations found in the OIHP film dissolves in the hydrogen-bonded solvents [26]. When exposed to polar aprotic solvents, the OIHP absorber layer readily bonds with the partially negative oxygen atoms

found in the aprotic solvents, dissociating the PbI_6 octahedral structure, degrading the OIHP layer [26]. Considering these, the HBP material was dissolved in the commonly employed chlorobenzene antisolvent to ensure minimal disruption to the underlying OIHP film [27]. Particularly, various concentrations of 0, 5, 10, and 20 mg/mL of HBP dissolved in chlorobenzene was spin coated between the OIHP and spiro-OMeTAD with excess solvents removed using heat treatment at 100 °C for 10 mins.

To understand the possible chemical interactions between the HBP and OIHP films, x-ray photoelectron spectroscopy (XPS) was utilized to investigate the changes in the composition of the OIHP films with and without HBP passivation. As seen in Figure 6.1a, oxygen acts as a characteristic peak indicative of the HBP molecule. Since the ratio of peaks is proportionate to the quantity of elements present, detection of larger oxygen to lead (O/Pb) ratio suggest the existence of the HBP film on the OIHP layer [2]. Estimation of the O/Pb ratios were carried out using quantitative intensities of the peaks obtained from Figure 6.1b & c. As calculated, the O/Pb ratio of the pristine OIHP film equates to 0.061 which is approximately half of that obtained for the HBP passivated OIHP film of 0.108. Hence, the high oxygen content found in the HBP passivated OIHP film greatly supports the successful adsorption of the HBP material on the surface of the underlying OIHP film [2,28]. Oxygen peaks found on the surfaces of the pristine OIHP film could be attributed to the unavoidable absorption of oxygen gas and moisture from the atmosphere. Figure 6.1d shows the Pb 4f spectra of the pristine and HBP passivated OIHP films in which the peak at 137.8 eV represents Pb 4f_{7/2} while the peak at 143.3 eV represents Pb 4f_{5/2}. With weaker Pb peak intensities in the HBP passivated OIHP film compared to the pristine OIHP film, the XPS spectra suggest successful passivation of the under-coordinated Pb^{2+} present found on the surface of the OIHP layer [29].

FTIR spectroscopy was also conducted for the pristine OIHP, pristine HBP, and HBP passivated OIHP films. The complete spectra are represented by Figure 6.1e whereby multiple bands found in the HBP spectrum clearly identifies the aromatic ring with signature out of plane (oop) C-H bending absorptions peaks between 675 to 1000 cm^{-1} [31–32]. In good agreement with several references, Figure 6.1f shows the pristine HBP

film showed characteristic peak at 1601 cm^{-1} , while the pristine OIHP film showed characteristic peak at 1610 cm^{-1} , representing the aromatic carbonyl ($\text{C}=\text{O}$) stretching and amine ($\text{N}-\text{H}$) bending, respectively [12,30,31]. After deconvolution of the broad peak found in the HBP passivated OIHP film, the FTIR pattern suggests presence of both carbonyl and amine groups. The small shift towards higher wavenumbers could be attributed to the slight reinforcement of the carbonyl group since intramolecular hydrogen bonding is weakened upon interaction with the OIHP surface [12,30,31].

Figure 6.1 (a) Molecular structure of HBP [32]. O 1s XPS peak found in the (b) pristine and (c) HBP passivated OIHP films. (d) Pb 4f XPS peaks. The (e) complete and (f) magnified FTIR

spectra of the as-prepared films, showing the presence of C=O and N–H in the HBP passivated perovskite film.

The effects of HBP passivation on the crystallinity of the OIHP film were also investigated using XRD. As seen in Figure 6.2, the films exhibit similar diffraction patterns despite various HBP concentrations employed. All samples possess a tetragonal structure with similar characteristic peaks [33]. Furthermore, all samples display characteristic peak of PbI_2 at 12.5° since excess PbI_2 is added to the OIHP precursor solution. Sharp peaks displayed in Figure 6.2 suggest that the addition of HBP does not affect the quality of the underlying OIHP films to which all films are of high quality.

Figure 6.2 XRD pattern of the pristine and HBP passivated OIHP films. Note that • represents peaks belonging to cubic PbI_2 while the remaining peaks represent the OIHP film.

