Impact of metal oxide/bulk-heterojunction interface on performance of organic solar cells

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Impact of Metal Oxide/Bulk-heterojunction Interface on Performance of Organic Solar Cells

WU Zhenghui

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Principal Supervisor: Prof. ZHU Furong

Hong Kong Baptist University

July 2015
DECLARATION

I hereby declare that this thesis represents my own work which has been done after registration for the degree of PhD at Hong Kong Baptist University, and has not been previously included in a thesis or dissertation submitted to this or any other institution for a degree, diploma or other qualifications.

Signature:

Zhenghui WU

July 2015
Abstract

Organic photovoltaics have shown much promise as an alternative photovoltaic technology for application in low-cost, large-scale and flexible solar cells. The application of metal oxides in organic solar cells (OSCs) and the impact of the properties of metal oxide/organic hetero-interfaces on cell performance have attracted a lot of attention. The metal oxide/organic interfaces have a crucial impact on interfacial charge transfer, charge collection and the overall device performance. This thesis is aimed at clarifying the principal interfacial phenomena occurring at the metal oxide/organic hetero-interfaces as well as effective engineering of those interfacial properties in OSCs. Photo-generated electrons and holes undergo different recombination processes, e.g., bimolecular recombination and trap-assisted recombination, before being collected by the electrodes in OSCs. Light intensity-dependent current density–voltage (J–V) characteristics of OSCs were analyzed to study the effect of recombination on charge collection efficiency. Effect of metal oxide/organic hetero-interfaces on charge transfers at organic/electrode interface was analyzed using transient photocurrent (TPC) measurements. Light intensity-dependent J–V characteristics and TPC characteristics were applied to explore the charge recombination dynamics in OSCs with a metal oxide interlayer. This project concentrated on an in-depth investigation of the physics and the interface phenomena such as interfacial exciton dissociation, charge recombination processes, charge collection and interface engineering for high performing OSCs.

The fundamentals about light intensity-dependent J–V characteristics for OSCs were summarized. The relationship between the charge recombination dynamics and light intensity-dependent J–V characteristics in OSCs were developed. Light intensity-dependent $J_{SC}$, $V_{OC}$ and
FF in OSCs made with different bulk-heterojunction (BHJ) systems of PTB7:PC$_{70}$BM, PTB7-Th:PC$_{70}$BM and PNB4:PC$_{70}$BM were investigated. It is found that bimolecular recombination is the most prominent factor limiting the performance of OSCs. For freshly made OSCs fabricated based on the commercial polymers, e.g. PTB7 & PTB7-Th, and the new polymer PNB4 synthesized in-house, the trap-assisted charge recombination process in the BHJ active layer plays a relatively small role. This suggests that reducing the bimolecular recombination in OSCs through selecting proper materials and device structures is crucial for enhancing the power conversion efficiency (PCE) of OSCs. In this work, device structures which enable reducing bimolecular recombination in OSCs were investigated.

The effect of ZnO interlayer at the interface between BHJ and Al cathode on the performance of PTB7:PC$_{71}$BM based OSCs was studied by a combination of theoretical simulation and experimental characterization techniques, e.g., using light intensity-dependent $J$–$V$ characteristic and $TPC$ measurements etc. It shows that ZnO interlayer has a profound effect on the performance of the PTB7:PC$_{70}$BM-based OSCs, although it does not have a significant influence on the maximum absorptance in the active layer. The origin of the improvement in the cell performance is associated with the efficient charge collection due to the favorable exciton dissociation at the electrode/active layer interface. It is shown that the presence of the ZnO interlayer allows using a thinner active layer without moderating the absorption in the optically optimized control OSCs without the ZnO interlayer. OSCs with a ~10 nm thick ZnO interlayer are found to be favorable for the efficient charge collection, and thereby improving the cell performance. The $TPC$ measurements also reveal that the dissociation of excitons at the metal/organic interface of regular OSCs hinders the electron collection. The unfavorable interfacial exciton dissociation can be removed by interposing a ZnO interlayer at the Al/organic
interface, thus bimolecular recombination at the electrode/active layer interface can be reduced for improving the charge collection efficiency. PCE of the OSCs using ZnO interlayer was 6.5%, which is about 20% higher than a control cell (5.4%), having an identical device configuration without a ZnO interlayer.

Solution-processed anode interlayer, a mixture of solution-processed MoO$_X$ and PEDOT:PSS, was adopted for application in inverted PTB7:PC$_{71}$BM-based OSCs. The ratio of MoO$_X$ to PEDOT:PSS in the mixed solution was optimized for achieving the best cell performance. A PCE of 7.4% was obtained for OSCs with an optimal MoO$_X$-PEDOT:PSS based interlayer, interposed between the BHJ active layer and Ag anode, which means 10% enhancement over the PCE of control cell made with an evaporated MoO$_X$ interlayer. Light intensity-dependent $J$–$V$ characteristics implied that the bimolecular recombination in OSCs with a MoO$_X$-PEDOT:PSS interlayer was reduced. $TPC$ measurements showed that the favorable exciton dissociation occurs at the organic/MoO$_X$ interface for the inverted OSCs. The favorable interfacial exciton dissociation generates an electrical field within a very small space near the interface, contributing significant additional photocurrent when the effective bias across the active layer in the OSCs is low, and thereby assisting in an efficient charge collection at the organic/electrode interface. In addition to the improvement in the cell performance, the solution-processed MoO$_X$-PEDOT:PSS interlayer does not require a post-annealing treatment, which is beneficial for application in solution-processed tandem and flexible OSCs.
Acknowledgement

First, I would like to express my genuine gratitude to my supervisor Prof. Furong Zhu, for providing me with the continuous support and patient guidance in my research work and writing of this thesis during my PhD study. I would also thank him for providing me with the tremendous opportunity to take part in the international research activities related to organic electronics. I have also benefited a lot from his guidance in the precise attitude for academic research. Without his selfless support, this thesis would have never been possible.

I would also like to express my sincere gratitude to the members from our research group: Dr. Hoi Lam Tam, Dr. Wing Kin Chan, Dr. Bo Wu, Dr. Qingyi Yang, Mr. Wing Hong Choi, Mr. Hanxiao Liu, Mr. Yanlian Lei, Miss Weixia Lan and Mr. Min Hsuan Lee, for the stimulating discussions and close cooperation in this research work, and for the great fun we have had in the last four years. This is a warm and loving family.

I would like to thank the people from the Department of Physics. Great acknowledgements go to my co-supervisor Prof. Kok Wai Cheah. Special thanks also go to: Mr. Leung Siu Cheong, Benson, Ms. Li Yuen Yee, Eve, Mr. Tsang Kin Wa, Adam and Mr. Luk Yu Man, Raymond for the technical and administrative support provided

I would also like to acknowledge all the members from Prof. Wenjing Tian’s group in Jilin University, Prof. Man Sing Wong and Dr. Bao Wang from the Department of Chemistry, for their support on experimental techniques and synthesis of functional materials. Finally, I would like to express my gratitude to my family for giving me continuous encouragement for my pursuit in academic research.

Zhenghui Wu
July 2014, Hong Kong
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Abbreviations

OSC                                  Organic solar cell
ZnO NPs                                Zinc oxide nano-particles
ITO                                    Indium Tin Oxide
PEDOT: PSS                            Poly (3, 4-ethylenedioxythiophene) poly (styrenesulfonate)
Al                                       Aluminum
MoO₃                                    Molybdenum oxide
Ag                                       Silver
PC₇₁BM                                  [6, 6]-phenyl-C71-butric acid methyl ester
PCBM (PC₆₁BM)                          [6, 6]-phenyl-C71-butric acid methyl ester
VASE                                    Variable Angle Spectroscopic Ellipsometer
P3HT                                    Poly (3-hexylthiophene)
PTB7                                    Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6
diy][3-fluo-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]]
PCDTBT                                  Poly[N-9-heptadecanyl-2,7-carbazole-alt-5,5-(4,7-di-2-thienyl
2,1,3-benzothiadiazole)], Poly[[9-(1-octynonyl)-9H-carbazole -2,7diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl]
PFN                                    Poly [(9,9-bis(3'-N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-
(9,9–dioctylfluorene)]
PCE                                    Power conversion efficiency
AFM                                    Atomic force microscope
J-V/I-V                                Current density to voltage/current to voltage
UV                                      Ultraviolet
TPC                                    Transient photocurrent
PV                                      Photovoltaic
HOMO                                    Highest occupied molecular orbitals
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<th>Abbreviation</th>
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<tr>
<td>$V_{oc}$</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>ETL</td>
<td>Electron transport layer</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent conducting oxides</td>
</tr>
<tr>
<td>$J_{sc}/I_{sc}$</td>
<td>Short circuit current density/ short circuit current</td>
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<td>$IPCE (EQE)$</td>
<td>Incident photon-to-electron conversion efficiency</td>
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<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbitals</td>
</tr>
<tr>
<td>HTL</td>
<td>Hole transport layer</td>
</tr>
<tr>
<td>$FF$</td>
<td>Fill factor</td>
</tr>
<tr>
<td>DCB</td>
<td>Dichlorobenzene</td>
</tr>
<tr>
<td>CB</td>
<td>Chlorobenzene</td>
</tr>
<tr>
<td>DIO</td>
<td>1, 8-octanedithiol</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square</td>
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<tr>
<td>$O_2$</td>
<td>Oxygen</td>
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Chapter 1

Introduction

1.1 Background and Motivation

As predicted by the International Energy Agency, human energy consumption will continue to rise, especially in the developing countries as shown in Fig. 1.1. In the past several decades, energy supply in the world was mainly supported by natural energy resources of fossil fuels such as coal, natural gas and oil. Energy resources have expanded into many categories which can be seen in Fig. 1.2. However, these fossil fuels take a long time to form and are considered to be limited energy resources with a risk of being unsustainable in the near future when it is unable to meet the energy demands of the society. A detrimental side effect of using these energy resources includes air pollution generated by the burning of these fuels. China for many years has suffered from serious air pollution and this has been the flip side of the past decade’s economic boom. Another harmful by-product of burning fossil fuels is the release of carbon dioxide which is a key factor that contributes to global warming. Due to global warming effect, the annual average temperature at the Earth’s poles has been increasing since 1980s. Another consequence of global warming is shrinking of the Arctic sea ice area (reducing to the lowest recorded surface area of 4.1 million square kilometers in Aug 2012) referenced from the National Aeronautics and Space Administration (NASA). Such climate changes tend to bring more disasters such as storms and droughts. The limited resources and harmful side effects of these fuels have pushed people to seek alternatives to meet their energy demands. As shown in Fig. 1.2, nuclear energy is one of the alternatives which have been widely used due to its
sufficiency and cleanliness. However, there are high risks associated with nuclear energy and can be seen from accidents such as the nuclear disaster in Fukushima Japan in 2011.

![Global energy demand projections from International Energy Agency in different areas.](image1)

**OECD**: Organization for Economic Cooperation and Development.

![Different sources for energy supply nowadays.](image2)

Fortunately, a lot of safe and environmentally friendly alternatives have been discovered by scientists. The several most important alternatives can be seen in Fig1.2. The amount and applications of some environmentally friendly energy resources such as biomass and geothermal
energy are limited. Electricity generated by wind has wide application due to its flexibility but it is often unstable. Solar energy can be seen as the most attractive source of renewable energy based on both its abundance and green energy. The photovoltaic (PV) device is one of the favorite devices for solar energy harvesting and has undergone much research in recent years. PV devices have been largely applied in power generation and we can see the evolution of the global PV cumulative installed capacity\(^4\) in Fig. 1.3.

![Fig. 1.3: Evolution of global PV cumulative installed capacity 2010-2013. APAC: Asia Pacific and Africa, MEA: Middle East, RoW: Rest of the World.](image)

The word “photovoltaic” combines the meaning of “photon” and “voltage” and the energy from solar irradiance can be directly converted to electricity by a photovoltaic cell, i.e. solar cell. Tremendous studies have been focused on various kinds of solar cells fabricated from inorganic and organic semiconducting materials over the last several decades. Over the past 35 years, the PCE of solar cells has increased dramatically (see Fig. 1.4). In 1954, the first practical photovoltaic cell based on silicon p-n junction was invented at Bell Laboratories by D. Chapin, C. S. Fuller and G. Pearson\(^5\). Though over 40% efficiency of inorganic material based solar cells
have been achieved\textsuperscript{6}, it is still too costly to be widely accepted in the industry. The fabrication of inorganic photovoltaic devices is usually processed under high temperature and ultra-high vacuum. It also costs too much time to complete the fabrication, resulting in a high price of inorganic solar cells. Some disadvantages include surface area restrictions, design inflexibility for certain applications limit the use of inorganic solar cells in the industry. Flexible thin film PV cells have already been applied in commercial goods and industry products. Fig. 1.5 shows one example of thin film PV product from Hanergy online shop (http://www.hanergyshop.com/). It is a folding solar cell charger for portable electronic devices. So far most of the thin film solar cell commercial products are made from Copper-Indium-Gallium-Selenium (CIGS) compounds. However metal Gallium is toxic while Indium is too expensive due to its scarcity. All these factors have been propelling the research of a new generation of PV cells. The new generation of PV cells, organic solar cells (OSCs), is very promising due to the advantages over their inorganic counterparts including:

- Solution processability of OSCs enables economies of scale, lowering the cost of manufacturing.
- Being light weight and flexible makes it easier to transport and install solar panels and also creates better design opportunities for new solar cell applications.
- There are no toxic byproducts of OSCs as these materials can be degraded to carbon dioxide and water. There is also an abundant supply of these natural resources (carbon, hydrogen and oxygen) on earth to synthesize organic materials for PV applications.
- With the easily controlled optical and electrical properties of organic materials, the application of OSCs can be extended into different industries.
Fig. 1.4: Best research-cell efficiencies of different solar cells (from NREL).

Fig. 1.5: Folding solar cell charger made by Hanergy Thin Film Power Group Ltd.
1.2 Frontiers of Organic Photovoltaics: Opportunities and Challenges

Significant improvements in OSCs have been made since the discovery of the PV effects of chlorophyll in plants by C. W. Tang in 1975\(^7\), in which a 0.001\% efficiency of OSC was shown. In the next decade after this discovery, the \(PCE\) of OSCs was never close to 1\% though a lot of new organic materials have been tried. The next breakthrough was also made by C. W. Tang by introducing a bilayer heterojunction consisting of one p-type and one n-type organic semiconducting materials\(^8\). With the concept of combining the n-type and p-type semiconductors, a bulk-heterojunction was introduced, in which the two types of semiconducting materials were mixed together instead of one depositing onto the other. Thus the \(PCE\) of OSCs was quickly boosted to 5\% by blending the p-type polymer P3HT and the fluorine derivative PCBM to form a bulk-heterojunction\(^9\). This is almost the upper limit of the \(PCE\) of OSCs based on the most classical blend system P3HT: PCBM. Even now, most of the labs in the world cannot achieve such high performances using P3HT: PCBM bulk-heterojunction. Later people found that the HOMO level of polymers was closely related to the \(V_{oc}\) of OSCs\(^10\), and polymers with a deep HOMO level are desired for achieving high \(V_{oc}\). On the other hand, the narrow absorption spectrum and high HOMO level in P3HT limits the photocurrent and \(V_{oc}\) in P3HT based OSCs. Guided by this rule and assisted by solvent additives, the OSCs based on new p-type polymer PCDTBT with a deep HOMO level achieved high \(V_{oc}\) (\(>0.9\)V) and high \(PCE\) (\(\sim7\)%\(^11\)). Then researchers noticed that the deep HOMO level will give high \(V_{oc}\), but on the other side, it limits the amount of light absorbed and thus photocurrent in OSCs. In 2010, PTB7, a p-type polymer with more suitable HOMO level was synthesized by Yongye Liang\(^12\) and the \(PCE\) OSCs based on this polymer increased to 7.4\% by using a simple device structure. Nowadays, single junction
OSC\(\text{\textregistered}\)s based on the newest polymer without complicated device structures approach \(PCE\) of \(>10\%\).\(^{13}\)

To improve the performances of OSC\(\text{\textregistered}\)s further or to explore new applications of OSC\(\text{\textregistered}\)s, new and smart device structure designs have also been introduced and studied, in addition to the introduction of more suitable polymers for OSC\(\text{\textregistered}\)s. For example, TiO\(_2\) was used as a cathode buffer layer in OSC\(\text{\textregistered}\)s to improve both the internal quantum efficiency to 100\% and the stability of PCDTBT based OSC\(\text{\textregistered}\)s\(^{14}\). Inverted device structures, in which the properly modified ITO contact worked as the cathode and metal top electrode worked as the anode, were first introduced to extend the lifetime of OSC\(\text{\textregistered}\)s in 2004\(^{15}\). The PBT7 based inverted OSC\(\text{\textregistered}\)s with \(PCE\) of \(>8\%\) have been reported\(^{16}\). The new cathode interfacial material PFN was then designed and applied for use in PTB7 based inverted OSC\(\text{\textregistered}\)s to further improve the \(PCE\) to 9.2\%\(^{17}\). Two cells with different absorption spectra were combined in series by an interconnection layer to form tandem solar cells. In 1982, the tandem OSC was invented by Joseph J. Hanak\(^{18}\). J. G. Xue et al\(^{19}\) introduced the first tandem OSC which easily outperformed the classic P3HT based single junction solar cell and achieved an efficiency output of over 5.5\%. More recently, OSC\(\text{\textregistered}\)s with \(PCE\) as high as 12\% reported by the solar cell company Heliatek were also based on tandem structure\(^{20}\). Flexible OSC\(\text{\textregistered}\)s\(^{21}\) with large surface areas and semitransparent OSC\(\text{\textregistered}\)s\(^{22}\) have also been investigated to make OSC\(\text{\textregistered}\)s suitable for new applications.

Though great success has been made on OSC\(\text{\textregistered}\)s, there is still a long way before the relevant technologies can bring about practical benefits. The highest \(PCE\) recorded is at 12\% which is quite challenging to replicate in the industry. There is still much room for research and improvement not only in terms of efficiency, but also in its design, lifetime and efficient operation of different types of OSC\(\text{\textregistered}\)s. Therefore, the basic physics in OSC\(\text{\textregistered}\)s and the mechanisms
behind these designs and treatments still require additional thorough studies in order to be used as a guidance to improve its stability and efficiency. In this thesis, studies were focused on the device physics to better understand the principal interfacial phenomena occurring at the metal oxide/organic hetero-interfaces, including the charge transfer dynamics at the organic active layer/metal oxide interfaces and the effective engineering of those interfacial properties for performance enhancement of OSCs.