6.3.2 Morphological Studies

FESEM was employed to investigate the effects of HBP passivation on the grain size of the underlying OIHP film. Figure 6.3 shows the top-view FESEM images and the corresponding distribution charts of the pristine and HBP passivated OIHP films at various concentrations. Evident in all samples, the as-prepared OIHP films show excellent compactness and surface coverage. In general, regardless of concentration utilized, the average grain size of HBP passivated OIHP films are larger than that in the pristine OIHP film. Particularly, the largest average grain size is found in the 5 mg/mL HBP passivated OIHP film of 347 nm while the smallest average grain size is found in the pristine OIHP grain size of 277 nm. Further increment in HBP concentration, however, does not result in larger grains whereby the average grain size of 337 and 329 nm in the 10 and 20 mg/mL HBP passivated OIHP films. The increased average grain size in the HBP passivated OIHP films could be attributed to the coarsening of grains promoted by the increased coordination between the Pb^{2+} ions with the passivation material [2].

Figure 6.3 FESEM image and grain size distribution of the (a & b) pristine, (c & d) 5 mg/mL, (e & f) 10 mg/mL and (g & h) 20 mg/mL HBP passivated OIHP films.

6.3.3 Optical and Electronic Studies

To investigate the impact of HBP passivation on the OIHP layer, UV–vis spectroscopy was employed. Specifically, for the investigation, pristine OIHP and various concentrations of HBP passivated OIHP films were deposited on glass substrates. As seen in Figure 6.4a, absorption intensity increases with the addition of HBP passivation with the largest absorption obtained by the 5 mg/mL HBP passivated OIHP film and the smallest absorption observed in the pristine OIHP film [34]. The increased grain size explains the increased absorption observed in the 5 mg/mL HBP passivated OIHP film.

As shown in Figure 6.1a, the HBP molecule can be considered as a Lewis base since it possesses both ketone and phenol groups [35]. Seeing that defects sites are often found at the OIHP/HTL interface, addition of the HBP film should, theoretically, reduce nonradiative recombination through effective passivation of the recombination sites via the donation of electrons from the HBP molecules to the under-coordinated Pb^{2+} trap states [14,35]. It is evident from Figure 6.4b that the addition of HBP, regardless of concentration, provides effective passivation of defects. With similar PL emission peak at 757 nm, the HBP passivated films showed increased PL intensities with the highest intensity observed in the 5 mg/mL HBP passivated film, approximately twice that observed in the pristine OIHP film. The lowered PL intensity in the 10 and 20 mg/mL HBP passivated OIHP films, compared to the 5 mg/mL HBP passivated film, could be due to the disproportionate employment of HBP molecules. With excessive amounts of passivation material utilized, the HBP film could induce more trap states at the OIHP/HTL interface instead [31]. Henceforth, it is essential to employ optimal concentration of passivation material such that paramount defect passivation is achieved.

Figure 6.4 (a) UV-vis absorbance and (b) PL spectra of the pristine and HBP passivated OIHP films at various concentrations.

6.3.4 Energy Band Level Alignment

To evaluate the effects of HBP passivation on the valence band maximum (E_{VBM}) and conduction band minimum (E_{CBM}) energy levels of the underlying OIHP film, UPS and UV-vis spectroscopy were engaged. Calculation of the E_{VBM} was conducted using the equation $E_{\text{VBM}} = -[21.22 - (E_{\text{cutoff}} - E_{\text{onset}})]$ for both the pristine OIHP and the HBP passivated OIHP films. Using the E_{cutoff} and E_{onset} values obtained from Figure 6.5a & b, the calculated E_{VBM} energy levels of the OIHP films with and without HBP are -5.74 and -5.72 eV, respectively. On the other hand, the band gap (E_g) of the as-prepared films was calculated using the Tauc Equation of $(\alpha h\nu) = A(h\nu - E_g)^{0.5}$ to which α , h , ν , and A represents the absorption coefficient, Plank constant, radiation frequency, and constant, respectively. Figure 6.5c shows the $(\alpha h\nu)^2$ against $h\nu$ plots of the pristine and the HBP passivated OIHP films. By extrapolating the curves across the energy axis, band gaps of the pristine and HBP passivated OIHP films were estimated to be 1.60 and 1.58 eV, respectively. With minimal difference in E_{CBM} in the pristine OIHP film of -4.12 eV and HBP passivated OIHP film of 4.16 eV, Figure 6.5d shows little influence of HBP passivation on the energy levels on the as-prepared OIHP absorber films. Hence, it is suggestive that the addition of HBP does not hinder both electron and hole transportation.

Figure 6.5 Enlarged (a) cutoff and (b) onset energy regions of the UPS spectra. (c) $(\alpha h\nu)^2$ against $h\nu$ plots of the pristine and HBP passivated OIHP films. (d) Band diagram of the complete OIHP device.