1.3 Thesis Objectives

The performance of OSCs is hampered by limited light absorption. Due to the low charge mobility in organic materials, there exists a mismatch between the charge transport scale and the optical absorption length. The thickness of the active layer in OSCs is limited due to poor charge transport, resulting in insufficient light absorption. The optimized thickness of the organic active layer is a tradeoff between light absorption and the efficiency of charge collection. Apart from the efficient absorption in the OSCs, high charge collection efficiency at the organic/electrode is also critical for the performance of OSCs.

Various approaches have been reported for achieving high performing OSCs, including incorporating metal nanoparticles, surface plasmonic structures and a textured substrate template in OSCs to boost light absorption. Utilization of photonic structures in OSCs is widely used. With photonic structures, enhancement of light absorption in the organic active layer can be achieved without the increase in the active layer’s thickness. The use of a metal oxide interlayer between an organic active layer and a metal electrode is another approach for improving the cell performance which is often adopted in planar OSCs. In addition, the surface of the metal oxide interlayer can be modified and optimized to facilitate an efficient charge collection at the
organic/electrode interface. On the other hand, charge collection efficiency in OSCs is a complicated issue since it is affected by numerous factors. Typical approaches to improve the charge collection efficiency in OSCs include morphology control of an organic active layer, smart design of organic active materials and effective interfacial engineering.

The use of metal oxides for application in OSCs has been widely reported. Various working mechanisms were introduced to explain the enhancement in PCE of OSCs with the presence of metal oxide interlayers in different cases. In this thesis, the impact of metal oxide/bulk-heterojunction interface on performance of conventional and inverted OSCs was analyzed through a comprehensive study. This includes the effect of metal oxide interlayers on light absorption, charge recombination and charge transfer dynamics at the organic/electrode interface in OSCs. Finally, the principal interfacial phenomena occurring at the metal oxide/organic hetero-interfaces as well as effective engineering of those interfacial properties for attaining high performing OSCs are discussed.

In conventional devices, a 10 nm thick solution processed ZnO NPs interlayer is interposed between an organic active layer and a metal (e.g., Al) cathode. Numerical simulation based on optical admittance analyses was applied to study the effect of ZnO cathode interlayer on the optical properties of OSCs. The effect of ZnO cathode interlayer on charge recombination was analyzed using light intensity dependent $J-V$ characteristics of OSCs made with and without ZnO cathode interlayer. In inverted devices, solution processed anode interlayer, a mixture of solution-processed MoO$_X$ (sMoO$_X$) and PEDOT:PSS, was interposed between the organic active layer and Ag anode. The effect of sMoO$_X$-PEDOT:PSS mixture and evaporated MoO$_X$ (eMoO$_X$) on the performance of inverted OSCs was investigated. Light intensity dependent $J-V$ characteristics of the OSCs were measured to study the charge recombination and collection in
the inverted OSCs. Transient photocurrent measurements were applied to study the impacts of metal oxide interlayer on the charge transfer dynamics at the interface between the organic active layer and electrode in OSCs. The aims of this thesis are summarized below and the processes to study these problems are shown in Fig. 1.6.

Objectives:

1) To better understand the impact of metal oxide interlayers on light absorption, charge recombination and charge transfer dynamics in OSCs.

2) To study the principal interfacial phenomena occurring at the metal oxide/organic hetero-interfaces, and

3) Effective engineering of those interfacial properties for attaining high performing OSCs.

![Diagram](image)

**Fig. 1.6: Flow of research work in this thesis.**

**1.4 Organization of This Thesis**
There are seven chapters in this thesis. Chapter 1 introduces the perspectives of energy revolution and the motivation of the research on OSCs carried in this thesis. The advantages, challenges and the recent development of OSCs are also discussed in Chapter 1, followed with the objectives of this research work. Chapter 2 introduces the fundamental knowledge of OSCs. The charge transport and energy diagram in organic semiconducting materials are briefly reviewed, followed by the introduction of excitonic processes in OSCs under illumination. More specifically, the background of oxide interlayer, e.g., ZnO and MoOx, and their interfacial engineering for application in OSCs are reviewed.

Chapter 3 describes the experimental details including materials processes, device fabrication, characterization, and theoretical simulation. The details of the device fabrication processes include material formulation, substrate cleaning, thin film deposition by spin-coating and thermal evaporation. The $J-V$ characteristics and incident photon-to-electron conversion efficiency ($IPCE$) of the devices were measured. The surface morphology of the function layers was examined using atomic force microscopy. Variable angle spectroscopic ellipsometry (VASE) was used to determine the optical properties of materials. Light intensity-dependent $J-V$ characteristics and transient photocurrent ($TPC$) of the devices are measured. The basic principles of optical admittance analysis are also discussed.

The relevant theories on charge collection and recombination in OSCs are summarized in chapter 4. The charge recombination dynamics and charge collection behaviors in OSCs, made with some commercial polymers of PTB7 & PTB7-Th and new polymer PNB4, was analyzed systematically using light intensity-dependent $J-V$ characteristics. The information on trap-assisted recombination and bimolecular recombination processes in OSCs provides useful insight in assisting with device design and interfacial engineering for improving the PCE of OSCs.
In chapter 5, the effects of ZnO interlayer between organic active layer and Al cathode on the performance of PTB7:PC\textsubscript{70}BM based OSCs were studied by theoretical simulation and experimental characterization. 20% increase in \textit{PCE} of the OSCs with a ZnO interlayer was observed compared to that of a structurally identical control cell without a ZnO interlayer. The experimental results and optical simulation revealed that the presence of a ZnO interlayer had two effects: (1) ZnO interlayer allowed improving light absorption in a thinner organic active layer compared to the optically optimized control cell that required a thicker active layer, (2) ZnO interlayer helped to reduce the bimolecular recombination processes at the organic/electrode interface, and therefore improved charge collection efficiency.

The results of inverted PTB7:PC\textsubscript{70}BM OSCs with a solution-processed MoO\textsubscript{X}-PEDOT:PSS anode interlayer are discussed in chapter 6. Significant improvements in the performance of OSCs with an optimal MoO\textsubscript{X}-PEDOT:PSS-based interlayer is achieved over that of the control cell with 2 nm evaporated MoO\textsubscript{X} as anode interlayer. The interfacial exciton dissociation and charge transfer dynamics at the organic/anode interface were analyzed using \textit{TPC} measurements. Research findings, experimental results, and the main conclusions derived from this work are summarized in chapter 7. Finally, the outlook of future research work in this field is discussed.
Chapter 2

Physics of Organic Solar Cells

2.1 Fundamentals of Organic Solar Cells

In this section, the fundamentals of OSCs including physics of organic semiconductors, excitonic processes, charge transport mechanisms, charge collection/extraction, device configuration, and device characterization are discussed.

2.1.1 Physics of Organic Semiconducting Materials

Small molecule organic materials and conjugated polymers are used for application in OSCs. The most promising OSCs through easy fabrication are usually based on conjugated polymers. Conjugated polymers are usually organic semiconductors being used as an electron donor in OSCs and polymer P3HT is a representative. Fluorine derivatives are organic semiconductors that are used as electron acceptors in OSCs and PCBM is a representative. Other fluorine derivatives widely used in OSCs include PC_{70}BM and ICBA. Although remarkable $PCE$ of OSCs has been realized based on P3HT, the wide band gap of P3HT limits its light absorption within the short wavelength region of solar spectrum and leaves light with longer wavelength unused. Recently, copolymers containing both an electron donating group and an electron accepting group in the repeating units are very popular for applications in OSCs since the electronic properties of the copolymers can be easily engineered. Polymers PCDTBT and PTB7 are such examples. The molecular structures of some of commonly used organic semiconducting materials are showed in Fig. 2.1.
The charge transport and energy levels of organic semiconducting materials are crucial for the performance of organic electronic devices. The backbone of polymers is composed of carbon-carbon (C-C) bonds. The mechanism of charge transport in semiconducting polymers, e.g., using the simplest conducting polymer of polyacetylene, is described in the following discussion. The outermost electron orbitals of one carbon atom in the backbone of polyacetylene consist of three s-p hybridized orbitals and one p orbital. As shown in Fig. 2.2, the electrons in one of the s-p hybridized orbital of a carbon atom form $\sigma$ type covalent bonds with a hydrogen atom. The electrons in the other two s-p hybridized orbitals of a carbon atom form $\sigma$ bonds with the s-p hybridized orbitals of two adjacent carbon atoms. The electrons in the p orbitals of two adjacent carbon atoms form $\pi$ bonds. The binding energy between electrons in $\pi$ bonds is much weaker than that in $\sigma$ bonds, as the electron clouds in $\pi$ bonds are relatively far away from the atomic nuclei. However, the electron clouds in two adjacent $\pi$ bonds are closer than those of two
adjacent σ bonds and their wave functions can easily overlap. This makes it easier for electrons to transfer among adjacent π bonds resulting in good conductivity for polyacetylene. Polymers used in OSCs are usually amorphous with localized trap states caused by the disordered structure. The charge transport in conjugated polymers originates from hopping between localized trap states induced by the thermal activation.

Fig. 2.2: Schematic diagram of the molecular structure and chemical bonds including π bonds and σ bonds in polyacetylene.

A lot of physical processes in organic semiconductors essentially depend on the energy levels of organic materials. Therefore it is helpful to review their energy levels and compare them to the band structures of inorganic semiconductors. In inorganic semiconductors, conduction band (CB) and valence band (VB) are two important concepts. Fig. 2.3(a) shows the typical band structure including CB and VB of a perfect crystal inorganic semiconductor with the vertical axis representing the energy levels. There are energy states at each energy level within the gap of CB and VB, while there are no energy states between the gap of CB and VB. The horizontal axis in Fig. 2.3(a) represents the density of energy states. As shown by the green curves in Fig. 2.3(a), the densities of energy states are different at different energy levels. When all the electrons in
semiconductors are in ground state, the energy states within the VB are filled with electrons and all the energy states in CB are empty. After the semiconductors are thermally and optically excited, an electron in the VB has the probability to gain an extra energy exceeding the bandgap to be excited into the energy states within CB. The electrons excited into CB are free to move and thus the materials become semiconducting. For single crystalline semiconductors, the edges of CB and VB are very clear and the energy levels at edges are defined as $E_C$ and $E_V$ respectively.

Fig. 2.3: Band structures for (a) single crystal inorganic semiconductors; (b) amorphous organic semiconductors.

In organic materials, band conduction in disordered organic polymers is not allowed. Instead of CB and VB, the concepts of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) are used. For organic semiconductors, the energy levels and the charge transport in the disordered polymers used in OSCs are distinctively different from
those in the crystal inorganic semiconductors. As shown in Fig. 2.3(b), the edges of HOMO and LUMO essentially are not clearly defined, though a specific value for HOMO or LUMO level is usually experimentally determined by cyclic voltammetry through interpolation. The bandgap of organic semiconductors is the difference between HOMO and LUMO. As shown by the green curves in Fig. 2.3(b), the densities of energy states around the edge of HOMO and LUMO decrease sharply but still extend into the bandgap, which are the so-called band tail states. The origins of tail states in organic semiconductors are comprehensively studied previously\textsuperscript{23,24}. Quantitatively, the density of energy states in the band tail is usually characterized by Gaussian model or exponential model. In Gaussian distribution model, the distribution of energy states in the band tail is expressed by Eq. 2.1\textsuperscript{25}:

\[
g_{D/A}(E) = \frac{N_{D/A}}{\sigma \sqrt{2\pi}} \exp \left[ - \frac{\left( E \mp E_{HOMO,D/LUMO,A} \right)^2}{2\sigma^2} \right],
\]

where \( E \) is energy level, \( N_{D/A} \) is the total density of hole or electron states, and \( \sigma \) is defined as the width of Gaussian distribution of the energetic disorder parameter. The tail states in organic semiconductors have great impact on charge generation processes in OSCs, which will be discussed in more details in the next section.

\textbf{2.1.2 Working Principles of Organic Solar Cells}

In an organic semiconducting material, the mobilities of electrons and holes usually vary far away from each other. So there is no ambipolar charge transport in organic semiconductors, which is one of the key differences about charge transport characteristics compared to inorganic semiconductors. This difference requires two kinds of organic materials in OSCs to transport
holes and electrons in two separate channels. This requirement results in very different device structures for OSCs compared to inorganic solar cells. It is necessary to review the unique device structures of OSCs before the description of working principles of OSCs.

*Device Structures*

The typical device architecture is shown in Fig. 2.4.

![Fig. 2.4: Schematic diagram of typical OSC structure.](image)

Indium tin oxide (ITO) is one of the most commonly used transparent conducting oxides (TCOs), e.g., 100~200 nm thick ITO-coated glass or transparent plastic substrates, for application in OSCs. Other TCOs such as aluminum doped zinc oxide (AZO) and fluoride doped tin oxide (FTO) have been also used in OSCs\textsuperscript{26,27}. The cathode and anode interlayers in the OSCs are carefully chosen according to the properties of organic materials and device structures to facilitate the efficient charge collection by electrodes. A bulk-heterojunction (BHJ) composes of a blend of polymer donor and fluorine or fluorine-derivative based acceptor. The microstructure
of a typical BHJ is schematically shown in Fig. 2.5. Some low work function metals, such as Al and Ag, are examples of commonly used metal electrodes in OSCs.

![Fluorine based derivative](image)

**Fig. 2.5: Schematic diagram of a BHJ.**

Some chemically reactive or environmental sensitive cathode materials, e.g., Ca and lithium fluoride (LiF/Al), are often used for obtaining high charge collection efficiency. However, the use of the chemically reactive materials has a limitation and also is not compatible with large area OSCs fabricated through all solution process approach. The development of solution-processable n-type metal oxides is desired and becomes mature. Therefore OSCs with conventional structures usually contain a layer of metal oxides at cathode side, as shown in Fig. 2.6(b). OSCs with reverse device architecture are designed and studied for improving the OSC performance. One of the representatives is inverted structure where ITO is modified to serves as the front cathode, while the top metal layer acts as the anode electrode. The architectures for conventional and inverted OSCs are schematically shown in Fig. 2.6, where HTL is the hole transport layer and ETL represents the electron transport layer.
Fig. 2.6: Device structures for (a) inverted OSCs and (b) conventional OSCs.

The stability of inverted OSCs, with a cell structure shown in Fig. 2.6(a), is better than that of the conventional cells with a layered structure illustrated in Fig. 2.6(b). In the conventional devices, PEDOT:PSS is often coated on ITO surface to serve as HTL. However, the interfacial contact property at the ITO/PEDOT:PSS interface can be easily damaged by the acidity of PEDOT:PSS, resulting in poor long term stability of OSCs with PEDOT:PSS as HTL. In inverted OSCs, there is no need to use PEDOT: PSS. The most commonly used HTL at the top metal electrode side in inverted OSCs is thermally evaporated molybdenum oxides (eMoO$_x$).

In order to improve the PCE of OSCs by absorbing wider range of solar spectrum, tandem structure is used. In the tandem structure, two sub-cells with BHJs absorbing different parts of solar spectrum are stacked. The intermediate layer, which connects the two sub-cells, plays a role of charge recombination site. The structure of typical tandem OSCs is shown in Fig. 2.7(a). The device concept of semi-transparent OSCs, as illustrated in Fig. 2.7(b), has also been demonstrated. Semi-transparent OSCs, with different colors and transparency, can be integrated into window panels in homes, skyscrapers and automobiles.
Fig. 2.7: Schematic diagram of (a) OSCs with tandem structure; (b) semi-transparent OSCs.

In tandem OSCs, the balance between the hole extracted from sub-cell 2 and the electron extracted from sub-cell 1 by the intermediate layer is crucial for the performance. In semi-transparent OSCs, the semi-transparent electrode and the associated ETL are the dominant factor affecting the performance of semi-transparent OSCs. For application in semi-transparent OSCs, the semi-transparent electrode must have such properties as high transparency in visible spectrum, good electrical conductivity, smooth surface and good stability.

*Physical Processes in Energy Conversion*

Generally, there are four processes occurred in the OSCs during the conversion from solar energy to electricity, i.e. (1) light absorption and exciton generation, (2) exciton diffusion, (3) exciton dissociation and (4) charge transport. Fig. 2.8(a) illustrates the energy diagram of active materials and four primary excitonic processes in the OSCs and Fig. 2.8(b) elucidates these processes occurred in the BHJ-based OSCs.
Fig. 2.8: Four physical processes for energy conversion in OSCs.

Light absorption and exciton generation

Most conjugated polymers have a much higher absorption coefficient ($\sim 10^5 \text{ cm}^{-1}$) than that of the crystalline silicon$^{28}$. Due to the low charge mobility in organic materials, there exists a mismatch between the charge transport scale and the optical absorption length. Despite their high absorption coefficient, OSC performance is hampered by limited light absorption due to the mismatch. The thickness of the organic active layer in the OSCs is much thinner ($\sim 100 \text{ nm}$) than
that of the crystalline silicon (~2 µm) typically used in the inorganic solar cells. From the view of quantum mechanics, only the photons with energy larger than or equal to the bandgap of the polymers can be absorbed in the OSCs. The large bandgap of organic semiconductors is the main concern for light absorption in OSCs. Photons with the long wavelength in solar spectrum are just wasted as shown in Fig. 2.9.

Fig. 2.9: The solar spectrum and the spectrum response of a typical solar cell based on PTB7:PC$_{71}$BM BHJ.

Upon photon absorption, the electrons in the HOMO of donor are excited into its LUMO as shown in Fig. 2.8(a). However, free charge carriers cannot be directly generated by photoexcitation in OSCs. The electrons excited into the LUMO and holes left in the HOMO are bound together by the Coulombic attraction to form excitons$^{29}$. The Coulombic force can be expressed as $\frac{q^2}{4\pi\varepsilon r}$, where $q$ is the elementary charge, $r$ is the distance between the electrons and holes and $\varepsilon$ is the dielectric constant of organic active layer. As opposed to a few meV binding
energy of the excitons in inorganic semiconductors, the binding energy of the excitons is as high as 0.1~1.4 eV due to localized electron and hole wavefunctions and low dielectric constant $\varepsilon$ in organic semiconductors\textsuperscript{30,31}. It is known that phonon energy at room temperature is only about 25 meV, so the excitons can rarely be separated automatically in OSCs.

*Exciton diffusion*

The photo-generated excitons diffuse in the organic materials before they dissociate or decay back into the ground state. The distance that the excitons can travel before they decay is defined as the exciton diffusion length, which is about ~20 nm for most of organic semiconductors\textsuperscript{32}. In a BHJ, the donor-acceptor phase separation length should be similar to the exciton diffusion length so that most of the excitons can find a donor-acceptor (D-A) interface within their lifetime. For efficient power conversion, the excitons in OSCs should diffuse to a heterojunction interface for dissociation.