6.3.5 Device Performance and Reproducibility

Equipped with the passivation capabilities of the HBP film when deposited on the surface of the OIHP film, photovoltaic performances of the pristine and HBP passivated OIHP devices were investigated. Using the planar n-i-p structure, Figure 6.6a and Figure 6.6b show the schematic and cross-sectional image of the complete HBP passivated OIHP device. Table 6.1 records the photovoltaic parameters of the as-prepared OIHP solar devices obtained during J-V measurements at simulated solar conditions of 100 mWcm^{-2} at AM 1.5G. As seen in Figure 6.6c, the photovoltaic performances of all HBP passivated

OIHP device outperforms that of the pristine perovskite device. To illustrate, higher PCEs of 19.28, 18.64, and 18.25 % were obtained with the addition of HBP at respective concentrations of 5, 10, 20 mg/mL compared to the pristine OIHP device with lower PCE of 17.87 %. Figure 6.6d shows the IPCE spectra of the devices in which the integrated current densities are in good agreement with the J–V results of 20.7 and 20.2 mAcm⁻² for the 5 mg/mL HBP passivated and pristine perovskite devices, respectively. Stabilized power output was also carried out in which the HBP passivated perovskite devices show better photo-stability with average PCE of 18.2%, unlike the pristine perovskite device which has an average PCE of 16.6% after 120 s, as seen in Figure 6.6e & f, respectively. Unsurprisingly, hysteresis also saw improvement when 5 mg/mL of HBP molecules were deposited on top of the OIHP film. Calculated using the equation hysteresis index (HI) = $\frac{\text{PCE (reverse)} - \text{PCE (forward)}}{\text{PCE (reverse)}}$, HI obtained from the 5 mg/mL HBP passivated OIHP device is approximately 0.101 while HI of the pristine OIHP device saw larger HI value of 0.214 [36,37]. The smaller degree of hysteresis in the 5 mg/mL HBP passivated OIHP device could be attributed to the successful passivation of defects, reducing the susceptibility of trapping and detrapping of charge carriers thought to play a part in hysteresis behaviour [38].

Table 6.1 Photovoltaic parameters of as-prepared OIHP devices.

OIHP Device	V _{OC} (V)	J _{SC} (mAcm ⁻²)	FF	Champion PCE (%)	Average PCE (%)
Pristine	1.06	21.42	78.21	17.87	16.41
5 mg/mL HBP	1.10	21.95	79.38	19.28	18.77
10 mg/mL HBP	1.10	21.33	78.07	18.64	17.72
20 mg/mL HBP	1.10	21.34	77.49	18.25	17.71

Figure 6.6 (a) Device architecture and (b) cross-sectional SEM image of the HBP passivated OIHP device. (c) Champion J–V curves and (d) IPCE spectra of both pristine and 5 mg/mL HBP passivated OIHP devices. Stabilized photocurrent and power output as a function of time for the (e) 5 mg/mL HBP passivated and (f) pristine OIHP devices.

To understand the trends and device reproducibility of the solar devices with and without HBP passivation, 20 devices of each device configuration was conducted as seen in the

statistical distribution represented by Figure 6.7. It is evident that the addition of HBP, regardless of concentration employed, achieved superior efficiency attributed to the heightened V_{OC} and FF. Particularly, the highest average PCE was attained in the 5 mg/mL HBP passivated OIHP device of 18.77 % owing to the high average V_{OC} and FF of 1.11 V and 78.31, respectively. Unsurprisingly, pristine OIHP devices showed the poorest average PCE of 16.41 % with relatively low average V_{OC} and FF of 1.02 V and 75.4, respectively. Enhancement in V_{OC} and FF suggest effective defect passivation provided by the HBP molecules [39–41]. However, devices with higher concentrations of HBP showed reduced photovoltaic performances especially in V_{OC} . Decreased V_{OC} in the 10 and 20 mg/mL HBP passivated OIHP devices can be attributed to the increased interfacial recombination sites. Supported by the PL spectra represented by Figure 6.4b, introduction of high concentrations of HBP materials possibly introduced undesirable trap states at the OIHP/HTL interface. That being said, all HBP passivated OIHP devices exhibited enhanced photovoltaic performances and device reproducibility compared to the pristine OIHP devices. Improvements in V_{OC} and FF can be attributed to the superior passivation capabilities of the HBP molecules in which beneficial interaction occurred between the functional groups of HBP and the under-coordinated Pb^{2+} dangling bonds found on the surface of the OIHP crystals [39–41]. However, when the concentration of the HBP is too high, reductions in all photovoltaic parameters were observed, with major decrease in average V_{OC} . In good agreement with the previous characterizations, the decrease in V_{OC} suggests the introduction of undesired interface recombination sites when concentrations of utilized passivation material are too high. Decrease in FF can be explained by the increase in series resistance due to excessive use of HBP, retarding the electron transport process and thus impeding the performance of the OIHP solar device. Nonetheless, all passivated OIHP devices displayed superior photovoltaic parameters and reproducibility compared to pristine OIHP devices.

Figure 6.7 Statistical distribution of the photovoltaic parameters, specifically the (a) V_{oc} , (b) J_{sc} , (c) FF, and (d) PCE. Note that the empty square in each box plot represents the average value achieved.

6.3.6 Long-Term Stability

Besides the enhanced photovoltaic performances and reproducibility, addition of the HBP passivation film could improve device stability since the hydrophobic benzene ring found in the HBP molecule could act as a protective shield. When used at the OIHP/HTL interface, the HBP film could act as a moisture barrier to protect the underlying OIHP layer from the hydroscopic spiro-OMeTAD layer [2,42]. To investigate changes in hydrophobicities with the addition of HBP, contact angle measurements were conducted for the pristine OIHP film along with the HBP passivated OIHP films at concentrations of 5, 10, and 20 mg/mL. As seen in Figure 6.8, contact angle increases with increasing concentration of

HBP utilized. Specifically, the smallest contact angle was obtained between the water droplet and the surface of the pristine OIHP film of 49.4° while the largest angle was obtained in the 20 mg/mL HBP passivated OIHP film of 72.1° . This could be understood from the molecular structure of HBP whereby the oxygen atoms anchor the molecule to the Pb–I framework found in the OIHP structure through interaction with the under-coordinated Pb^{2+} ion, leaving the hydrophobic benzene ring tilted away from the perovskite layer to provide appropriate moisture protection [13,42]. The enhanced hydrophobic interaction of OIHP films after the introduction of HBP suggests improved stability against attack of humid air in which the HBP film shelters the underlying sensitive OIHP layer from moisture and air.

Figure 6.8 Contact angle measurements for both pristine and HBP passivated OIHP films.

In good agreement with the results obtained from the contact angle measurements, addition of the HBP interlayer tremendously improved the device stability, even when a small amount of 5 mg/mL was utilized. Stored in the dark and exposed to ambient air at 40% relative humidity, 5 perovskite devices of each composition without encapsulation were used for long-term stability analysis. As seen in Figure 6.9, each data point shows the average value represented by a filled circle symbol together with the standard deviation (error bars) obtained from the 5 devices. It is evident that the HBP passivated OIHP devices

exhibited much better long-term stability. In the absence of HBP, the pristine OIHP devices observed a large drop in average PCE to 84 % of its initial PCE after 120 days. On the other hand, the 5 mg/mL HBP passivated OIHP devices showed minimal decrease in average PCE, maintaining 93 % of its initial PCE even after 120 days. As seen in Figure 6.9c, pristine OIHP devices suffer tremendous decrease in average FF from 77.73 in day 1 to 66.83 in day 120. The average FF of the HBP passivated perovskite device, however, suffered small reduction after 120 days from 78.78 to 73.26. Minor losses in FF found in the HBP passivated perovskite device could be explained by the suppression of recombination at the perovskite/HTL interface, allowing efficient hole transportation and performance [13,43]. Furthermore, the enhanced hydrophobic interaction between the HBP and OIHP films supports improved stability against attack from ambient atmosphere to which the HBP layer acts as a protective coverage to the underlying OIHP layer.

Figure 6.9 Stability histogram of pristine and 5 mg/mL HBP passivated OIHP devices over 120 days, divided into their respective photovoltaic parameters of (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) PCE.

Note that the average (filled circle) and standard deviation (error bar) were calculated from 5 devices of each configuration.

6.4 Conclusion

In summary, deposition of the HBP film at the OIHP/spiro-OMeTAD interface demonstrated effective passivation to which reduction in nonradiative recombination and enhanced hole transportation resulted in significant improvements in V_{OC} and FF of the OIHP solar cells, respectively. When optimal concentration of HBP was employed, nonpareil PCE, reproducibility, and device stability was attained. To illustrate, the 5 mg/mL HBP passivated OIHP device achieved paramount PCE of 19.26 %, attributed to the heightened FF and V_{OC} attained. Excellent long-term stability was also exhibited to which 93 % of initial PCE was retained after 120 days in the absence of encapsulation. Therefore, this study demonstrates the significance of using a premeditatedly designed material to passivate the OIHP/HTL interface. By lowering the density of trap states and improving the charge transport between the OIHP and HTL layers, the use of suitable passivation materials acts as simple yet low-cost approach to simultaneously boost photovoltaic performances, reproducibility, and stability of OIHP solar devices.

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Chapter 7

Discussion and Future Work

In this chapter, the correlations between various chapters are brought together. Hypotheses established in chapter 1 are also substantiated and validated against the findings presented in chapters 4–7. Key findings and significance of the dissertation are also highlighted. Finally, opportunities derived from reconnaissance work which did not warrant a complete chapter are also shown.