*Exciton dissociation*

The energy level alignment of the donor and acceptor in a BHJ is shown in Fig. 2.8(a). Because of a sudden change in potential level of different materials, a strong electrical field exists at the D-A interface. This strong electrical field is essential for exciton dissociation. Therefore, the energy difference between the LUMO of donor and LUMO of acceptor should be comparable or larger than the binding energy of excitons to ensure efficient exciton dissociation. After exciton dissociation, the photo-generated electrons and holes are in two different phases and the Coulombic attraction between them is much weaker than that in their excitonic status\textsuperscript{33}. This intermolecular electron-hole pair sometimes is also called charge transfer (CT) complex, in which the electron and hole may recombine to form exciton again or dissociate into free carriers.
depending on the local electrical field\textsuperscript{34,35}. There is a built-in potential across the BHJ in OSCs due to the difference in the work function of two electrodes. Assisted by this potential, the CT complex can be separated into free carriers.

\textit{Charge transport and collection}

After exciton dissociation, free carriers are generated and concentrated at the D-A interface at first. Due to the concentration gradient, the carriers are drifted away from the interface. On the other hand, a built-in electric field is formed due to the difference in the work function between the anode and cathode. Under the built-in electric field, the holes are transported to anode and electrons are transported to cathode. Finally, the holes and electrons are collected by anode and cathode respectively. During the transport of free carriers, energy loss is highly dependent on the carrier mobility. In OSCs, free carriers are actually not really free to move as like the free carriers in inorganic semiconductors. The carriers in organic semiconductors are in localized states and their transport is via the hopping mechanism as illustrated in Section 2.1. The localized states, also referred to as the charge trap states and the depth of trap states are internally dependent on the band tail states of organic materials and externally dependent on the purity, doping and residual contamination in the organic materials. After the dissociation, carriers will first fall into the trap states. Next they are thermally activated by phonons and de-trapped. Thus the carrier mobility in organic semiconducting materials is highly dependent on band tail states and temperature as shown in the following equation\textsuperscript{36,37}:

\[
\mu(\Delta, T) = \mu_0 \exp\left(-\frac{\Delta}{kT}\right),
\]

where \(\mu_0\) is a prefactor depending on the basic electrical properties of the organic materials, the activation energy \(\Delta\) is also called the trap depth and \(k\) is the Boltzmann constant. On the other
hand, the potential barrier and charge accumulation at the electrode interface will affect the charge transfer dynamics at organic/electrode interface. The recombination loss during charge transport and transfer at organic/electrode interface will be discussed in the Chapter 4 and Chapter 5.

2.1.3 Fundamental characteristics

The current density-voltage (J-V) characteristic is one of the most important characteristics of OSCs. Typical current-voltage (I-V) characteristics of an OSC in dark condition and under illumination are respectively showed as the blue curve and red curve in Fig.1.3, where \( I=J \cdot A \), \( A \) is the effective area of a cell.

![Typical I-V curves of an OSC in dark and under illumination.](image)

Fig. 2.10: Typical I-V curves of an OSC in dark and under illumination.

In the dark condition, the I-V curve of an OSC is very similar to that of a typical p-n junction diode. To get fair comparisons of the performance of OSCs, a standard condition of the illumination should be defined. Conventionally, AM1.5G (global spectrum) solar spectrum, as shown in Fig. 2.9, is the standard condition of illumination in the measurement of J-V curves.
The optical air mass is an important parameter determining the total solar incident power under clear conditions. Due to absorption in the atmosphere, solar irradiance arrived at earth surface is related to the angle of incidence. As shown in Fig. 2.11, air mass at incident angle $\theta$ is calculated by $1/\cos\theta$, where $\theta$ is angle between the incident direction of solar irradiation and the radial direction of earth. Sunlight is attenuated by about 30% in its passage through the Earth’s atmosphere. AM1.5G corresponds to a defined terrestrial standard to this standard at 1000 W/m$^2$, a value calculated at $\theta$ of 48.2°.

![Fig. 2.11: Air mass at incident angle $\theta$.](image)

Under illumination, the photocurrent is generated due to drift of the photo-generated carriers under the built-in potential in the cell. During the measurement, an external bias, usually swept from -1 V to 1 V, is applied across the OSCs. When the external bias is 0, represented by point a in Fig. 2.10, the output current is short circuit current ($I_{SC}$). Dividing $I_{SC}$ by the effective area of the cells is short circuit current density ($J_{SC}$). As represented in Fig.1.3, the diffusion current and injected current are cancelled off by each other at point b, resulting in the total zero current in the OSC. At point b, the value of the applied forward bias equals to $V_{OC}$. Only the fourth quadrant in Fig. 2.10 represents the output power which equals to the product of applied voltage and the output current. As shown in Fig. 2.10, a certain point between a and b, denoted by c, represents the condition of maximum output power. The output current and the forward bias applied at
point c are denoted as $I_{MPP}$ and $V_{MPP}$, respectively. Therefore the PCE of an OSC can be calculated by the Equation 2.3.

$$PCE = \frac{P_{\text{out}}}{P_{\text{in}}} = \frac{I_{MPP} \times V_{MPP}}{P_{\text{in}}}$$  \hspace{1cm} 2.3

Fill factor ($FF$) is another important cell parameter, defined by:

$$FF = \frac{P_{\text{out}}}{I_{sc} \times V_{oc}} = \frac{I_{MPP} \times V_{MPP}}{I_{sc} \times V_{oc}}$$  \hspace{1cm} 2.4

The spectral response is also an important characteristic of an OSC. To determine the spectral response, the photocurrent generated by monochromatic light with wavelength increased from 350 nm to 850 nm by a step of 5 nm is measured using a Lock-in Amplifier. This parameter related to spectral response is called $EQE$ or $IPCE$, which is defined by the ratio of the number of carriers collected ($n_c$) to the number of incident photons ($n_{ph}$) as shown in Equation 2.5.

$$IPCE = \frac{n_c}{n_{ph}} = \frac{I_{sc}hc}{P_0 \lambda q}$$  \hspace{1cm} 2.5

where $c$ is the speed of light, $P_0$ is the incident optical power, $\lambda$ is the wavelength and $q$ is the electron charge. As the numerator in Eq. 2.5 means the total charges collected by electrodes, which is dependent on light absorption and charge collection efficiency, $IPCE$ not only provide information about light absorption, but also about charge exciton dissociation, charge transport and collection processes. The typical $IPCE$ spectrum of a practical device is plotted in Fig. 2.12.
2.2 Electrode/Organic Hetero-interfaces in Organic Solar Cells

2.2.1 Interfacial Engineering in Organic Solar Cells

As mentioned in Section 2.1.2, the built-in electrical field, caused by the difference in the work function between the anode and cathode, is critical to the charge transport in OSCs. In addition, charge transfer at electrode/organic interfaces is greatly influenced by the alignments of energy levels at the interfaces. Consequently, the characteristics of OSCs including $J_{SC}$, $V_{OC}$ and $FF$ are very dependent on the nature of electrical contact of the electrode/organic interfaces. A comprehensive review on the roles of oxide interfacial layers on the performance of OSCs is discussed below.
Electrode/organic interfacial energy level alignment

The intrinsic $V_{OC}$ of OSCs is determined by the energy difference between the Fermi levels of the photogenerated free holes and electrons under illumination\textsuperscript{38}. However, Schottky barrier at the electrode/organic interfaces in practical devices makes the resultant $V_{OC}$ lower than the intrinsic $V_{OC}$\textsuperscript{39}. As shown in Fig. 2.13, the mismatch between the work functions (WF) of the electrodes and the Fermi levels of photogenerated carriers can be alleviated by suitable interfacial materials. As illustrated in Fig. 2.13, such mismatch is actually alleviated through the modification of WF of electrodes. If interfacial layers are inserted into electrode/organic interfaces, the $V_{OC}$ in practical cells approaches to its intrinsic value. According to the previous studies, the change in WF of electrodes originates from the surface interfacial dipole formed at the electrode/organic interface after suitable interfacial material is applied\textsuperscript{40}.

![Fig. 2.13: The alignments of energy levels at electrode/organic interfaces in OSCs with and without interfacial layers.](image_url)
Electrode selectivity and contact resistance

Generally, the photogenerated holes are collected by anode and electrons are collected by cathode in OSCs. However, the photoactive layer in OSCs is BHJ, which means that holes or electrons may be collected by the opposite electrodes if the alignment of energy levels at the organic/electrode interfaces is not properly controlled. Since both of electrons and holes are transferred to the same electrode, the resultant charge recombination and exciton quenching at the organic/electrode interface induce appreciate amount of energy loss in OSCs. So the charge selecting properties of interfacial layers are very important to improve the performance of OSCs. At anode side, p-type interfacial materials or HTL are applied, which have good selectivity on holes. On the other hand, n-type interface materials or ETL are applied at cathode side, which have good selectivity on electrons. As shown in Fig. 2.14, the HOMO level of an ideal HTL should be equal to the $E_{F,h}$ of the BHJ layer and its LUMO level should be well above the $E_{F,e}$ of the BHJ layer. On the contrary, the LUMO level of an ideal ETL should be equal to the $E_{F,e}$ of the BHJ layer and its HOMO level should be well below the $E_{F,e}$ of the BHJ layer. With ideal interfacial layers, there will be no opposite carriers collected by the electrode as shown in Fig. 2.14. In addition to the suitable energy alignments, good hole (electron) mobility is also desired for p-type (n-type) interface materials to reduce the contact resistance. For those interfacial materials with suitable energy levels but low carrier mobility, doping with other materials with high conductivity is an effective way to improve the device performance$^{41}$. 

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Fig. 2.14: Charge transfer dynamics at organic/electrode interfaces in OSCs with and without interfacial layers.

Application in OSCs with plasmonic structure

As discussed in Chapter 1, metallic nanostructures are widely used in OSCs to enhance light absorption through the surface plasmon resonance effects. Various approaches have been reported including incorporating metal nanoparticles, surface plasmonic structures and a textured substrate template in OSCs to boost light absorption. The localized surface plasmon resonance (LSPR) around metal nanoparticles (NPs) can enhance light absorption in the surrounding absorbers. Direct blending of metal NPs into the BHJ is a simple method to utilize the LSPR of metal NPs. However, it sometimes induce other problems: e.g. both holes and electrons can be easily trapped and recombined with each other around the metal NPs embedded in the BHJ. On the other hand, the metal NPs or the associated legends may be detrimental to the morphology of BHJ. With interfacial materials in OSCs, the plasmonic structures can be incorporated into the
interfacial layers without deteriorating the morphology and charge transport properties of the BHJ. Semitransparent Ag based interlayer electrode is another example adopted for absorption in OSCs\textsuperscript{44}. When less than 10 nm of Ag is deposited onto the BHJ, Ag actually doesn't form continuous thin film resulting very poor conductivity of the Ag based semitransparent electrodes. Ag particles with high temperature will penetrate into the BHJ and induce damage to organic materials. If a suitable interfacial layer, working as seeding layer to improve compatibility with ultra-thin Ag layer, is deposited onto the BHJ before evaporating Ag, the Ag semitransparent electrode can possess both high conductivity and transmittance\textsuperscript{45}. All the works introduced above demonstrate the importance of interfacial layers in optical engineering for achieving high performance and new applications of OSCs. Interfacial layers, such as TiO\textsubscript{2} and ZnO, can also bring advantages for absorption enhancement in conventional OSCs with planar device structure. More details about this will be discussed in the Section 2.2.2 and Chapter 5.

\textit{BHJ morphology and device stability}

The morphology of the BHJ layer is closely related to the surface energy of the underlying interfacial layer\textsuperscript{46}. When the interfacial layers are polymers, the backbone and side chains of the interfacial polymer should be carefully designed considering their influence on the morphological evolution in BHJ. It was reported that the ITO surface, e.g., modified with an organic hydrophobic interfacial layer on ITO surface, can improve the BHJ morphology resulting in enhanced $J_{SC}$ and $FF$ in OSCs\textsuperscript{47}. It was also reported that adding a polar phosphonate moiety on the side-chains of organic interfacial layer can improve the smoothness of the organic active layer due to its more compatible surface energy\textsuperscript{48}. Finally, the interfacial layer in OSCs can improve the device stability since the organic active materials are sandwiched between the interlayers and they protected from the permeation of water and oxygen.
The widely used p-type interfacial materials include polymers such as PEDOT:PSS and transition metal oxides such as MoO$_x$, WO$_3$, NiO, etc. And n-type interfacial materials include polymers such as PFN and transition metal oxides such as TiO$_2$, ZnO, Al doped ZnO, etc. In this thesis, n-type ZnO and p-type MoO$_x$ were used as and the cathode and anode interlayers in OSCs.

2.2.2 Impact of Metal Oxide Interlayer on Performance of Organic Solar Cells

N-type metal oxide interlayer in OSCs

Insertion of a metal oxide interlayer between the BHJ layer and Al cathode in OSCs was first introduced by J. Y. Kim in 2006\textsuperscript{49}. In that work, the enhanced $J_{SC}$ in OSCs with TiO$_x$ interlayer between BHJ and Al cathode was mainly attributed the enhancement of light absorption caused by the redistribution of light intensity. Fig. 2.15 schematically demonstrates the effect of TiO$_x$ interlayer on light intensity redistribution.

![Fig. 2.15: Schematic representation of the spatial distribution of light intensity in control device and device with a TiO$_x$ interlayer.](image)

Then the application of metal oxides in OSCs and the impact of the properties of metal oxide/organic hetero-interfaces on cell performance have attracted a lot of attentions. For
example, the use of a titanium suboxide\textsuperscript{50} or ZnO interlayer\textsuperscript{51} between the active layer and the reflective electrode in OSCs has been shown to increase the absorption in the active layer. The enhancement in the photocurrent generation due to the ZnO interlayer is found to be more beneficial in OSCs with a thin active layer (<60 nm), but has less effect in device with a thicker layer (>90 nm). The ZnO interlayer also serves as a hole blocking layer to reduce the recombination rate.\textsuperscript{52} Despite numerous reports about the improvement on OSCs due to the incorporation of metal oxide interlayer, mechanisms of improving cell performance due to oxide interlayer in OSCs are still inconclusive and controversial. Inganäs et al.\textsuperscript{53} reported that no beneficial effect can be expected by interposing a metal oxide interlayer in OSCs with an already optimized active layer thickness. In a recent work, we found that the insertion of a ZnO interlayer between the active layer and the metal contact enables to eliminate the unfavorable exciton dissociation that would otherwise occur at the organic/metal interface, thereby improving the charge collection efficiency. This suggests that the removal of the unfavorable interfacial exciton dissociation is a perquisite for high performing OSCs\textsuperscript{54}. However, studies about the effects of metal oxide interlayer at the top electrode of OSCs on charge transport and collection and exciton dissociation were less sufficient. A thorough and comprehensive study about the effects of metal oxide interlayer on those physical processes will be conducted in Chapter 5 of this work, which makes this work distinguishable from previous related work.

\textit{P-type metal oxide interlayer in OSCs}

PEDOT:PSS is widely used as HTL in OSCs. However, the interfacial contact property at the ITO/PEDOT:PSS interface can be easily damaged by the acidity of PEDOT:PSS, resulting in poor long term stability of OSCs with PEDOT:PSS as HTL\textsuperscript{55}. On the other hand, the interface between the low work function metal cathode and the organic active layer in regular OSCs is
unstable because the metal with low work function is easy to be oxidized\textsuperscript{56}. To improve the PCE and stability of regular OSCs, p-type transition metal oxides, such as MoO\textsubscript{3}, V\textsubscript{2}O\textsubscript{5}, NiO, and WO\textsubscript{3} have been used as alternatives to PEDOT:PSS\textsuperscript{57,58}. Thin films of these metal oxides are usually deposited by thermal evaporation. However, thermal evaporation is less compatible with large area solution-processed fabrication approach. So far different solution-processing methods to deposit these metal oxides thin films have been demonstrated. Application of colloidal V\textsubscript{2}O\textsubscript{5} and MoO\textsubscript{X} nanoparticle dispersions in OSCs was reported\textsuperscript{59,60}. But the electronic and electrical of the metal oxides are difficult to control and the thin film cast from the dispersion shows low quality. More recently, solution processed V\textsubscript{2}O\textsubscript{5} and MoO\textsubscript{X} (sV\textsubscript{2}O\textsubscript{5} and sMoO\textsubscript{X}) via the sol-gel process have been applied in OSCs\textsuperscript{61,62}. The advantages of sol-gel processed metal oxides include precise composition control and high homogeneity of the interlayer thin film. This method is favorable for large area and low cost fabrication. The requirement of high temperature treatment in sol-gel process limits the application of p-type metal oxides in inverted OSCs. MoO\textsubscript{X} thin film cast from the solution of hydrogen molybdenum oxides bronzes (HMoO\textsubscript{X}) at room temperature was reported\textsuperscript{63}. The conductivity of room temperature processed sMoO\textsubscript{X} is highly sensitive to the synthesis process of the HMoO\textsubscript{X} solution. To ensure good conductivity of the resulting MoO\textsubscript{X} thin film, solution blend with an appropriate ratio of HMoO\textsubscript{X} to PEDOT:PSS was also proposed\textsuperscript{64}. These works were primary focused on the solution formulation, electronic and electrical properties of resulting thin film rather than its impact on the performance of the whole device. OSC is a multilayer device, in which every layer imposes influences on each other. The effect of p-type metal oxides on the exciton generation and dissociation, charge collection and recombination in inverted OSCs has not been systematically studied previously. Chapter 6 of this work demonstrates a comprehensive study about these physical processes.
Chapter 3

Experiments and Optical Simulation

In this chapter, the experimental techniques for material formulation, device fabrication and characterization are presented. Most of the experimental facilities during all the experimental processes are described in both pictures and schematic diagrams. For optical simulation, the fundamental principle of optical admittance analysis is also discussed.

3.1 Material Preparation and Device Fabrication

The main facilities for material preparation and device fabrication in the lab include glove box (MBraun MB200B), fume hood and vacuum chamber systems. The glove box is purged with high purity nitrogen gas. Solution–processed samples can be transferred between the glove boxes and the connected vacuum chambers for cell fabrication and encapsulation without exposure air. A gas circulatory system is connected to the glove box to keep the gas pressure between 1.2 mbar and 5 mbar. A gas purifier system and a solvent absorbing system are connected to the glove box to remove water (H₂O), oxygen (O₂) and organic solvents. As a result, both of the residual H₂O and O₂ levels inside the glove box are below 0.1 parts per million (ppm). As shown in Fig. 3.1, the multi-chamber vacuum system composed of sample preparation chamber, thermal evaporation chamber and sputtering chamber connects in sequence with the glove box through an anti-chamber. The transmission rod installed inside the anti-chamber helps to transfer the samples between the glove box and vacuum system. This design can make sure that the samples are protected from the contamination of ambient atmosphere during the fabrication processes.
3.1.1 Formulation of Solution-processed Metal Oxides and Donor/Acceptor Solutions

The materials used in the study of OSCs include organic active materials and inorganic functional materials. The ITO/glass substrates, metals and metal oxides for thermal evaporation deposition were purchased from Sigma Aldrich. The solution-processed metal oxides, including ZnO NPs in methanol and MoO\textsubscript{X} in ethanol, were formulated in-house.