7.1 Conclusions

Merits of low-cost, simple processibility, compatible energy level alignment, thermal and chemical stabilities, has crowned titanium dioxide (TiO_2) as the most popular electron transfer material in OIHP solar cell application. As a result, plenty of certified record efficiencies were achieved in TiO_2 ETL based devices. That being said, pristine TiO_2 as an ETL is far from ideal. To illustrate, the electron mobility in TiO_2 is a few magnitudes smaller than that in OIHP materials. Hence, transport of photogenerated electrons would take a longer time through the TiO_2 ETL than the bulk OIHP absorber itself. In addition, the existence of trap states such as low valence Ti^{3+} sites and oxygen vacancies at the surface of the TiO_2 ETL could increase recombination tendencies at the TiO_2 /OIHP interface. Numerous strategies have attempted to improve the intrinsic properties of TiO_2 ETL in OIHP solar cells while reducing the recombination rate at the interface. A universal approach is to introduce foreign atoms into the TiO_2 lattice whereby the introduction of dopants modifies the properties of the pristine ETL. In this thesis, Al and In were co-doped into the TiO_2 lattice where the improvements in TiO_2 photovoltaic parameters were investigated. While the above-mentioned method shows clear improvements in the optoelectronics of OIHP solar cells, efficiency and stability of devices remain unsatisfactory, especially in planar configurations. In addition, the use of heterogeneous ETL was developed to reduce the amount of trapped states on the surface of the TiO_2 based ETL via passivation using a thin SnO_2 film.

First, the influences of Al and In dopants on the compact TiO_2 (c- TiO_2) ETL in the mesoporous configuration are studied in Chapter 4. Comprehensive characterization such as UV-Vis spectrophotometry, impedance spectroscopy, and J-V measurements reveal superior optoelectronic properties of the co-doped film to which enhanced transparency is attributed to the addition of aluminium (Al), while increased charge transportation is due to the addition of indium (In). These improvements resulted in heightened short-circuit current (J_{sc}), fill factor (FF), and open-circuit voltage (V_{oc}), respectively.

That being said, the mesoporous configuration limits commercialization of OIHP solar cells due to the tedious fabrication process. Instead, synthesis of planar OIHP solar cells is facile. The lack of the mesoporous TiO_2 layer means reduced surface area, limiting charge transport efficiency. The mesoporous layer also reduces the occurrence of shunt pathways. Tin oxide (SnO_2) ETL based device demonstrates superior efficiency and stability owing to the high electron mobility and passivating characteristic. However, solution processed SnO_2 ETL based devices are unsuitable for commercialization due to the inconsistent device performance, with high susceptibilities to shunting pathway formations. When AlIn-TiO_2 (AITO) and SnO_2 are utilized together, the heterogenous ETL based devices exhibit unrivalled photovoltaic performances, stability, and reproducibility. This could be due the synergistic benefits which builds on the strengths of the individual ETLs, beyond that of homogeneous ETLs.

However, interfacial engineering at the ETL/OIHP interface itself is insufficient since the OIHP solar cell has a complex multilayer architecture, where recombination is not restricted to the ETL/OIHP interface. In particular, interfaces adjacent to the OIHP absorber and charge transport layers represent one of the largest limiting factors suppressing charge carrier collection and transport efficiencies. In chapter 5, we demonstrate the importance of passivation to reduce energetic losses and surface recombination at the OIHP/HTL interface. The use of 2-hydroxybenzophenone (HBP) molecules provides Lewis base passivation through intentional coordination of lone pair in the HBP molecules to the under-coordinated lead ions. Experimental results reveal improvements in power conversion efficiencies (PCEs) in the HBP passivated devices compared to the pristine OIHP devices. The enhancements are attributed to the reduction in surface defects and strengthened charge transport properties, further supported by the enhanced open-circuit voltage (V_{OC}) and fill factor (FF), respectively. Increase in contact angle between the OIHP surface and water droplet is also observed with the addition of HBP. The higher hydrophobicity could be attributed to the molecular structure of HBP. Oxygen atoms in the HBP molecules anchor to the under-coordinated Pb^{2+} ions in the OIHP film such that the hydrophobic benzene rings point away from the OIHP absorber.

As such, HBP provides moisture protection to the underlying OIHP layer from water and air attack, supplementing the long-term stability of the HBP passivated OIHP device.