Zinc acetate dehydrate (ZnAc•2H\textsubscript{2}O) and potassium hydroxide (KOH), from Sigma-Aldrich and used without further treatment, were used for making ZnO Nano-particles (NPs). ZnO NPs were synthesized following the procedure described by Hermann-Jens.\textsuperscript{65} In this experiment, 780 mg ZnAc•2H\textsubscript{2}O and 390 mg KOH powders were loaded into two separate beakers inside the glove box. They were then transferred out of the glove box for making different solutions. ZnAc•2H\textsubscript{2}O solution was formed by dissolving 780 mg ZnAc•2H\textsubscript{2}O powder in 50 ml methanol, and KOH solution was formulated by dissolving 390 mg KOH powder in 28 ml methanol. ZnAc•2H\textsubscript{2}O solution was then transferred to a three-necked flask. The reaction of ZnAc•2H\textsubscript{2}O...
and KOH solutions was taken place by gradually adding KOH solution in the flask. The reaction was kept at 60 °C constant temperature using a water bath for 2 hours. The ZnO NPs thus synthesized were purified and re-dissolved in methanol forming the ZnO NPs solution. The concentration of the ZnO NPs solution was ~0.01 mol/L. A thin film of ZnO layer can then be formed on the organic layer without post-annealing by spin-coating approach.

The processes to synthesis solution-processed MoOₓ were reported in previous work. The molybdenum powder were bought from Sigma-Aldrich and stored in glove box. 100mg molybdenum powder was weighted by an electronic analytical balance and then loaded into a colorless transparent bottle with a volume of 20 ml. 10 ml ethanol was added into the bottle and the molybdenum suspension was stirred for several minutes. 0.35 ml hydrogen peroxide (H₂O₂) (30%) solution was then added into the metal power suspension solution, allowing for 18 hour reaction to form HMoOₓ solution. The concentration HMoOₓ solution was ~0.1 mol/L. After the MoOₓ suspension was diluted 20 times by ethanol, it can be directly used to cast MoOₓ thin film in OSCs without post annealing. Another interfacial material PEDOT:PSS (Baytron P VP Al4083) was purchased from Bayer.

Commercial polymers of PTB7 (purchased from 1 Materials), PTB7-Th (purchased from Solarmer Materials Inc) and new polymer PNB4 synthesized in-house were used for cell fabrication. The chemical structure of the commercial polymer PTB7 is shown in Fig. 2.1. The new polymer PNB4 was synthesized by colleagues from the Department of Chemistry. The chemical structures of PNB4 and PTB-Th are shown in Fig. 3.2. The fluorine derivative PC₇₁BM was purchased from NanoC. The organic solvents such DCB and CB and the organic additive DIO were purchased from Sigma Aldrich. To prepare the organic solution, all organic materials were weighted by the electronic analytical balance in the glove box and were loaded into the
semitransparent brown bottles. The solvents and additives were then added into the bottle in the glove box. After the organic solutions were prepared, a stir bar was added into each of the bottle. The organic solvents were magnetically stirred at 60 °C at least overnight before they were used for thin film preparation.

Fig. 3.2: Chemical structures of PNB4 (left) and PTB7-Th (right).

### 3.1.2 Device fabrication

Before thin films were deposited onto the ITO/glass substrates, they were cleaned following the procedure below:

- The ITO/glass substrates were vertically loaded into glassware. Then some detergent was poured into the glassware until the ITO/glass substrates were fully immersed. The glassware was put into an ultrasonic cleaner for 30 min to remove the large grained particulates and lipid contamination.
- The substrates were then rinsed by deionized water and subject to ultrasonication clean for another 30 min to remove the residual of detergent.
Replace the deionized water by acetone and the ultrasonic cleaning was kept for another 20 min to dissolve any remaining non-polar solvent contamination.

Replace the acetone by isopropyl alcohol (IPA). Keep the ultrasonic cleaning for 20 min to remove the residual of acetone. Then IPA was removed and the glassware containing ITO/glass substrates was kept in an oven (Mennert UNE 200) to dry up the solvent residual at 100 °C.

Prior to the cell fabrication, wet cleaned ITO substrates were sent to the sample preparation chamber for O₂ plasma treatment. There are two reasons to do this: (1) Contaminants on the ITO surface such as stable particles, adsorbed organic molecules and moisture can be removed by the plasma; (2) modify the surface properties of ITO. Fig. 3.3(a) schematically shows the working mechanism of O₂ plasma treatment. The flow rate of O₂ in the chamber was kept constant at 100 sccm (standard-state cubic centimeter per minute) for O₂ plasma treatment. On the other hand, a rotary pump was used to pump out the gas in the chamber to achieve a balanced gas pressure of ~64 Pa. The gas molecules between the two electrodes will be ionized by the high frequency alternating electrical field. The surface properties of ITO were modified by the ions, radicals, electrons, UV radiation and molecules in excited states generated by the ionization of gas molecules. Originally, the surface of ITO was hydrophobic and it was difficult to form a smooth PEDOT:PSS thin film on its surface. After O₂ plasma treatment, the surface of ITO substrates was converted to hydrophilic through adding new functional hydrophilic molecular groups. Then the contact angle on ITO surface was reduced as shown in Fig. 3.3(b).
Fig. 3.3: (a) Mechanism of O$_2$ surface plasma treatment; (b) change of the contact angle, illustration of the effect of O$_2$ plasma treatment on changing the surface hydrophilicity of ITO.

The functional layers of PEDOT:PSS, ZnO, sMoO$_x$ and organic active layer used in OSCs were deposited by spin-coating method. Fig. 3.4 illustrates the processes of spin coating. The substrates were placed on the center of the spin plate and were sucked by vacuum pump. A small amount of solution was dropped onto the center of the substrate. The substrate was then rotated at high speed ranging from 500 rpm to 3500 rpm in to spread the coating material by centrifugal force. Rotation kept from a period from 30 s to 150 s to obtain films with different thicknesses. During the rotation, the solution was spread over the substrates and some solution spun off the edges of the substrate. Usually the solvent to dissolve the coating materials are volatile and it will be dried and evaporated during the rotation, leaving the coating material to form thin films on the substrates. The applied solvent is usually volatile, and simultaneously evaporates. So, the higher the rotation speed, the thinner the film. The thickness of the film also depends on the viscosity, concentration of the solution and the solvent used in the formulation of the solution. The factors
that affect the final film thickness and the morphology of the film include the concentration, viscosity and drying rate of the solution, the final spin speed, acceleration in the startup of spin as well as the gas turbulence above the substrate. One of the most important considerations in spin coating is repeatability, as subtle variations in the processing factors mentioned above can result in significant differences in the coated film.

![Schematic diagram of a spin coater](image)

**Fig. 3.4: Schematic diagram of a spin coater.**

The spin coater Laurell (WS-650Mz-23NPP) was applied to coat the aqueous solution such as PEDOT:PSS in ambient atmosphere. Other layers such as ZnO NPs, organic blend active layer and sMoOx were spin coated using the spin coater SAWATEC located inside the glove box.

Metal electrodes and MoO$_x$ in controlled inverted OSCs were deposited through thermal evaporation in the vacuum chamber. Fig. 3.5 schematically illustrates the thermal evaporation and mechanism and process.
As shown in Fig. 3.1, the evaporation chamber and sample preparation chamber are connected with glove box. The samples were transferred to the evaporation chamber without air exposure after the deposition of the solution-processed layers. As shown in Fig. 3.5, the chamber was also connected to the pump system consisting of a mechanical pump and a turbine molecular pump. Before heating, the chamber was evacuated by the pump system to keep chamber at high vacuum below $5 \times 10^{-4}$ Pa. The pressure in the chamber was monitored by a resistance vacuum pressure gauge and an ionization vacuum pressure. Then the metal or MoO$_X$ were heated and evaporated at a given rate. The evaporation rate was monitored by a quartz crystal resonator.

In the fabrication of conventional OSCs, Al grains were used for the deposition of cathode. In the fabrication of inverted OSCs, MoO$_X$ powder and Ag grains were loaded into two separate boron nitride crucibles in the vacuum chamber and were thermally evaporated sequentially to complete the deposition of the anode.
3.2 Characterization of Materials and Devices

3.2.1 Current Density-Voltage Characteristics

The most important measurement of performance for OSCs is $J-V$ characteristics. The apparatus of $J-V$ characteristic measurement is shown in Fig. 3.6(a). A voltage signal gradually sweeping from -1 V to 1 V was generated by the signal generator and was then exerted across the sample cell. Then the output voltage and current from the sample cell were recorded. The shutter in front of the solar simulator could be closed or open so that the $J-V$ characteristics of the cell could be measured in dark or under illumination.

![Image of measurement setup]

Fig. 3.6: The apparatus of $J-V$ characteristics measurement system; (b) SAN-EI ELECTRIC XEC-301S solar simulator.

The measurement accuracy of $J-V$ characteristics is highly dependent on whether the illumination condition is very similar to the AM1.5G 100 mW/cm$^2$ condition. As shown in Fig. 3.6(b), a Xeon lamp with tunable intensity was used to simulate AM1.5G 100 mW/cm$^2$ condition in the experiments. As the output current density of a standard c-Si cell under AM1.5G
100mW/cm$^2$ condition is well known, it was used to calibrate light intensity of the Xeon lamp. The spectrum of the Xeon lamp when its integrated intensity was calibrated to 100 mW/cm$^2$ and the AM1.5G 100 mW/cm$^2$ were plotted in Fig. 3.7.

![Graph showing spectral irradiance vs. wavelength for AM1.5G and Xeon lamp](image)

Fig. 3.7: The spectra of standard AM1.5G 100 mW/cm$^2$ and the simulated illumination condition without using KG5 filter in the measurement.

However, the spectral response of OSCs is usually in the range of 400 nm to 800 nm, while it’s in the range of 400 nm to 1200 nm for c-Si cell. The integrated light intensity of the Xeon lamp within the spectral range of 400 nm to 800 nm is different from that under AM1.5G 100 mW/cm$^2$. This spectral mismatch will cause measurement errors. Therefore, a KG5 filter (only 300 nm to 800 nm can be transmitted) was used in the experiments to minimize the effect of spectral mismatch. The Table 3.1 shows the mismatch between the spectra of Xeon lamp and AM1.5G. In the table, $E(lamp)$ and $E(AM1.5G)$ are defined as:
\[ E(lamp) = \int_{\lambda_1}^{\lambda_2} R_{lamp}(\lambda) d\lambda , \tag{3.1} \]

\[ E(AM1.5G) = \int_{\lambda_1}^{\lambda_2} R_{AM1.5G}(\lambda) d\lambda , \tag{3.2} \]

where \( R_{lamp}(\lambda) \) and \( R_{AM1.5G}(\lambda) \) are the spectral irradiance for the lamp and AM1.5G 100 mW/cm\(^2\) condition as shown in Fig. 3.7 and \( \lambda_1 \sim \lambda_2 \) is the spectrum range considered.

Table 3.1: Spectral mismatch between the Xeon lamp and AM1.5G.

<table>
<thead>
<tr>
<th>Spectrum range</th>
<th>400~1200 nm</th>
<th>400~800 nm</th>
<th>800~1200 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{E(lamp)}{E(AM1.5G)} )</td>
<td>1.00</td>
<td>1.04</td>
<td>0.96</td>
</tr>
</tbody>
</table>

As can be seen from Table 3.1, there is mismatch between the spectra of the solar simulator and AM1.5G condition in the spectral range of 800 nm to 1200 nm. When the integrated light intensity of the solar simulator in the spectral range of 400 nm to 1200 nm is calibrated to 100 mW/cm\(^2\), light intensity in the spectral range of 400 nm to 800 nm of the solar simulator is actually higher than that under AM1.5G 100 mW/cm\(^2\) condition. Therefore, the performance of OSCs is overestimated without KG5 filter.

### 3.2 Incident Photon-to-electron Conversion Efficiency

The apparatus of IPCE measurement is shown in Fig. 3.8. Light from the Xeon lamp passed through an optical chopper with a certain frequency before entering into a monochromator. The optical chopper was connected with a lock-in amplifier. The wavelength of monochromatic light was swept from 300 nm to 850 nm with an interval step of 5nm. The output light from the
monochromator was focused and directed to the active area of the sample using a series of optical apparatus. The photocurrent generated by the sample was first amplified by a lock-in amplifier and recorded by the PC. Since the optical chopper was also connected with the lock-in amplifier, the photocurrent generated by the monochromatic light could be distinguished from the signal due to background noise and signal-to-noise ratio could be enhanced.

Turn on the Xeon lamp and wait for about 10 min to stabilize light intensity of the Xeon lamp. The photocurrent of a standard c-Si reference cell at different wavelength \( I_R(\lambda) \) was recorded. Then replace the reference cell by the sample cell and record the photocurrent of the sample cell at different wavelength \( I_S(\lambda) \). Since the \( IPCE \) of the reference cell is well known, the \( IPCE \) of the sample cell was calculated as:

\[
IPCE_S = \frac{I_S(\lambda)}{I_R(\lambda)} \times IPCE_R,
\]

where \( IPCE_R \) is the \( IPCE \) of the standard reference cell.
The $J_{SC}$ of sample cell can be calculated using the measured $IPCE$ by the following equation:

$$J_{SC} = \int_{\lambda=300nm}^{\lambda=850nm} IPCE \times \frac{q\lambda}{hc} P(\lambda) d\lambda,$$

where $q$ is elementary charge, $c$ is the speed of light, $h$ is the Planck constant and $P(\lambda)$ is the intensity of solar irradiation under AM1.5G 100 mW/cm$^2$ condition at different wavelength.

### 3.2.3 Light Intensity-dependent Current Density-Voltage Characteristics

The experimental facilities to do the characterization in this part were the same with those in the measurements of $J$-$V$ characteristics. The $J$-$V$ characteristics for the sample cells were measured under different illumination intensity of the solar simulator. The power supply for the Xeon lamp was tuned to change the illumination intensity. Light intensity of the Xeon lamp with different power supply was determined by the output current density of the standard reference c-Si cell. However it was found that the changes of illumination intensity of the Xeon lamp within different spectral ranges after the power supply was tuned were different. The spectral intensity distributions of the solar simulator at different integrated light intensities were measured using a portable Spectrometer Ocean Optics (USB2000+VIS-NIR). The working principle of the portable Spectrometer is illustrated in Fig. 3.9. The measured spectral intensity was normalized according to the equation below:

$$I_{N,E}(\lambda) = \frac{I_E(\lambda)}{E},$$

where $E$ is the integrated illumination intensity of the Xeon lamp and $I_{N,E}(\lambda)$, $I_E(\lambda)$ are the normalized spectral intensity and the measured spectral intensity when the integrated illumination intensity is $E$. 
The normalized spectral intensity at different integrated intensity was plotted in Fig. 3.10(a). It was found that the weight of the number of photons from spectrum range of 800 nm to 1000 nm was obviously increased. Therefore without KG5 filter, the values of two different light intensities calibrated by a standard c-Si cell actually doesn’t reflect the real differences between the two different light intensities within the spectral range of 400 nm to 800 nm. It can be seen from Fig. 3.10(b) that the spectral intensity distribution of the lamp nearly changed synchronous within spectral range of 400 nm to 800 nm when the power supply changed. With KG5 filter, it is feasible to measure light intensity-dependent $J-V$ characteristics through tuning the power supply of the lamp to change the intensity of light. On the other hand, a series of filters must be used to change light intensity if the spectral response range to the test sample extends to beyond 800 nm. In the experiments, the spectral response ranges of OSCs based on PTB7, PTB7-Th and PNB4 were all within 300 nm to 800 nm.
Fig. 3.10: Normalized spectral intensity distribution of Xeon lamp measured at different illumination intensities within the spectrum range of (a) 380 nm to 1000 nm and (b) 380 nm to 800 nm.

3.2.3 Transient Photocurrent Measurement

TPC measurement is a technique to study the transient dynamics of the photo-generated carriers with a time scale of ~10 ns in electronic devices. The apparatus for TPC measurement is shown in Fig. 3.11. In the experiments, the transient signal in sample devices was generated by an Nd:YAG pulsed laser with the wavelength of 355 nm and pulse duration of 5 ns. The metal electrodes of the devices were about 30 nm so that the laser could penetrate the semitransparent metal film and generated excitons and free carriers in the active layer. The transient photovoltage generated by the transient dynamics of excitons and free carriers was recorded by an oscilloscope (Agilent DSO8064A Infinium Digital Oscilloscope, with the bandwidth of 600 MHz). The transient photovoltage was converted to the corresponding transient photocurrent of the devices using the internal resistor (50 Ω) of the functional generator. In the dark, the transient current ($I_D$)
was recorded to reflect the noise and dark current. When the active layer was excited by the laser, the transient current ($I_L$) was recorded again. Then transient photocurrent ($I_{TPC}$) of the device was calculated by:

$$I_{TPC} = I_L - I_D.$$  \hspace{1cm} 3.5

Every kind of transient dynamics of excitons and free carriers may contribute to the transient photocurrent. However, the response time scale and the response to an external bias of these different transient signals are different. The external bias from the function generator is important to distinguish different transient currents from each other.

![Diagram of the TPC measurement system.](image)

Fig. 3.11: Schematic diagram of the TPC measurement system.

3.2.5 Atomic Force Microscope

DI Nanoscope-IV Multimode atomic force microscope (AFM) was used to characterize the surface morphology of the organic active layers and the solution processed interlayer on the organic active layers. AFM is a type of scanning probe microscopy with very high-resolution in
the order of 1nm. AFM can be used to observe the landscape of the sample surface and measure the roughness of the surface at a high resolution. The separation phase of an organic blend layer can also be studied by AFM. In the experiments, the scanning area of the AFM image was typically 5 μm × 5 μm. There was a tip on the end of a cantilever. AFM tapping mode was used to get a 2D image of the surface morphology of the samples. The information about the surface property was generated through the atomic force interaction between the tip and the sample surface. The setup of AFM was schematically shown in Fig. 3.12.

![Schematic diagram of the components of an AFM.](image)

Fig. 3.12: Schematic diagram of the components of an AFM.

The ZnO NPs thin film on the organic blend layer was difficult to observe by bare eyes and therefore it was not sure whether the organic blend layer could be fully covered by the ZnO NPs. As shown in Fig. 3.13, the AFM images for the surfaces of organic blend layer and the ZnO NPs interlayer on organic blend layer were very different. Two phases of the blend layer surface and the particles on the ZnO NPs surface could be clearly observed. The surface of the organic blend layer was fully covered by ZnO NPs. The surface morphology can be described by root mean square (RMS) roughness, which means the standard deviation of height from the average height
of a surface. The values of RMS for the two different surfaces were shown in Fig. 3.13. Therefore, the surface of the sample with a ZnO interlayer covered on the top of organic blend layer was smoother than the original blend layer surface.

![AFM images of P3HT:PCBM blend layer and ZnO NPs spin coated on P3HT:PCBM blend layer.](image)

Fig. 3.13: (a) AFM image of P3HT:PCBM blend layer; (b) AFM image of ZnO NPs spin coated on P3HT:PCBM blend layer.

### 3.2.6 Variable Angle Spectroscopic Ellipsometry

To conduct optical simulation, the optical constants, i.e. wavelength dependent refractive index $n(\lambda)$ and extinction coefficient $k(\lambda)$, are necessary to be determined for every layer in OSCs. The values of $n(\lambda)$ and $k(\lambda)$ for Al were from handbook. The values of $n(\lambda)$ and $k(\lambda)$ for ITO, PEDOT:PSS, PTB7:PC$_{70}$BM and ZnO were measured by variable angle spectroscopic ellipsometry (VASE). VASE is a very sensitive characterization technique and can be used to characterize the thicknesses of multilayer thin films, optical constants of thin films, composition and crystallinity of thin film and material microstructures. In practice, the thicknesses of thin
films were measured by an Alphastep Semiconductor Surface Profiler since its operation was much easier and quicker than that of VASE. The typical configuration and physical picture of an ellipsometry were shown in Fig. 3.14. The polarized light was transmitted through the surface of PTB7:PC$_{70}$BM and reflected by the surface of Si substrate. In the experiments, wavelength of the incident polarized light was swept from 300 nm to 900 nm. The amplitude and phase changes of the reflected light, which depended on the optical constant and thickness PTB7:PC$_{70}$BM blend layer, were recorded and analyzed by computer software. The amplitude and phase changes in the reflected polarized light were donated by the $\Psi$ and $\Delta$, respectively. The Fresnel coefficients of the reflected light were expressed as:

$$ r_p = \frac{N \cos \theta_i - \cos \theta_r}{N \cos \theta_i + \cos \theta_r}, \quad 3.6 $$

$$ r_s = \frac{\cos \theta_i - N \cos \theta_r}{\cos \theta_i + N \cos \theta_r}, \quad 3.7 $$

where $r_p$ was the projection of the electric field of the reflected light on p-plane, i.e. plane of incidence); $r_s$ was the projection of the electric field of the reflected light on s-plane, i.e. perpendicular to plane of incidence; $\theta_i$ and $\theta_r$ were the incidence and reflection angle; $N$ is the complex refractive index. The relationship between the Fresnel coefficients and measured values of $\Psi$ and $\Delta$ was expressed in Eq. 3.8. Combine Eq. 3.6, Eq. 3.7, Eq. 3.8 and Eq. 3.9 together, the $n(\lambda)$ and $k(\lambda)$ of the tested thin film were calculated.

$$ \tan(\Psi) \exp(i\Delta) = \frac{r_p}{r_s}, \quad 3.8 $$

$$ N(\lambda) = n(\lambda) + i \times k(\lambda). \quad 3.9 $$
Finally, the wavelength dependent values of $n(\lambda)$ and $k(\lambda)$ for PTB7:PC$_{70}$BM blend layer was calculated and plotted in Fig. 3.15.
3.2 Optical Admittance Analysis

The basic principles of optical admittance analysis are based on wave optics. It considers the reflection, refraction, transmission and the boundary conditions for both the electrical and magnetic field at the interface between two dielectric thin films. An OSC can be viewed as a multilayer thin film system and thus its optical properties can be investigated by optical admittance analysis. For a general understanding, it is assumed the OSCs consist of $m$ layers of dielectrics. The effective optical admittance $y_{\text{eff}}$ of the whole system can be calculated based on the following two equations:\(^{67,68}\):

$$\left( \begin{array}{c} B \\ C \end{array} \right) = \left[ \prod_{j=1}^{m} \left( \begin{array}{cc} \cos \delta_j & i \sin \delta_j \ y_j \\ i y_j \sin \delta_j & \cos \delta_j \end{array} \right) \right] \left( \begin{array}{c} I \\ y_{m+1} \end{array} \right),$$

$$y_{\text{eff}} = \frac{C}{B},$$

where $I$ is the unit matrix; $y_j$ and $y_{m+1}$ are the optical admittances for the $j$th layer and the substrate respectively. In practice, the substrate is air. $\delta_j$ is the angular phase, which is expressed as:

$$\delta_j = \frac{2\pi N_j d_j \cos \theta}{\lambda},$$

where $d_j$ is the thickness of $j$th layer; $N_j$ is the complex refractive index of $j$th layer and it is expressed in the form of $n_j(\lambda) - ik_j(\lambda)$. $\theta$ is light incident angle. After the value of $y_{\text{eff}}$ is determined, the reflectance of the whole system at different wavelength $R(\lambda)$ can be calculated by:
\[ R(\lambda) = \left| \frac{1 - y_{\text{eff}}}{1 + y_{\text{eff}}} \right|. \]  
(3.13)

And in the condition of normal incidence, i.e. \( \theta = 0 \), the transmittance of the whole system \( T(\lambda) \) can be calculated by the following two equations \(^{67,68}\):

\[ T(\lambda) = \left[1 - R(\lambda)\right] \prod_{j=1}^{m} \Psi_j, \]  
(3.14)

\[ \Psi_j = \frac{\text{Re}(y_{j+1})}{\text{Re}(y_j) \cos \delta_j + \frac{y_{j+1} \sin \delta_j}{N_j}}. \]  
(3.15)

where \( \text{Re}(y_{j+1}) \) and \( \text{Re}(y_j) \) are the real part of the optical admittances of \((j+1)\)th and \( j \)th layer.

Then the absorption spectrum of the \( j \)th layer can be expressed as \(^{67,68}\):

\[ A_j(\lambda) = \left[1 - R(\lambda)\right] \prod_{i=1}^{j} \Psi_i(\lambda). \]  
(3.16)

The integrated absorbance of any individual layer can be calculated as:

\[ \overline{A}_j = \frac{\int A_j(\lambda) F(\lambda) d\lambda}{\int F(\lambda) d\lambda}, \]  
(3.17)

where \( F(\lambda) \) is the flux of solar irradiation measured in Wm\(^{-2}\)nm\(^{-1}\). Thus the optical admittance analysis technique can be used as a method to quickly find the optimal thicknesses of each layer in OSCs so that the integrated absorbance in organic active layer achieves maximum. In practice, the optical properties of the PTB7:PC\(_{70}\)BM based OSCs were studied by Emissive Thin Film Optics Simulator (ETFOS). The wavelength of the incident light in the simulation was swept from 350 nm to 800 nm with a step of 2 nm.
Chapter 4

Monomolecular and Bimolecular Recombination Processes in Organic Solar Cells

4.1 Charge Collection in Organic Solar Cells

In previous works, the definition of charge collection efficiency was quite ambiguous. One of the interpretations for charge collection efficiency was the collecting ability of the electrodes, i.e. the percentage of the charges collected by the electrodes among the total charges arrived at the organic/electrode interfaces. However, it’s quite difficult to judge how many charges arrived at the organic/electrode interface. In some cases, the transport of electrons and holes is not balanced, which means that the amount of charges accumulated at anode and cathode are different. Based on the working principle of OSCs, a more practical method to define the charge collection efficiency was adopted in this thesis. It is interpreted by Eq. 4.1:

\[ IPCE = \eta_A \cdot \eta_{\text{diff}} \cdot \eta_{\text{CT}} \cdot \eta_C, \]  

where \( \eta_A \) is the photon absorption efficiency; \( \eta_{\text{diff}} \) describes the energy loss due to the relaxation of excitons before they diffuse to the D-A interface; \( \eta_{\text{CT}} \) is the exciton dissociation efficiency at the D-A interface; \( \eta_C \), the so-called charge collection efficiency, describes the total losses of charges during the free carrier transport in the organic active layer and the transfer at the organic/electrode interface. \( \eta_C \) reflects the energy losses due to the charge recombination and accumulation in the organic active layer and organic/electrode interface. The accumulated charges disappear via recombination processes eventually. Before the charge collection
efficiency is discussed in more details, several physical concepts will be defined. Applied bias on the OSCs is denoted as $V_a$. The built-in potential across the organic active layer, determined by the intrinsic properties of D-A interface and the difference in the work function between the two electrodes, is denoted as $V_0$. The value of $V_0$ equals to the applied voltage when $J_{ph}=J-J_D=0$, where $J_{ph}$ is photocurrent density, $J$ is the measured current density and $J_D$ is the current density in dark condition. Then the effective bias across the organic active layer is expressed as:

$$V_{eff} = V_0 - V_a.$$  \[4.2\]

There are two types of recombination for the photo-generated free carriers, i.e. bimolecular recombination and monomolecular recombination. Bimolecular recombination is the recombination that occurs between the photo-generated positive and negative charges when they meet each other. These charges usually meet at the D-A interface and organic/electrode interface. Monomolecular recombination happens when the photogenerated free electrons (holes) are captured by the traps and then recombine with the intrinsic free holes (electrons) in the acceptor (donor). As well known, $J_{SC}$ is the photocurrent when the applied bias is zero. However, the photocurrents at other applied biases are also important for the performance of OSCs, which actually are reflected by $FF$. Therefore examining the charge collection efficiency at the short circuit density condition is not enough to understand the energy loss during charge transport and collection processes. The travelling time of the free carriers in the bulk is affected by the applied bias, which will finally affect the bimolecular recombination loss. The probability for the free carriers to escape from the traps is also dependent on the electrical field across the organic active layer. On the other hand, the concentration of photo-generated free carriers, depending on the intensity of incident light ($I$), is also a key factor to determine the charge recombination loss.
The charge recombination loss during charge transport and transfer at the organic/electrode interfaces is characterized by charge collection efficiency, which is also a function of the effective bias and incident light intensity. The effective bias and intensity dependent charge collection efficiency is donated by $P(I, V_{\text{eff}})$. According to previous work, photocurrent under specific effective bias ($V_{\text{eff}}$) and the intensity of light ($I$) can be expressed as\textsuperscript{71, 72}:

$$J_{\text{ph}}(I, V_{\text{eff}}) = eLG(I)P(I, V_{\text{eff}}),$$

Eq. 4.3

where $e$ is the elementary charge, $L$ is the thickness of the active layer, $G(I)$ is light intensity-dependent generation rate of electron-hole pairs per unit volume. At high effective bias, i.e. large applied reverse bias, the recombination loss during transport and transfer is negligible since the photo-generated free carriers can be extracted easily by the large electrical field. It is reasonable to assume the charge collection efficiency $P(I, V_{\text{eff}}) = 1$, when the effective bias approaches $V_S$. $V_S$ here means effective bias corresponding the saturated current density $J_{\text{ph}}(I, V_S)$. Then the charge collection efficiency can be expressed as\textsuperscript{73}:

$$P(I, V_{\text{eff}}) = \frac{J_{\text{ph}}(I, V_{\text{eff}})}{J_{\text{ph}}(I, V_S)}. \quad 4.4$$

If the photocurrent density are normalized and define the saturated photocurrent density $J_{\text{ph}}(I, V_S)$ as the unit 1, the curves representing the effective bias dependent charge collection efficiency and the normalized effective bias dependent photocurrent density are the same. As an example shown in Fig. 4.1, the curve also representing the function $\eta_C = P(I, V_{\text{eff}})$. 

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Fig. 4.1: Normalized photocurrent density as a function of $V_{\text{eff}}$, illustrating the characteristics of the effective bias dependent charge collection efficiency.

4.2 Light Intensity-dependent Charge Recombination Dynamics

Bimolecular recombination and monomolecular recombination are two important factors that limit the charge collection efficiency. The charge collection efficiency shows the integrated effects of the two types of recombination processes. Study of light intensity-dependent $J$-$V$ characteristics is a useful technique to analyze the energy loss in OSCs due to different charge recombination processes. Since the bimolecular and monomolecular recombinations are affected by different factors, better understanding of them provide valuable guidance for the design of efficient OSCs. Next the fundamentals about light intensity-dependent $J_{SC}$, $V_{OC}$ and $FF$ will be introduced and a method to analyze the effects of the two types of recombination in OSCs will be developed.
4.2.1 Light Intensity-dependent Photocurrent

As known, the output power of OSCs is closely related to the intensity of solar irradiance. The intensity of light has a significant impact on the $J$-$V$ characteristics of the cells. The $J_{ph}$ of OSCs is closely related to the intensity of light. The empirical relationship between and $I$ was established through large scale of experimental work\textsuperscript{74, 75}. $J_{SC}$ and $I$ follow a power law relationship:

$$J_{SC} \propto I^{\alpha}, \quad 4.5$$

where the value of the exponent $\alpha$ is usually between 0.75 and 1. However, the experimental fact that $\alpha$ is usually less than 1 is not consistent with our physical intuition. The reasons for this inconsistency are still controversial. It is widely accepted that the bimolecular recombination, which can cancel out part of the photo-generated carriers, is responsible for the deviation of $\alpha$ from 1\textsuperscript{76, 77}. The percentage of photo-generated carriers that is lost due to bimolecular recombination increases with increase of the intensity of light\textsuperscript{78}. So there is a diminishing marginal increase in $J_{SC}$ with the increase of $I$, resulting in a value of $\alpha$ less than 1. If the intensity of light increases to several hundreds of W/cm$^2$ or higher, the value of $\alpha$ is well below 1 due to high charge loss in organic materials with poor charge transport capability\textsuperscript{73}. The $J_{SC}$ of OSCs is affected by the dark current $J_D$. Bimolecular recombination also depends on the effective potential difference across the organic active layer\textsuperscript{79}. Therefore it is more convenient to analyze the relevant physics by expressing the intensity dependence current as shown in the following equation\textsuperscript{80}. 

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\[ J_{ph} \propto (PI)^\alpha \sqrt{(V_0 - V_a)}, \]

where the photocurrent density \( J_{ph} = J_{SC} - J_D \), \( P \) is the exciton dissociation probability, \((V_0 - V_a)\) is the effective bias across the organic active layer.

It was also reported that there were numerous explanations other than bimolecular recombination for such deviations. The monomolecular recombination via defects or impurities\(^{73,81}\) and the accumulated space charges\(^{82}\) also contribute to the deviation of \( \alpha \) from unit. The accumulated charges, no matter in the bulk or at the electrode/organics interface, eventually disappear via bimolecular or monomolecular recombination. So the deviation of \( \alpha \) from unit is also an integrated effect of bimolecular and monomolecular recombination\(^{83}\). Any imperfections in the OSCs that can increase charge losses via bimolecular or monomolecular recombination processes contribute to the deviation of \( \alpha \) from 1. Two examples below demonstrate how to analyze experimental data regarding the relationship between light intensity and \( J_{ph} \).

Example 1: In Duren’s work, the charge recombinations in a set of devices with identically structure \((ITO/PEDOT:PSS/P3HT:PCBM/Al)\) but different ratios of P3HT to PCBM were studied through the measurement of light intensity-dependent photocurrent density\(^{73}\). It was found that the photocurrent densities in all of the devices followed a power law relationship with \( I \), but the values of \( \alpha \) were different in these devices. All the other factors, i.e. defects, impurities, sites for charge accumulation, are indifferent in these devices. Therefore, the significant differences in \( \alpha \) resulted from the different bimolecular recombination rates in these OSCs with different D-A interfacial properties. In addition to the D-A ratios, the morphology of the organic blend layer, selection of acceptors and annealing conditions all have great impact on the D-A...
interfacial properties. These factors also have great influences on the bimolecular recombination rate\textsuperscript{84} and the value of $\alpha$.

Example 2: In Kyaw’s work, the charge collection efficiencies in two devices, with structures of ITO/PEDOT:PSS/active layer/Al and ITO/PEDOT:PSS/active layer/ZnO/Al were analyzed through the measurement of light intensity-dependent $J$-$V$ characteristics\textsuperscript{85}. In the two devices, all of the layers were the same except for the organic/cathode interfaces. Therefore, any significant difference in the value of $\alpha$ resulted from the different bimolecular or monomolecular recombination processes at organic/electrode interfaces. If the barriers at the electrode/organics interface were high enough to cause significant resistance to the charge transfer across the interface, there were significant charge accumulation at the organic/electrode interfaces. The accumulated charges disappear via monomolecular recombination at the interfacial trap sites eventually. If the charge selectivity of the electrode is poor, then opposite charges will be collected by the electrodes at the same time, which increases the bimolecular recombination. To judge which mechanism was responsible for the deviation of $\alpha$ from 1 in the two OSCs, additional experimental data was need.

4.2.2 Light Intensity-dependent Open Circuit Voltage

Examining the relationship between $J_{SC}$ and $I$ is not enough to study the bimolecular and monomolecular recombination in OSCs. It’s worth to further analyze the relationship between the open circuit voltage ($V_{OC}$) and light intensity. Next a brief review of some fundamental theories about $V_{OC}$ for OSCs will be presented. In the previous work, it has been reported that $V_{OC}$ increases with the increase in the energy difference between the HOMO of donor and the LUMO of acceptor in OSCs. $V_{OC}$ is not so much affected by the work function of the electrodes\textsuperscript{86}.  

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The energy levels of HOMO and LUMO in organic semiconducting materials are analogous to the conduction band and valence band in inorganic semiconductors. Generally, organic materials used in OSCs are amorphous and disorders always exist, which may have significant effects on the performance of OSCs. The edges of conduction and valence bands in the amorphous materials are not clearly defined due to the disorder, instead, there will be tail states extended into the bandgap. Gaussian distribution is often used to approximate the density distribution of the band tail states. The disorder induced loss in $V_{OC}$ of OSCs can be expressed as $-\sigma^2/kT$, where $\sigma$ is related to the width of Gaussian distribution, $k$ is the Boltzmann constant and $T$ is the temperature.