7.2 Significant Contributions

Based on the studies carried out throughout the thesis, numerous novel findings and outcomes have been made as summarized below:

1. The direct impact of co-doping on the photovoltaic parameters of OIHP solar cells have been rarely reported. In chapter 4, we systematically showed the strengths of various dopants using a variety of characterization methods.
2. Demonstrates the use of heterogeneous ETL as a facile yet highly effective method to take advantage of various properties from various ETL compositions while, simultaneously, masking the shortfalls of individual films.
3. Confirms the importance of tailored interfacial engineering at various charge transport and OIHP interfaces whereby effective passivation significantly benefits the photovoltaic parameters and long-term stability of OIHP solar devices.
4. Reiterates the significance of optimization of passivation concentration whereby excessive use of passivation materials could greatly deteriorate device performance, stability, and reproducibility.

7.3 Reconnaissance Results and Future Work

7.3.1 Effects of Lewis acid Passivation and its Importance

Common passivation materials include molecules containing functional groups with Lewis acids and bases properties since defects found in OIHP solar cells are often ionic. Though we see an escalating number of studies employing Lewis base passivation, there is a huge

discrepancy in studies conducted on Lewis acid passivation [1–4]. However, it is important to passivate the Lewis base defects such as under-coordinated Γ^- , PbI_3^- antisite. Apart from poor device efficiency, stability, and reproducibility, iodine-rich defects could potentially migrate under applied field, producing ionic current and hysteresis [5–7]. By adding Lewis acid to the OIHP film, electrons from Lewis base defect states is accepted by the passivation material, reducing the amount electronic recombination centers. For example, Abate et al. added iodopentafluorobenzene on the surface of the OIHP film and reported successful passivation of the under-coordinated Γ^- , resulting in significant enhancement in V_{OC} and FF [5]. The use of a highly electron accepting passivation material, 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane, also demonstrated improvements in photovoltaic parameters whereby PCE improved from 15.3 to 18.1 % [7]. The authors attributed the improvements to the effective defect suppression whereby Kelvin probe force microscopy revealed homogenous surface potential across the perovskite film with the addition of F4TCNQ passivation, justifying the reduction in trapped states.

Here, we demonstrate the importance of passivating undercoordinated halide ions in minimizing carrier losses at the OIHP/HTL interface. By employing 4-chlorobenzene sulfonyl chloride (CBSC) as the Lewis acid passivation material, passivation of negatively charged defects were verified in the preliminary results, resulting in improved PCE. Interfacial passivation was conducted by depositing CBSC molecules dissolved in chlorobenzene on top of the annealed OIHP film, before annealing for another 10 mins to remove residual solvent. Chemical structure of the CBSC molecule is shown in Figure 7.1a. Although the chlorine (Cl) atoms found in the CBSC molecule have non-bonding valence electron pairs, the highly electronegative nature of the electron withdrawing chlorine atoms far outweigh the donation of electron density from the lone pair. As such, CBSC acts more like a Lewis acid than a Lewis base.

To understand the effectiveness of the passivated OIHP devices for photovoltaic application, current density against voltage (J–V) measurements tested at AM 1.5G illumination 100 mWcm^{-2} were conducted for the pristine and CBSC interface (CBSC-IN) passivated devices. The CBSC-IN OIHP solar device has a general configuration of FTO/

c-TiO₂/ SnO₂/ OIHP/ CBSC/ spiro-OMeTAD/ Au. Figure 7.1b represents the J–V curves of the CBSC passivated OIHP devices at various concentrations collected under reverse scan. Highest PCE was achieved in the 5 mg/mL CBSC–IN OIHP device, suggesting optimal concentration for photovoltaic performance. As seen in Table 7.1, the nonpareil photovoltaic performance in the 5 mg/mL CBSC–IN OIHP device attained short-circuit current density (J_{sc}) of 21.13 mAcm⁻², open-circuit (V_{oc}) of 1.03 V, FF of 78.53, and PCE of 17.03 %. It is notable that excessive use of CBSC passivation is detrimental for device performance possibly owing to the introduction of undesired trapped sites as resulting in lower V_{oc} and FF values, respectively. Given these points, use of optimal concentration of passivation material is paramount in effective defect passivation for superior device performance. Unsurprisingly, CBSC–IN passivation has little effect to the absorbance in absorbance intensity of the underlying film, as seen in Figure 7.1c. On the other hand, the superior performance in the CBSC–IN OIHP devices are due to the significant improvement in FF. As seen in Figure 7.1d, greatest passivation was attained in the 5 mg/mL CBSC–IN OIHP device while. When excessive amount of CBSC molecules is deposited on top of the OIHP film, photoluminescence (PL) intensity decreases, indicating reduced passivating capabilities. Excessive interfacial material act as trap states, explaining the reduced FF in the 7 mg/mL CBSC–IN OIHP device.