Another source of loss in $V_{OC}$ is monomolecular and bimolecular recombination. To understand the effect of charge recombination on the $V_{OC}$ of solar cells, it’s helpful to review the origin of $V_{OC}$ in OSCs. Shockley equation is derived based on the classical theory for $p$-$n$ junction and is used to describe the current-voltage behavior of a $p$-$n$ junction diode. The Shockley equation for a $p$-$n$ junction diode with an ideality $n$ is as:

$$J(V_a) = J_0[\exp\left(\frac{qV_a}{kT}\right)-1],$$

where $V_a$ is the externally applied voltage, $J_0$ is the saturation current under small reverse bias ($V_a<0$), $q$ is the elementary charge, $k$ is the Boltzmann constant and $T$ is the temperature. If the $p$-$n$ junction diode considered here is a solar cell, then the photocurrent $J_{ph}$ should be taken into consideration under illumination. Since the photogenerated carriers form current by diffusion, the direction of $J_{ph}$ is opposite to the current caused by a forward bias. Then the Shockley equation for solar cells under illumination becomes:
\[ J(V_a) = J_0[\exp(\frac{qV_a}{kT}) - 1] - J_{ph}. \]  

At an open circuit condition, the current density in the external circuit is 0, i.e. \( J(V_a=V_{OC}) = 0 \).

Thus \( V_{OC} \) can be expressed as:

\[ V_{oc} = \frac{mkT}{q} \ln(\frac{J_{ph}}{J_0} + 1), \]

where \( m \) is dependent on the ideality of the \( p-n \) junction diode.

It’s easy to see that light intensity can affect the \( V_{OC} \) since \( J_{ph} \) is directly related to light intensity. The reverse saturation current in dark \( J_0 \) depends on the fundamental semiconducting properties of the \( p-n \) junction. Under reverse bias in the dark, the dynamic equilibrium of minority carriers results in the saturation dark current density \( J_0 \). The dynamic equilibrium of the minority is actually constructed by the carrier injection of the electrodes and the carrier recombination. Therefore the recombination characteristics of a \( p-n \) junction diode have great impacts on its current-voltage characteristics.

The metal-insulator-metal model, in which the organic blend layer is regarded as equivalent to one semiconducting material with HOMO of donor as valence band and LUMO of acceptor as conduction band, is used to describe the charge carrier dynamics inside the OSCs.\(^{82, 92, 97}\) The following relationships be derived:\(^{79}\):

\[ np = n_i^2 \exp\left(\frac{qV_{oc}}{kT}\right), \]

\[ n_i = N_c \exp\left(-\frac{\Delta E}{2kT}\right), \]

where \( n/p \) is the electron/hole concentration inside the device, \( n_i \) is the intrinsic carriers
concentration (for both electrons and holes) in the organic active layer, $N_c$ is the effective density of states (for both conduction band and valence band) and $\Delta E$ is the difference between the LUMO of acceptor and the HOMO of donor. From Eq. 4.10 and Eq. 4.11, $V_{OC}$ can be expressed as:

$$V_{oc} = \frac{\Delta E}{q} + \frac{kT}{q} \ln\left(\frac{np}{N_c^2}\right).$$  \hspace{1cm} 4.12

It should be noted that $\Delta E$ should be modified if the Gaussian disorder in the organic materials is taken into consideration. Thus Eq. 4.12 can be more accurate:

$$V_{oc} = \frac{\Delta E}{q} - \frac{\sigma^2}{kT} + \frac{kT}{q} \ln\left(\frac{np}{N_c^2}\right).$$  \hspace{1cm} 4.13

The carrier concentration in the device is determined by the dynamics of mobile carrier generation and recombination, or mathematically,

$$\frac{\partial(n \cdot Vol)}{\partial t} = g_e - r_e,$$  \hspace{1cm} 4.14

where $Vol$ is the volume of the active region, $g_e$ is the number of photo-generated free electrons per unit time, $r_e$ is the number of free electrons reduced by recombination. Based on the metal-insulator-metal model and the concept expressed by Eq. 4.14, taking into consideration of space charge effects, the continuity equation becomes \(^98\):

$$\frac{1}{q} \frac{\partial}{\partial x} J_n(x) = PG - (1-P)R,$$  \hspace{1cm} 4.15

where $G$ is the exciton generation rate, $P$ is the exciton dissociation probability and $R$ is the recombination rate. The linear coefficient, linking the exciton generation rate (averaged photon
absorption ratio) and the intensity of the incident light \( (I) \), is donated as \( A \). At an open circuit condition, the current density inside the device is 0 everywhere and the correlation between \( I \) and the charge recombination \( (R) \) becomes:

\[
R = \frac{PA}{1-P} \cdot I. \tag{4.16}
\]

To express \( V_{OC} \) as a function of \( I \), a relationship between the recombination \( R \) and the free carriers \((n/p)\) is essential. Here the bimolecular recombination and monomolecular recombination are examined separately. Assume that only the bimolecular recombination exists in the system. The limiting factor on the rate of bimolecular recombination is the possibility to find the recombination partners. Therefore, the bimolecular recombination rate can be expressed as:

\[
R = \gamma(np - n_i^2). \tag{4.17}
\]

Under illumination, the intrinsic carrier concentration \( n_i \), excited by thermal energy and bias, is much lower than the photoexcited carriers. By neglecting the term \( n_i^2 \), using Eq. 4.13, Eq. 4.16 and Eq. 4.17, the \( V_{OC} \) of OSCs and the intensity of light can be related through the following equation:

\[
V_{oc} = \frac{\Delta E}{q} - \frac{\sigma^2}{kT} + \frac{kT}{q} \ln[\frac{PA}{\gamma(1-P)N_e^2} \cdot I]. \tag{4.18}
\]

From Eq. 4.18, a linear relationship between \( V_{OC} \) and \( \ln I \) with a slope of \( \frac{kT}{q} \) is obvious.

Assume that the recombination in the device is only in monomolecular form. Following assumptions that the limiting factor of monomolecular recombination is the possibility to find an
effective trap sites, the monomolecular recombination rate can be described by Schockley-Read Hall equation\textsuperscript{100,101}:

\[ R = \frac{C_n C_p \delta (pn - n_i^2)}{C_n (n + n_i) + C_p (p + n_i)}, \]  

where \( C_n \) and \( C_p \) are the capture coefficients of electrons and holes respectively, \( \delta \) is the density of the trap sites, \( p/n \) is the hole/electron density generated by photoexcitation, \( n_i \) is the intrinsic carrier concentration. Under illumination, the number of photo-generated electron and holes are about the same \( (p \approx n) \) since the electrons and holes are generated in pair. The number of photo-generated carriers is greater than that of the intrinsic ones. Assuming \( p \approx n > n_i \), Eq. 4.19 can be approximated as:

\[ R = \frac{C_n C_p \delta}{C_n + C_p} \cdot n = \gamma_m \delta \cdot n, \]  

where \( \frac{C_n C_p}{C_n + C_p} \) is equal to a constant \( \gamma_m \). Using Eq. 4.13, Eq. 4.16 and Eq. 4.20, correlation between the V\textsubscript{OC} of OSCs and \( I \) can be expressed as:

\[ V_{oc} = \frac{\Delta E}{q} - \frac{\sigma^2}{kT} - \frac{kT}{q} \ln \left( \frac{P^2 A^2}{\gamma_m^2 \delta^2 (1 - P)^2 N_c^2} \cdot I^2 \right). \]  

From Eq. 4.21, V\textsubscript{OC} and \( \ln I \) show a linear relationship with a slope of \( 2 \cdot \frac{kT}{q} \). For a high performance OSC, the densities of defects and impurities in the active layer are relatively low and the charge loss via bimolecular recombination is dominant at open circuit condition\textsuperscript{76}. So for OSCs, the slope is usually equal to or a little large than \( \frac{kT}{q} \). However, in some devices with
traps of high density and deep average depth, the slope can be well exceed $\frac{kT}{q}$ or even larger than $2\cdot\frac{kT}{q}$ \textsuperscript{102}. It needs further study to explain that the slope is sometimes larger than $2\cdot\frac{kT}{q}$. In summary, by studying the relationship between $V_{OC}$ and $I$, it is helpful to analyze the recombination losses in OSCs.

### 4.2.3 Light Intensity-dependent Fill Factor

It has been reported that the $FF$ of OSCs is also dependent on the intensity of light\textsuperscript{73,78}. According to the definition of $FF$ and its graphical interpretation discussed in Section 2.1.3, it is easy to understand that $FF$ is a measure of the shape of $J$-$V$ characteristics. $FF$ actually can be interpreted as the dependence of current density on the output voltage. From such a point of view, any factors that related to the bias dependent current density may affect the $FF$ of OSCs. As discussed in the previous sections, both of the bimolecular and monomolecular recombinations are dependent on the effective bias\textsuperscript{103,104}. The rates of bimolecular and monomolecular recombinations are affected by the intensity light. Therefore the study of light intensity-dependent $FF$ is important to understand the effect of device architecture on $FF$ of OSCs.

As the charge recombination can occur in the organic active layer or the organic/electrode interface, the factors limiting $FF$ can be divided into two parts: (a) free carrier loss in the organic active layer and (b) free carrier loss at the organic/electrode interfaces. These factors can be described using Eq. 4.22 and Eq. 4.23\textsuperscript{105}:

$$FF_{bulk} \propto \frac{Q_{free}}{Q_{total}} = \frac{Q_{free}}{Q_{free} + Q_{trap} + Q_{recombine}}, \quad 4.22$$
where the total free carriers in the active layer $Q_{\text{total}}$ can be divided into three parts: free carriers $Q_{\text{free}}$, trapped carriers $Q_{\text{trap}}$ and bimolecular recombined carriers $Q_{\text{recombine}}$. $Q_c$ represents the carriers collected finally, $Q_a$ represents the carriers accumulated at the organic/electrode interface and $Q_c + Q_a = Q_{\text{free}}$. The amount of carriers captured by the traps and recombined with each other in the active layer can be related to the amount of free carriers using Eq. 4.24 and Eq. 4.25.

\[ Q_{\text{trap}} = \frac{kT}{Q_{\text{free}}}, \quad Q_{\text{recombine}} = k_0 \cdot \text{free}^{\lambda+1}, \]

where $U_T$ is the Urbach energy of trap distribution, $k$ is Boltzmann constant, $T$ is temperature; $k_0$ is a constant depending on the properties of the organic materials and $\lambda+1$ is an empirical reaction order. Urbach energy characterizes the average trap depth due to the band tail states in organic materials. Using Eq. 4.22, Eq. 4.24 and Eq. 4.25, the expression for $FF_{\text{bulk}}$ changes to:

\[ FF_{\text{bulk}} \propto \frac{Q_{\text{free}}}{kT} \cdot \frac{1}{1 + Q_{\text{free}}^{\lambda+1} + k_0 Q_{\text{free}}^{\lambda}}, \]

When the Urbach energy $U_T > kT$ (≈25.8 meV at room temperature), the $FF_{\text{bulk}}$ increases first and then decreases with increase in the amount of transported free carriers $Q_{\text{free}}$ or light intensity $I$. $Q_{\text{free}}$ is proportional to light intensity $I$. When the Urbach energy for the band tail states is very large, the photogenerated carriers are easily captured by the traps. As the intensity of light increases, the photo-generated carriers are likely to fill in the traps first. With the increase in the
amount of photo-generated carrier, the percentage of transported carrier increases and thus $FF_{bulk}$ also increases. With further increase in the intensity of light, most of the traps are filled; the bimolecular recombination increases significantly due to the high concentration of transported carriers. Therefore, the percentage of transported carriers among the total photo-generated carriers decreases, which means a decreasing $FF_{bulk}$. In summary, $FF_{bulk}$ increases with the increase in the intensity of light under weak illumination condition, while $FF_{bulk}$ decreases with the increase in the intensity of light under strong illumination condition. When the Urbach energy $U_T < kT$, the $FF_{bulk}$ decreases monotonically with the increase in the intensity of light, as expressed by Eq. 4.26. In this case, the carrier loss in the active layer is mainly contributed by the bimolecular recombination.

The $FF$ of the OSCs combines the effects of charge loss in the bulk and at the organic/electrode interface, i.e. $FF = FF_{bulk} \times FF_{interface}$. If the carrier transfer at the organic/electrode interface is highly efficient, there will be little carriers accumulated at the interface. Then $FF_{interface}$ is almost equal to 100%, and therefore it becomes less sensitive to the intensity of light. As a result, the relationship between $FF$ and the intensity of light is mainly determined by light intensity-dependent $FF_{bulk}$. It is easy to observe the non-monotonic trends in $FF$ with increase in the intensity of light. If there is significant charge loss at the organic/electrode interface, the relationship between $FF$ and the intensity of light is mainly determined by light intensity-dependent $FF_{interface}$. The amount of accumulated charges usually increases with a faster rate than that of the collected charges due to the non-ohmic contact of organic/electrode interface. In this case, there is a monotonic decrease in $FF$ with the increase in the intensity of light.
4.3 Effect of Charge Recombination on Performance of Organic Solar Cells

The bimolecular recombination and monomolecular recombination in OSCs based on three widely used commercial polymers were studied. Carrier recombination dynamics in OSCs were analyzed using light intensity-dependent $J$-$V$ characteristics.

Inverted OSCs with structure of ITO/ZnO/BHJ/eMoO$_X$/Ag were fabricated. The ratio of donor to acceptor in different BHJs of PTB7: PC$_{70}$BM (1:1.5), PTB7-Th: PC$_{70}$BM (1:1.5) and PNB4: PC$_{70}$BM (1:2) was optimized for cell fabrication. The thicknesses of the BHJs for the three optimized devices were all ~100 nm. The $J_S$, $V_{OC}$, $FF$ and $PCE$ of the three devices are summarized in Table 4.1.

Table 4.1: Summary of the performance of PTB7: PC$_{70}$BM, PTB7-Th: PC$_{70}$BM and PNB4: PC$_{70}$BM based inverted OSCs.

<table>
<thead>
<tr>
<th>Optimized devices</th>
<th>$V_{OC}$ (V)</th>
<th>$J_S$ (mA/cm$^2$)</th>
<th>$FF$ (%)</th>
<th>$PCE$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB7: PC$_{70}$BM</td>
<td>0.73</td>
<td>13.3</td>
<td>69</td>
<td>6.7</td>
</tr>
<tr>
<td>PTB7-Th: PC$_{70}$BM</td>
<td>0.78</td>
<td>14.2</td>
<td>68</td>
<td>7.5</td>
</tr>
<tr>
<td>PNB4: PC$_{70}$BM</td>
<td>0.7</td>
<td>12.1</td>
<td>67</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Light intensity-dependent $J$-$V$ curves were measured for the three devices. Light intensity-dependent photocurrent densities for the three devices are shown in Fig. 4.2.
As discussed in the previous section, the photocurrent density and light intensity has a sublinear relationship: \( J_{ph} \propto I^\alpha \). The values of \( \alpha \) for different devices under different effective bias were summarized in Table 4.2.

![Fig. 4.2: Light intensity-dependent photocurrent density of (a) PTB7:PC\(_{70}\)BM, (b) PTB7-Th:PC\(_{70}\)BM and (c) PNB4:PC\(_{70}\)BM based inverted OSCs measured at different effective bias.](image-url)
Table 4.2: Sublinear coefficients $\alpha$ of light intensity-dependent photocurrent densities obtained for PTB7: PC$_{70}$BM, PTB7-Th: PC$_{70}$BM and PNB4: PC$_{70}$BM based inverted OSCs.

<table>
<thead>
<tr>
<th>$V_{eff} \approx 0.80V$</th>
<th>PTB7: PC$_{70}$BM</th>
<th>PTB7-Th: PC$_{70}$BM</th>
<th>PNB4: PC$_{70}$BM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha = 1.0$</td>
<td>$\alpha = 1.0$</td>
<td>$\alpha = 1.0$</td>
<td>$\alpha = 1.0$</td>
</tr>
<tr>
<td>$V_{eff} \approx 0.25V$</td>
<td>$\alpha = 1.0$</td>
<td>$\alpha = 1.0$</td>
<td>$\alpha = 0.99$</td>
</tr>
<tr>
<td>$\alpha = 0.99$</td>
<td>$\alpha = 0.94$</td>
<td>$\alpha = 0.90$</td>
<td>$\alpha = 0.90$</td>
</tr>
<tr>
<td>$V_{eff} \approx 0.15V$</td>
<td>$\alpha = 0.89$</td>
<td>$\alpha = 0.94$</td>
<td>$\alpha = 0.90$</td>
</tr>
</tbody>
</table>

The deviation of $\alpha$ from unit could only be observed under very low effective bias for all of the three devices. The high effective bias conditions, i.e. $V_{eff} = 0.83$, $V_{eff} = 0.88$ and $V_{eff} = 0.79$ corresponded to the short circuit conditions in the three OSCs. On the other hand, the low effective bias was achieved when the externally applied bias was closed to open circuit voltage. It is seen that the charge recombination during charge transport in the bulk and transfer at the organic/electrode interface in these cells had negligible impact on $J_{SC}$. However, deviation of $\alpha$ from unit was observed in the sublinear relationship between the effective bias dependent photocurrent and light intensity. Thus $FF$ could be largely affected by charge recombination. It has been reported that monomolecular recombination dominates the charge loss under high effective bias, while bimolecular recombination dominates the charge loss under low effective bias$^{109}$. This suggests that the energy loss during charge transport in the bulk and transfer at the organic/electrode interfaces was dominated by bimolecular recombination. This was also supported by the $V_{OC}$-$I$ characteristics measured for the three devices, as shown in Fig. 4.3. Therefore, reduction of bimolecular recombination is one of the main considerations for attaining high efficiency OSCs.
Fig. 4.3: Light intensity-dependent open circuit voltages measured for PTB7:PC\textsubscript{70}BM, PTB7-Th:PC\textsubscript{70}BM and PNB4: PC\textsubscript{70}BM based inverted OSCs.

Results in Fig. 4.3 show that there is a linear relationship between $V_{OC}$ and $\ln(I)$. The slopes of $d(V_{OC})$ vs $d[\ln(I)]$ for different OSCs are given in Fig. 4.3. For comparison, the slopes of $d(V_{OC})$ vs $d[\ln(I)]$ for amorphous silicon and single crystal silicon solar cells are $1.7\left(\frac{kT}{q}\right)$ and $2\left(\frac{kT}{q}\right)$ respectively\textsuperscript{110}. However, the slopes for most of the OSCs are closed to $\frac{kT}{q}$. This implies that the recombination in silicon based solar cells is primary associated with the trap-assisted recombination, while the recombination loss in most of OSCs are mainly attributed to bimolecular recombination. According to the theoretical study in the previous section, FF-$I$ characteristics as shown in Fig. 4.4, also suggest that bimolecular recombination is the mechanism in the energy loss responding for the poor FF in these OSCs. For all of the three devices, fill factors monotonically decreased with the increase of light intensity, showing that the
trap-assisted recombination in BHJ played a negligible role for energy loss in these OSCs. Compared to the recombination loss in BHJ, the charge accumulation and recombination at organic/electrode interfaces was more prominent in these OSCs.

Bimolecular recombination is an intrinsic characteristic for OSCs due to the strong Coulombic attraction between electrons (Chapter 2). To improve the performance of OSCs, main effort was focused on suppressing the bimolecular recombination in these cells. Other than the intrinsic properties of organic materials, both of the morphology of BHJ and the imperfection at the organic/electrode interface also contribute the bimolecular recombination. Based on the discussions above, two practical approaches to suppress bimolecular recombination and improve the performance of OSCs include: (a) to optimize the D-A phase separation so that the transports of holes and electrons are balanced; (b) to improve the carrier selectivity of the electrodes so that carriers arrived at the interface cannot meet with the opposite carriers. In the next two chapters, modification of electrodes that can reduce bimolecular recombination and enhance the performance of OSCs will be investigated.
Fig. 4.4: Light intensity-dependent fill factor for PTB7: PC$_{70}$BM, PTB7-Th: PC$_{70}$BM and PNB4: PC$_{70}$BM based OSCs.

4.3 Summary

In summary, charge collection efficiency and charge recombination dynamics are studied in this Chapter. The charge collection efficiency of an OSC is described by the effective bias dependent normalized photocurrent density, $J_{ph}$ and $I$ follow a power law relationship under different effective bias across the active layer. The power law relationship is characterized by the exponent $\alpha$, which describes the total recombination loss in the processes of charge transport in the active layer and the charge transfer at the organic/electrode interfaces. $V_{OC}$ and $\ln(I)$ follow a linear relationship. When the Urbach energy, depending on the band tail states of organic materials, is large, $FF$ increases first and then decreases with the increase in the intensity of light.
When the Urbach energy is low, $FF$ decreases with the increase in the intensity of light. The charge recombination dynamics in PTB7:PC$_{70}$BM, PTB7-Th:PC$_{70}$BM and PNB4:PC$_{70}$BM based inverted OSCs was analyzed using light intensity-dependent $J-V$ characteristics. The dominant recombination process that affects the charge collection efficiency and therefore performance of these OSCs was identified as bimolecular recombination at the organic/electrode interface.
Chapter 5

An Insight on Zinc Oxide Cathode Interlayer in Organic Solar Cells

5.1 Optimization of Conventional Cells with ZnO/Al based Cathode

In this chapter, a systematic study of the effect of ZnO interlayer on the performance of OSCs, based on PTB7:PC$_{70}$BM-blend system, is carried out. Two sets of conventional devices with device structures, shown in Fig. 5.1 were fabricated. The set of control cell with a structure of ITO/PEDO:PSS/PTB7:PC$_{70}$BM/Al, having different active layer thicknesses, was fabricated for comparison studies.

Fig. 5.1: Schematic cross-sectional view of (a) an OSC with an upper ZnO cathode interlayer; (b) a structurally identical control cell without the ZnO cathode interlayer.

ITO/glass substrates with a sheet resistance of 10 Ω/square were used for the OSC fabrication. They were cleaned in ultrasonic bath, followed by the in situ oxygen plasma
treatment prior to the cell fabrication. The PTB7:PC$_{70}$BM blend in a weight ratio of 1:1.5 was fully dissolved in CB with 3% 1, 8-Diiodooctane (DIO) (Sigma-Aldrich) at 60 °C before use. A set of structurally identical OSCs with different BHJ layer thicknesses ranging from 60 nm to 130 nm was then fabricated on PEDOT:PSS-covered ITO/glass substrates by spin-coating inside the glove-box. A ~10 nm thick ZnO interlayer was deposited on the BHJ surface by spin-coating inside the glove-box. The samples were then transferred to the adjacent vacuum system with a base pressure of < 5.0×10$^{-4}$ Pa to form a 100 nm thick Al top contact, evaporated at an evaporation rate of 1 Å/s.

A 90 nm thick active layer was optimized and used in the control cell and the device with a ~10 nm thick upper ZnO cathode interlayer. The $J$–$V$ characteristics measured for the two sets of the optimized cells are plotted in Fig. 5.2 for comparison. As shown by the summary in Table 5.1, $V_{OC}$, $J_{SC}$ and $FF$ of the OSC with an upper ZnO cathode interlayer between the active layer and the Al cathode increased from 0.725 V to 0.735 V, 13.7 mA/cm$^2$ to 14.5 mA/cm$^2$ and 65% to 73%, respectively, leading to an overall 20% increase in $PCE$ from 6.48% to 7.77%. Steady improvements in $J_{SC}$ and $FF$ as can be seen in Fig. 5.2, are the main factors contributing to the enhancement in the cell performance. This suggests that both light absorption and the transport of photo-generated carriers are more favorable in OSCs made with an upper ZnO cathode interlayer.
Fig. 5.2: $J$–$V$ characteristics measured for the control cell and the OSC with a 10 nm thick ZnO interlayer between the active layer and the Al contact.

Table 5.1: The characteristics of optimized devices with/without ZnO interlayer. The values of $J_{SC}$ and $PCE$ calibrated using $IPCE$ measurements are also given in the parentheses for comparison.

<table>
<thead>
<tr>
<th>Devices</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$FF$ (%)</th>
<th>$PCE$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control cell</td>
<td>0.725</td>
<td>13.3 (13.7)</td>
<td>65.1</td>
<td>6.28 (6.48)</td>
</tr>
<tr>
<td>Cell with 10 nm ZnO</td>
<td>0.735</td>
<td>14.0 (14.5)</td>
<td>72.9</td>
<td>7.50 (7.77)</td>
</tr>
</tbody>
</table>

$IPCE$ spectra of a control cell and the OSC with a $\sim$10 nm thick ZnO interlayer between the active layer and the Al contact were also measured and are plotted in Fig. 5.3. The $IPCE$ of an OSC not only reveals information about the absorption spectrum of the device, but also about the exciton dissociation, charge transport and collection processes in OSCs. Although the control cell and the OSCs with a 10 nm thick ZnO interlayer have comparable light absorption in their active layers, cells with a ZnO interlayer apparently possess a higher internal electric field across
the active layer, and therefore an efficient charge transport and a higher drift current are expected. The change in the IPCE spectra at wavelength < 500 nm and the wavelength region from 500 nm to 750 nm, as shown in Fig. 5.3, is due to the interference effect in the OSCs. There is a slight decrease in the IPCE measured for the OSCs with a ZnO interlayer at wavelength < 500 nm, and an obvious increase in IPCE over a spectral region from 500 nm to 750 nm. PTB7 does not have a strong absorption below 500 nm. Incorporation of a ZnO interlayer in the cells still benefit from an overall absorption enhancement over the wavelength region from 500 to 750 nm, attaining a ~6% increase in $J_{SC}$ as compared to the control cell. $J_{SC}$ calculated using IPCE spectra of the control cell and the OSCs with a ZnO interlayer also agrees with measured $J$–$V$ characteristics, showing that the improvement in performance of the OSCs with a ZnO interlayer contributes the improvement in $J_{SC}$ and $FF$. A summary of device parameters obtained for both types of the OSCs is listed in Table 5.1.

Fig. 5.3: The IPCE spectra measured for the control cell and the OSC with a 10 nm thick ZnO interlayer between the active layer and the Al contact.
5.2 Effect of ZnO Interlayer on Light Absorption

To understand the effect of ZnO interlayer on absorption enhancement in the OSCs, the integrated absorbance ($A\lambda$) in OSCs with a configuration of ITO/PEDOT:PSS (30 nm)/PTB7:PC$_{70}$BM/Al (100 nm) (control device) and that of the structurally identical cells with a ZnO interlayer inserted between the active layer and the metal contact: ITO/PEDOT:PSS (30 nm)/PTB7:PC$_{70}$BM/ZnO/Al (100 nm), was calculated using optical admittance analysis. Defining $F(\lambda)$ as the flux of the sun light incident on an OSC, e.g., AM1.5G solar irradiation flux measured in W·m$^{-2}$·nm$^{-1}$, the integrated light absorption in the active of the OSCs can be calculated using the following equation:

$$\int_{-\lambda}^{\lambda} A(\lambda) \cdot F(\lambda) d\lambda$$

where $A(\lambda)$ is the wavelength dependent absorption of the organic active layer. $A(\lambda)$ is calculated using Emissive Thin Film Optics Simulator (ETFOS) software, which is based on the principles of optical admittance analysis. Equation 5.1 allows to evaluate the optimal active layer (e.g., PTB7:PC$_{70}$BM) thickness through maximizing its integrated absorptance.

The integrated absorptance of the PTB7:PC$_{70}$BM layer, calculated for the control OSC and the structurally identical cells with different ZnO interlayer thicknesses of 10 nm, 20 nm and 30 nm, as a function of its layer thickness ranging from 40 to 240 nm is shown in Figure 5.4. It is clear that the integrated absorbance displays an oscillation behavior with increase in the active layer thickness, having a relative absorption maximum occurred at the blend layer thickness of ~105 nm for a control OSC. However, the thickness of the PTB7:PC$_{70}$BM layer corresponding to the absorption maximum in the integrated absorptance becomes thinner, e.g., ~90 nm for OSC
with a 10 nm thick ZnO interlayer. As shown in Fig. 5.5, a slight decrease in the maximum integrated absorbance is observed when the thickness of the ZnO interlayer further increases from 10 nm to 30 nm. This suggests that the insertion of an oxide interlayer between the organic active layer and the metal contact does not have an obvious contribution to the absorption enhancement in active layer as compared to that in an optically optimized control cell.

![Graph showing integrated absorbance vs. thickness of blend layer](image)

**Fig. 5.4:** Calculated integrated absorbance of the active layer in the control cell and the OSCs with different ZnO interlayer thicknesses of 10 nm, 20 nm and 30 nm.
From the optical point of view, the distribution of light intensity in the devices is intrinsically determined by the interference between the transmitted light and reflected light at each interface. The dispersive refractive indices for PTB7:PC$_{70}$BM blend layer and ZnO are very similar and both in the range of 1.75~1.8. Therefore, the addition of an organic blend layer/ZnO interface in the device has negligible contribution to light interference in the cell. When ZnO interlayer is added between the organic layer and metal electrode, the interference pattern within the organic stack will almost remain the same. Therefore, no matter in control OSC or OSC with a ZnO interlayer, light intensity distribution in the organic layer is always a result of the interference between incident light and light reflected by metal electrode. This implies that the photon harvesting is almost dependent only on the sum of the thickness of active layer and ZnO interlayer. It is also easy to understand that the optimal active layer thickness of the devices with a ZnO interlayer is thinner than that of the optically optimized control devices. So actually the
simulation results shown in Fig. 5.4 are based on the essence of the basic physical laws rather than a coincidence.

Although a thin oxide interlayer alone cannot account for light absorption enhancement in the already optically optimized control device, OSCs with an optimized ZnO interlayer is still beneficial for efficient device operation. The results in Fig. 5.4 reveal that OSCs with an appropriate ZnO interlayer (~10 nm thick) permits a thinner active layer (~90 nm) to achieve the similar maximum light absorption as compared to an optimized thicker active layer (~105 nm) used in the control cell. The inset in Fig. 5.4 is the cross-sectional view of the OSC. Due to the low charge mobility in organic materials, there exists a mismatch between the charge transport scale and the optical absorption length. The thickness of the active layer in OSCs is limited due to poor charge transport, resulting in insufficient light absorption. The use of a thinner organic active layer without a fall in light absorption, enabled in OSCs with a ZnO interlayer, as shown in Fig. 5.4, helps to create a higher internal electric field across the active layer, thereby reducing the exciton recombination losses and improving the charge transport. It shows that ZnO interlayer is advantageous for the efficient operation of the PTB7:PC_{70}BM-based OSCs. The presence of the ZnO interlayer allows using a thinner active layer without moderating the absorption in the optimized control cells with a thicker active layer. A combination of the efficient absorption and higher internal potential favors the efficient charge transport, and thereby improving the cell performance.

The relevance of the above discussion in the absorption in the active layer can be seen by measuring the performance of the control cell and the OSCs with a thin ZnO interlayer. Two sets of structurally identical OSCs, ITO/PEDOT:PSS (30 nm)/PTB7:PC_{70}BM/Al(100 nm) and ITO/PEDOT:PSS (30 nm)/PTB7:PC_{70}BM/ZnO (~10 nm)/Al(100 nm), with different active
thicknesses of 60, 70, 80, 90, 100, and 105 nm, were made for comparison studies. $J_{sc}$ of both sets of the OSCs as a function of the active layer thickness was measured and plotted in Fig. 5.6. The correlation between the $J_{sc}$ and the active layer thickness, measured for both types of the OSCs, is very similar to the simulation results.
Fig. 5.6: $PCE$ and $J_{SC}$ measured for a set of (a) control cells and (b) structurally identical OSCs with a ~10 nm thick ZnO interlayer as a function of the active layer thickness over the thickness range from 40 nm to 130 nm.

The performances of the two sets of cells, i.e., control set and the set with a ~10 nm thick ZnO interlayer are shown in Fig. 5.6. A maximum $PCE$ was obtained for control cells with an active layer thickness of ~90 nm, while the maximum value of $J_{SC}$ was achieved with an active layer thickness of ~105 nm. The results suggest that decrease in the performance of the control cells with a thicker active layer, e.g., above 90 nm, the poor charge transport and deteriorated charge collection became the dominant factors limiting the cell performance, due to the mismatch between the absorption depth and the charge transport scale in the organic semiconductors. The details of the improvement in charge collection efficiency of the cells with ZnO interlayer will be further elaborated in Section 5.3. As shown in Fig. 5.6(b), both the $PCE$ and $J_{SC}$ were obtained for ZnO contained OSCs with an optimal active layer thickness of ~90 nm. As shown in Fig. 5.7, the $V_{OC}$ and $FF$ of both sets of cells were dependent on the active layer thickness. It is shown that $V_{OC}$ and $FF$ become less sensitive to the change in the active layer thickness when a ZnO interlayer was inserted between the active layer and Al contact.
Fig. 5.7: Comparison of (a) $V_{OC}$ and (b) $FF$ measured for the control cells and the OSCs having a ~10 nm thick ZnO buffer as a function of the active layer thickness.
For the control cells, $J_{SC}$ reaches to the relative maximum value of 13.1 mA/cm$^2$ for cells with a 105 nm thick active layer, while a higher $J_{SC}$ (13.6 mA/cm$^2$) for OSCs with a ZnO interlayer occurred at a thinner active layer of ~90 nm, following with a graduate decay which is consistent with the simulation results. The optical admittance analysis agrees well with the experimental results in showing that OSCs having an optimal ZnO interlayer between the 90 nm thick active layer and the Al contact corresponded to the best cell performance. It is clear that a PTB7:PC$_{70}$BM blend layer thickness optimized for maximum light absorption in OSCs, e.g., achieving highest $J_{SC}$, does not give rise to the highest PCE. Such a deviation in the optical optimization and device performance essentially reflects the mismatch between the optical absorption length and charge transport scale in the organic semiconductors.

### 5.3 Effect of ZnO Interlayer on Charge Collection Efficiency

As shown in Table 5.1, both $V_{OC}$ and $FF$ in the cell were improved when a ZnO interlayer was inserted between the active layer and cathode, which could not be explained by optical study. The charge collection properties in the devices, affected by the insertion of an oxide interlayer between the active layer and the metal contact, also play an important role in determining the cell performance. To further understand the origin of the enhancement in the performance of the OSCs with an upper ZnO cathode interlayer as compared to a control cell, the charge recombination characteristics in the OSCs were analyzed. Fig. 5.8 shows the double logarithmic plot of photocurrent $J_{ph}$ ($J_{ph} = J_L - J_D$, where $J_L$ is the current density measured under AM1.5G irradiation of 100 mW/cm$^2$ and $J_D$ is the dark current) as a function of the effective voltage $V_{eff}$ ($V_{eff} = V_0 - V_b$, where $V_0$ is the built-in voltage measured at $J_{ph} = 0$, and $V_b$ is the applied bias),
measured for the OSC with a 10 nm thick ZnO cathode interlayer and a control cell. In this work, $V_0$ of both devices is approximately 0.8 V. The saturated photocurrents $J_{sat}$ of both types of the OSCs are also shown in Fig. 5.8. $J_{sat}$ in the OSCs depends only on the charge generation as $J_{ph}$ saturates at high $V_{eff} (>1.0$ V), giving rise to almost 100% collection of the photo-generated charges. As discussed in Chapter 4, the ratio of $J_{ph}$ to $J_{sat}$ reflects essentially a measure of an overall loss in the photo-excited charges, e.g., due to bimolecular recombination, trap-assisted defect states, occurred during transport processes prior to the collection by the electrodes.

Fig. 5.8: Photocurrent densities as a function of effective bias across the active layer measured for a control cell and the OSC with a 10 nm thick ZnO cathode interlayer.

The charge recombination would increase and not all the photo-generated carriers can be collected by the electrodes when $V_{eff}$ in the cell decreases, leading to a poor charge collection. As shown in Fig. 5.8, $J_{ph}$ obtained for a control cell decreases much faster than the photocurrent generated in the OSC with a ZnO interlayer at $V_{eff} <0.5$ V. The loss due to the monomolecular
recombination or bimolecular recombination is obviously much higher in the control cell than that in the OSCs with a ZnO interlayer at $V_{eff} < 0.5$ V. Both types of OSCs have identical anode contact and the active layer thickness, the change in the $J_{ph}-V_{eff}$ characteristics at low $V_{eff}$ region is seemingly associated with the change in the interfacial properties at the organic/cathode contact. This reveals that the presence of a 10 nm thick ZnO interlayer between the active layer and the Al cathode augments the photocurrent in this $V_{eff}$ region, revealing improvement in charge collection efficiency at the cathode contact.

Light intensity dependent $J-V$ characteristics of the OSCs were also measured to analyze recombination and extraction of the photo-generated charges. As discussed in Chapter 4, the empirical relationship between $J_{ph}$ and light intensity ($I$) is:

$$J_{ph} \propto I^{\alpha}, \quad 5.2 \text{ w}$$

Here the exponent $\alpha$ is usually less than one. Recombination of the photo-generated charges in the device generally results in $\alpha$ deviating from 1.

With increase in light intensity, charge accumulation in the active layer of a high performing OSC will be quickly saturated due to the limited trap states. Therefore, less “bright” light irradiation can be used to analyze the charge accumulation processes in the OSCs. The double logarithmic plot of $J_{ph}-I$ characteristics measured for the OSC with a 10 nm thick ZnO interlayer and a control cell are shown in Fig. 5.9(a) and 5.9(b). The power law dependence of $J_{ph}$ on light intensity is clearly seen. The power exponents of $J_{ph}-I$ characteristics measured for both cells approach to one at $V_{eff}$ of $> 0.25$ V. This suggests that most photo-generated charges can be collected at the organic/electrode contacts without charge accumulation in the cell at high $V_{eff}$.
Fig. 5.9: Double logarithmic plot of photocurrent density as a function of light intensity for (a) a control cell and (b) the OSC with an upper ZnO cathode interlayer under different effective voltages.