Figure 7.1 (a) Chemical structure of a CBSC molecule. (b) J–V, (c) UV–vis absorbance, and (d) PL spectra of the pristine and CBSC–IN OIHP devices at various concentrations.

Table 7.1 Photovoltaic parameters of the pristine and CBSC–IN OIHP devices.

OIHP device	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
Pristine	21.12	0.99	76.33	16.00
3 mg/mL CBSC-IN	21.02	1.01	78.19	16.64
5 mg/mL CBSC-IN	21.13	1.03	78.53	17.03
7 mg/mL CBSC-IN	21.29	1.02	76.34	16.51

To confirm the presence and effects of CBSC–IN passivation, x-ray photoelectron spectroscopy (XPS) measurements were carried out on the as-prepared OIHP films. Figure

7.2a shows the deconvoluted Cl characteristic peaks at 200.9 and 201.3 eV representing the Cl 2p_{3/2} and 2p_{1/2} peaks. The lack of Cl peak in the pristine OIHP film unlike CBSC-IN OIHP film strongly supports the successful addition of CBSC molecules. Successful incorporation of the CBSC molecules is further affirmed by the XPS spectra of the O 1s peaks. As seen in Figure 7.1db, peak intensity of the CBSC-IN OIHP film is much higher than the pristine OIHP film with deconvoluted peaks at 532.6 eV which represents the O²⁻ ions at intrinsic sites from the lattice (O_{lat}) and another peak at 533.2 eV which represents oxygen vacancies and loosely bound oxygen that was adsorbed onto the surface of the film. Note that the O_{abs} peak is prominent in the CBSC-IN OIHP film. This could be due to the hydrophilic character of the CBSC molecules. When deposited on top of the OIHP film, the CBSC molecules unavoidably adsorb more moisture from the ambient condition during testing, explaining the higher intensity.

The highly electronegative chlorine atoms in the CBSC molecule inductively withdraw electron density from the sulfur (S) atom within the sulfonyl group (R-S(=O)₂-R'), leaving behind a partial positive charge on the sulfur element. Hence, the sulfur atom acts as an electron acceptor to form coordination bonds with negatively charged defects such as Pb-I antisite (PbI₃⁻) and/or undercoordinated I⁻ ions. Due to the electron accepting nature of sulfonyl functional group, we postulate that CBSC acts as a Lewis acid to adduct with negatively charged defects. Figure 7.2c & d shows the signals of the lead (Pb) 4f and iodine (I) 2p peaks, respectively. The Pb element is represented by 2 main peaks namely, Pb 4f_{7/2} and Pb 4f_{5/2} at respective binding energies of 138.2 and 143.3 eV. On the other hand, the I element is represented by 2 main peaks namely, I 3d_{5/2} and Pb 4f_{3/2} at respective binding energies of 619.2 and 630.6 eV. With the reduction in peak intensity for both Pb and I spectra in the CBSC-IN OIHP film, it is clear that the addition of CBSC molecules at the OIHP/spiro-OMeTAD do passivate the defects. It is interesting to note that no metallic Pb (Pb⁰) peaks were found in the CBSC-IN OIHP films while Pb⁰ peaks at 136.8 and 141.5 eV are present in the pristine OIHP film, further justifying the effectiveness of CBSC passivation.

Figure 7.2 XPS spectra of the pristine and 5 mg/mL CBSC-IN OIHP devices, specifically (a) deconvoluted Cl 2p, (b) deconvoluted O 1s, (c) Pb 4f, and (d) I 3d elements.

7.3.2 Passivation at Grain Boundaries compared to Interfaces

Although the effects of defects found at interfaces are relatively straightforward, such is not the case for grain boundaries (GBs) since the role of GBs are contradictory and unclear. Several studies have indicated increased non-radiative recombination at GBs while others argued that aggregation of PbI₂ at GBs encourages defect passivation, reducing the susceptibility of non-radiative recombination instead [8–11]. That being said, works regarding passivation of GBs have shown tremendous enhancement in photovoltaic performance and device stability. To date, several materials have been tested, such as the use of cations, polymers, and Lewis base/acids to which these additives are commonly added to the GBs via entry with the perovskite precursor solution or antisolvent [12–15, 27–30]. For example, Bi et al. added poly (methyl methacrylate) (PMMA) to the

antisolvent to which passivation of PbI_2 defects resulted in negligible hysteresis, and elevated V_{OC} and FF from 1.10 to 1.14 V and 0.74 to 0.78, respectively [16]. Remarkable stability of 3.3 % decay were also observed in the unsealed passivated device.

Here, we hope to unravel the contribution of interfacial passivation and GB passivation in OIHP solar cells by comparing their effects using various characterization techniques. To investigate and compare the effects of grain boundary passivation compared to interfacial passivation, CBSC molecules were deposited at the GBs and OIHP/HTL interface (section 7.3.1), respectively. In both cases, CBSC were utilized as the Lewis acid passivation material to which CBSC molecules act as electron acceptors and bind to negatively charged undercoordinated halide ions and Pb–I antisite defects (PbI_3^-). GB passivation was conducted 15 s into the second step of the spin coating procedure whereby CBSC molecules were dissolved in the chlorobenzene antisolvent and dropped onto the OIHP film during antisolvent treatment to form the CBSC grain boundary passivated (CBSC–GB) OIHP film. Interfacial passivation, on the other hand, was conducted by depositing CBSC molecules dissolved in chlorobenzene on top of the annealed OIHP film (section 7.3.1). Even though the same passivation material and concentration of 5 mg/mL were employed for both passivation methods, chemical interaction between the CBSC molecules with the GBs and interface can vary greatly. This could result in dissimilar properties and vastly different photovoltaic performances.

Figure 7.3a&b represents the top-view field emission scanning electron microscope (FESEM) morphologies along with their respective grain size histograms (Figure 7.3c&d). Average grain size is larger in the CBSC–GB OIHP films of 356 nm compared to the CBSC–IN OIHP film of 310 nm. Likewise, cross-sectional FESEM images of the revealed that the thickness of the CBSC–GB OIHP film is larger. As seen in Figure 7.3e&f, it is evident that thicknesses of various layers surrounding the OIHP film remain relatively consistent across the various configurations while the thicknesses of the OIHP layers differ considerably. Hence, results obtained from FESEM suggest that CBSC passivation at the GBs greatly influence the nucleation and growth of the OIHP film as compared to the CBSC–IN OIHP film.

Figure 7.3 FESEM images and respective histograms of the (a&c) 5 mg/mL CBSC-IN and (b&d) 5 mg/mL CBSC-GB OIHP films. Cross-sectional FESEM of the (e) 5 mg/mL CBSC-IN and (f) 5 mg/mL CBSC-GB OIHP devices.

This is in good agreement with the higher absorbance intensity in the CBSC-GB OIHP film, as seen in Figure 7.4a. Hence, adding CBSC molecules to the GBs greatly increases the grain size and absorption, which should also improve the J_{sc} values of the corresponding devices. Figure 7.4b, however, shows higher PL intensity in the CBSC-IN OIHP film suggesting stronger defect passivation when CBSC molecules are added to the OIHP/spiro-OMeTAD interface compared to the GBs.

Figure 7.4 (a) UV-vis absorbance, and (b) PL spectra of the CBSC-IN and CBSC-GB OIHP devices.

XPS measurements were conducted on the 5 mg/mL CBSC-GB and 5 mg/mL CBSC-IN OIHP films. Figure 7.5a shows the deconvoluted Cl 2p peak while Figure 7.5b shows the deconvoluted O 1s peak, indicating successful incorporation of the CBSC molecules is regardless of method of deposition. It is interesting to note the O_{abs} peak is more prominent in the CBSC-IN OIHP film. This could be because the hydrophilic CBSC molecules are less exposed to moisture in the CBSC-GB OIHP film, as such showing little oxygen adsorption. Figure 7.1c & d shows the signals of the lead (Pb) 4f and iodine (I) 2p peaks, respectively. Extent of passivation is higher in the CBSC-IN OIHP film compared to the CBSC-GB OIHP film as evident from the smaller Pb and I peak intensities, in good agreement with the higher PL intensity. Hence, it is expected that the CBSC-IN OIHP device achieves higher FF value while the J_{SC} value should be higher in the CBSC-GB OIHP device.

Figure 7.5 XPS spectra of the CBSC-IN and CBSC-GB OIHP films, specifically the (a) deconvoluted Cl 2p, (b) deconvoluted O1s, (c) Pb 4f, and (d) I 3d peaks.

7.4 Recommendations for Future Work

1. Design an equation comprising on various the most important factors regarding ETL material selection such as electron mobility, energy level alignment, transparency since there are multiple factors affecting the effectiveness of the ETL for OIHP solar cells. By having this equation, it would allow researchers to better optimize the ETL through well-designed experiments.

2. Draw correlations with various critical ETL factors to photovoltaic parameters for clear understanding and significance of ETL metrics in OIHP solar cell. This would allow researchers to better optimize the OIHP device through intentional tuning.

3. Apply passivation layers as possible encapsulation materials to improve stability for both thermal and humidity protection of OIHP solar cell, without compromising on device performance. This would greatly encourage the commercialization road map for OIHP solar cells

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