As the charge mobility in organic materials is field dependent, less efficient charge transport and collection in the OSCs would occur at low $V_{\text{eff}}$, leading to the build-up of space charges that gives rise to higher bimolecular recombination, and thereby a lower power exponent in the $J_{\text{ph}} - I$
characteristics. As shown in Fig. 5.9(a), the exponent of $J_{ph}$-$I$ characteristics observed for the control cell decreases to 0.67 at $V_{eff}$ of 0.085 V. A higher exponent value of 0.87 is obtained for OSC with a ZnO interlayer under the same effective voltage. When the $V_{eff}$ is larger than 0.25 V (i.e. applied bias $> V_{MPP}$), trap-assisted recombination dominates the charge loss in OSCs. On the contrary, bimolecular recombination dominates the charge loss in OSCs when $V_{eff}$ is lower than 0.25 V. The exponent $\alpha$ appears different only at low $V_{eff}$, suggesting that the different charge collection efficiencies in the control cells and cells with an upper ZnO cathode interlayer are attributed to the different strengths of bimolecular recombination in the two types of the devices. This conclusion is also supported by light intensity dependent $V_{oc}$, as shown in Fig. 5.10. The slopes of $d[V_{oc}]$ vs $d[\ln(I)]$ for both the control cell and the cell with a ZnO cathode interlayer are around $\frac{kT}{q}$. The slope of $V_{oc}$-$\ln(I)$ correlation for the cell having a ZnO interlayer is a little bit higher than that of the control cell. The above results reveal that at open circuit condition, almost all the photo-generated free carriers disappear via bimolecular recombination.

![Fig. 5.10: Light intensity-dependent $V_{oc}$ for the control cell and the cell with an upper ZnO cathode interlayer.](image)

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As both cells have the same anode/organic contact and blend system, it can be considered that the charge accumulation behaviors at the anode contact and in the active layer of both cells are very similar. Fig. 5.11 shows light intensity dependent $FF$ of the two devices. The $FF$ of the controlled device monotonically decreases with increase in light intensity. But the $FF$ of the device with a ZnO cathode interlayer shows non-monotonic dependence on light intensity. According to the results discussed in Chapter 4, charge accumulation in the organic active layer is responsible for the increase of $FF$ with increase in light intensity, while the charge accumulation at the electrode/organic layer interfaces is responsible for the decrease of $FF$ with increase in light intensity. Charges accumulated in the bulk eventually disappear via trap-assisted recombination, while the charges accumulated at the organic/electrode interface mainly disappear via bimolecular recombination. Charge accumulation in the bulk can be quickly saturated due to the limited trap states in high performance OSCs with the increase in the intensity of light, while charge accumulation and recombination at the organic/electrode interface increases faster and faster (i.e. there is no saturated value). So the effects of charge accumulation in the bulks can only be observed at low intensity of light intensity, and the amount of charges accumulated or recombined at the organic/electrode interface is relatively small. However, the identical stack of the organic active layers was used in both devices, suggesting that the impacts of charge accumulation and trap-assisted recombination in the bulks on the performances of the two devices should be the same. The difference in the $FF-I$ characteristics measured for the two devices imply that the recombination loss at the cathode/organic interface in the controlled cell is much stronger. Therefore, the effects of the charge accumulation in the bulks are totally covered and not observable even at a very low light intensity of 20 mW/cm$^2$. 


Fig. 5.11: Light intensity-dependent $FF$ of the control cell and the cell with an upper ZnO cathode interlayer.

Dissociation of the photo-excited excitons occurs at the interface between the two dissimilar materials, e.g., organic/electrode and donor/acceptor interfaces, the later process dominates the photocurrent generation in the OSCs. The dissociated charges at the donor/acceptor interface are drifted under the internal built-in potential forming field dependent drift current in the cell. The transient photocurrent in OSCs comprises the drift current formed in the active layer and the contribution from the interfacial exciton dissociations occurred at the organic/electrode interfaces. The drift current is a function of the internal electric field, while the current generated via interfacial exciton dissociation is independent on the effective internal electric field. Contributions to the transient photocurrent due to the drift current and the interfacial exciton dissociation cannot be decoupled in the $J$–$V$ characteristics of the cells measured at the steady
state condition. However the behavior of exciton dissociation at the organic/electrode interfaces and its contribution to the transient current can be analyzed by applying an opposite external bias to suppress the drift current in the transient photocurrent measurements. It then becomes possible to exam the interfacial exciton dissociation in the absence of internal built-in potential. Therefore, the correlation between the interfacial exciton dynamics and recombination loss at organic/electrode interface can be obtained by measuring transient current for devices at different biases. In this work, charge collection and the interfacial exciton dissociation processes at the organic/cathode interface in the cells were investigated using $TPC$ measurements.

To analysis the effect of the interfacial exciton dissociation on charge collection at the organic/Al cathode interface, two devices with layered structures of ITO/ PEDOT:PSS/ $\text{PC}_{70}\text{BM}(400 \text{ nm})/\text{Al}(30 \text{ nm})$ (control device) and ITO/PEDOT:PSS/$\text{PC}_{70}\text{BM}(400 \text{ nm})/\text{ZnO}(\sim10 \text{ nm})/\text{Al} (30 \text{ nm})$ were made for $TPC$ measurements. The transient photocurrents measured for both devices at different biases are plotted in Fig. 5.12(a) and Fig. 5.12(b), respectively. The positive transient photocurrent decays were observed for both devices without the external bias, suggesting that the electric field drifted currents were dominated in both devices. However, when the $TPC$ measurements were performed for both devices with an opposite external bias, very different transient photocurrent behaviors were observed. A clear rapid negative transient photocurrent signal for the control device was observed at a reverse bias of 0.4 V, shown in Fig. 5.12(a). The prompt negative transient photocurrent, originated from the fast interfacial exciton dissociation at the $\text{PC}_{70}\text{BM}/\text{Al}$ interface, is apparently unfavorable for the electron collection. In comparison with the flow of the transient photocurrent generated at the $\text{PC}_{70}\text{BM}/\text{Al}$ interface shown in Fig. 5.12(a), there was an obvious positive transient photocurrent seen in the device with the presence of a 10 nm thick ZnO cathode interlayer between the active layer and Al.
contact at a reverse bias of 0.9 V, shown in Fig. 5.12(b). It becomes clear that the interfacial exciton dissociation at the organic/Al interface in the control cell impedes the electron collection. In contrast, the presence of a 10 nm thick ZnO interlayer between the active layer and the metal cathode in the OSCs promotes an efficient charge collection through elimination of the adverse interfacial excition dissociation that would otherwise occurred in the control cell. The \( TPC \) results agree well with the analysis based on the \( J_{ph}-V_{eff} \) characteristics of the cells shown in Fig. 5.8. It is clear that the enhanced \( J_{ph} \), observed in the OSCs with a ZnO interlayer at the low \( V_{eff} \), arises from the favorable interfacial exciton dissociation that inhibits the interfacial bimolecular recombination.

![Fig. 5.12: Transient photocurrent signals, due to the interfacial exciton dissociation at (a) PC\textsubscript{70}BM/Al and (b) PC\textsubscript{70}BM/ZnO/Al interfaces.](image-url)
5.4 Summary

In summary, a comprehensive study of the effect of ZnO cathode interlayer on the performance of PTB7: PC\textsubscript{70}BM based OSCs was carried out. OSCs with a mismatch between optical absorption length and charge transport scale in conjugated polymers, such as PTB7: PC\textsubscript{70}BM based OSCs, can benefit from ZnO interlayer in two ways. It can enhance the optical absorption with a thinner active layer to increase the internal electric field for reducing recombination loss of the photo-generated charges. It also can reduce the bimolecular recombination among photo-generated charges at the cathode/organic interface. The lower bimolecular recombination rate discovered in the OSCs made with a ZnO cathode interlayer at low effective bias is mainly responsible for the enhancement in $FF$. The removal of the unfavorable exciton dissociation at the organic/cathode interface in the cell with a 10 nm thick ZnO cathode interlayer between the organic active layer and Al cathode is the essential factor to suppress the bimolecular recombination in the cells. This simple yet effective implementation can improve the device performance in all aspects including $J_{SC}$, $V_{OC}$ and $FF$ and the total device $PCE$ by 20%.
Chapter 6

An Insight on MoO$_X$ Anode Interlayer in Inverted Organic Solar Cells

6.1 Optimization of Inverted Cells with MoO$_X$/Ag based Anode

In this chapter, the effect of solution-processed sMoO$_X$ and hybrid sMoO$_X$-PEDOT:PSS anode interlayers on the performance of PTB7: PC$_{70}$BM based inverted OSCs was investigated. The process of the hybrid sMoO$_X$-PEDOT:PSS interlayer does not require the post-annealing treatment, making it very suitable for application in large area OSCs through solution fabrication processes. Though method to apply sMoO$_X$ in inverted OSCs was reported several times previously, the repeatability of the performance of the inverted OSCs with sMoO$_X$ anode interlayer was rather poor. However, it was difficult to achieve the similar performance of the inverted OSCs with a sMoO$_X$ anode interlayer as compared to that in inverted OSCs with an eMoO$_X$ anode interlayer$^{113}$. Mixing sMoO$_X$ and PEDO:PSS together is a good approach to achieve high performance for OSCs with good repeatability. On the other hand, there are many articles reporting the interfacial engineering in OSCs with a thin metal oxide interlayer,$^{114,115,116}$ the effect of metal oxide anode interlayer on interfacial exciton dissociation and charge collection in OSCs is not fully understood yet.

Inverted OSCs with a structure shown in Fig. 6.1 were made. The pre-patterned ITO substrates, with a sheet resistance of ~10 $\Omega$/square, were cleaned by ultrasonication sequentially with detergent, deionized water and isopropanol for 15 min. The blend of PTB7 and PC$_{70}$BM in
a weight ratio 1:1.5 was dissolved in chlorobenzene. The organic blend layer, with a thickness of ~90 nm was spin coated after the solution was stirred overnight. Structurally identical inverted OSCs with four different HTLs of 2 nm thick eMoOX, ~15 nm thick sMoOx, ~15 nm thick hybrid sMoOx-PEDOT:PSS and ~15 nm PEDOT:PSS were fabricated. Before the spin coating of sMoOx, the as prepared sMoOx was diluted by ethanol in a volume ratio of 1:20. The mixing ratio between the diluted sMoOx and PEDOT:PSS varied from 20:1 to 20:8. All solution-processed HTL layers were spin coated in the glovebox. The samples were transferred to the adjacent vacuum system without exposure to air. Then 2 nm eMoOx /100 nm Ag or 100 nm Ag (for devices using solution processed HTL) were deposited by thermal evaporation at a base pressure of < 5×10⁻⁴ Pa. Then the devices were transferred back to the glovebox for encapsulation. J-V characteristics, light intensity-dependent characteristics and IPCE of the devices were measured following the characterization procedures described in Chapter 3.

![Diagram of device structure](image)

Fig. 6.1: Device structures for the inverted OSCs with different anode interlayers of a 2 nm thick eMoOx, a ~15 nm thick sMoOx, a ~15 nm thick hybrid sMoOx-PEDOT:PSS, and a ~15 nm thick PEDOT:PSS.
The $J$-$V$ characteristics for the devices with a sMoO$_X$-PEDOT:PSS anode interlayer were plotted in Fig. 6.2. The volume ratio of the diluted sMoO$_X$ to PEDOT:PSS in the mixed solution varied from 20:1 to 20:8. $J$-$V$ characteristics of devices with pristine PEDOT:PSS and pure sMoO$_X$ anode interlayers were also plotted together. The characteristics of these devices were also summarized in Table 6.1. The repeatability of inverted OSCs with a sMoO$_X$ anode interlayer was poor and the average $PCE$ is less than 4%. This can be ascribed to the poor conductivity of the sMoO$_X$ layer that was formed without the post-annealing. Due to the good conductivity of PEDOT:PSS, high $PCE$ was achieved in inverted OSCs with a hybrid sMoO$_X$-PEDOT:PSS anode interlayer. The best inverted device with an optimized hybrid sMoO$_X$-PEDOT:PSS anode interlayer achieved a $PCE$ of ~7.4%, with a volume ratio of the diluted sMoO$_X$ to PEDOT:PSS at 20:5. When the volume ratio of PEDOT:PSS in the mixed solution increased from 0 to 8:20, the $PCE$ of the inverted OSCs showed significant enhancement first and then gradually decreased as the volume ratio of PEDOT:PSS in the mixed solution further increased. $J_{SC}$, $FF$ and $PCE$ changed almost in the same way with the increase in the volume ratio of PEDOT:PSS in the mixed solution. But the $V_{OC}$ of the inverted OSCs increased from 0.54 V to 0.78 V with the increase in volume ratio of PEDOT:PSS in the mixed solution. If a pristine PEDOT:PSS HTL was used, $V_{OC}$ and $FF$ of the OSCs experience a dramatic sudden drop, though $J_{SC}$ remained unchanged, resulting in very poor performance of inverted OSCs with a pristine PEDOT:PSS HTL. As known, direct deposition of Ag by thermal evaporation on the surface of organic materials may induce unexpected interfacial defects at the organic/Ag interface. Therefore, PEDOT:PSS, though it is an excellent HTL in conventional OSCs, leads to very poor performance of inverted OSCs. On the other hand, combination of MoO$_X$/Ag was shown to be a good anode that can be directly deposited on the surface of organic materials through thermal
evaporation. Therefore, the sMoO$_X$-PEDOT:PSS mixed solution actually combines the advantages of high conductivity of PEDOT:PSS and the suitable energy alignments at the organic/MoO$_X$/Ag interfaces.

![J-V characteristics for inverted OSCs with different kinds of HTL](image)

Fig. 6.2: The $J$-$V$ characteristics for inverted OSCs with different kinds of HTL. The ratio by volume of sMoO$_X$ to PEDOT:PSS changes from 20:1 to 20:8.

### Table 6.1: The characteristics of inverted OSCs with different HTL, including sMoO$_X$, sMoO$_X$-PEDOT:PSS and PEDOT:PSS.

<table>
<thead>
<tr>
<th>sMoO$_X$ to PEDOT:PSS</th>
<th>$PCE$ (%)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>$FF$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20:0 (only sMoO$_X$)</td>
<td>3.80</td>
<td>12.0</td>
<td>0.54</td>
<td>57.0</td>
</tr>
<tr>
<td>20:1</td>
<td>5.16</td>
<td>14.0</td>
<td>0.60</td>
<td>59.8</td>
</tr>
<tr>
<td>20:3</td>
<td>6.31</td>
<td>13.9</td>
<td>0.72</td>
<td>63.5</td>
</tr>
<tr>
<td>20:5</td>
<td>7.37</td>
<td>14.1</td>
<td>0.76</td>
<td>69.0</td>
</tr>
<tr>
<td>20:6</td>
<td>7.19</td>
<td>13.7</td>
<td>0.77</td>
<td>68.3</td>
</tr>
<tr>
<td>20:8</td>
<td>6.68</td>
<td>13.0</td>
<td>0.78</td>
<td>66.1</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>4.83</td>
<td>13.9</td>
<td>0.64</td>
<td>54.1</td>
</tr>
</tbody>
</table>
In addition, inverted OSCs with eMoOx as anode interlayer were also fabricated. The $J$-$V$ characteristics for inverted OSCs with sMoO$_X$-PEDOT:PSS in optimized condition, eMoO$_X$ and PEDOT:PSS were shown in Fig. 6.3 for comparison. And their characteristics were summarized in Table 6.2.

![Image of J-V characteristics](image)

**Fig. 6.3:** The $J$-$V$ characteristics of inverted cells with different anode interlayers of sMoO$_X$-PEDOT:PSS, eMoO$_X$ and PEDOT:PSS.

**Table 6.2:** The characteristics of inverted OSCs with different HTLs of an optimal hybrid sMoO$_X$-PEDOT:PSS, an eMoO$_X$ and a PEDOT:PSS.

<table>
<thead>
<tr>
<th>Anode interlayer</th>
<th>$PCE$ (%)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>$FF$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sMoO$_X$-PEDOT:PSS</td>
<td>7.37</td>
<td>14.1</td>
<td>0.76</td>
<td>69</td>
</tr>
<tr>
<td>eMoO$_X$</td>
<td>6.70</td>
<td>13.3</td>
<td>0.73</td>
<td>69</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>4.83</td>
<td>13.9</td>
<td>0.64</td>
<td>54.1</td>
</tr>
</tbody>
</table>
The IPCE of the three devices were shown in Fig. 6.4. The calculated $J_{SC}$ based on the IPCE data were 14.7mA/cm$^2$, 13.9mA/cm$^2$ and 14.4mA/cm$^2$ for inverted OSCs with sMoO$_X$-PEDOT:PSS in optimized condition, eMoO$_X$ and PEDOT:PSS as anode interlayer, respectively.

$\text{IPCE} (%)$

Wavelength (nm)

300 400 500 600 700 800

sMoO$_x$-PEDOT:PSS

30 40 50 60 70

eMoO$_x$

0

10 20 30

PEDOT:PSS

$\text{IPCE} (%)$

Wavelength (nm)

Fig. 6.4: The IPCE of inverted cells with sMoO$_X$-PEDOT:PSS in optimized condition, eMoO$_X$ and PEDOT:PSS as anode interlayer.

6.2 Charge Collection Efficiency in Inverted Organic Solar Cells

Bias dependent charge collection efficiencies of inverted OSCs with sMoO$_X$-PEDOT:PSS in optimized condition, eMoO$_X$ and PEDOT:PSS as anode interlayer were studied. $J_{ph}$ is equal to the difference between the current densities under illumination and in the dark, i.e. $J_{ph} = J_L - J_D$. $J_{ph}$ is dependent on the effective bias ($V_0 - V_a$) across the organic blend layer. When the $J_{ph} = 0$, the applied voltage $V_a$ is equal to the built-in potential $V_0$. Thus the built-in potentials in the inverted OSCs with sMoO$_X$-PEDOT:PSS in optimized condition, eMoO$_X$ and PEDOT:PSS as
anode interlayer was determined to be 0.86 V, 0.83 V and 0.80V, respectively. When the externally applied bias $V_a$ swept from -1V to 1V in the measurement, the effective bias across the organic blend layer in the devices changed correspondingly. When the effective bias was very large in the device, all the photo-generated carriers are swept out of the device, which implied that the charge collection efficiency is nearly 100% and the photocurrent density achieves the saturated value $J_{\text{sat}}$. For the three devices, the photocurrent density achieved saturated value when the effective bias was $\sim$1.3 V as shown in Fig. 6.5. The effective bias dependent normalized photocurrent densities of the three devices, which essentially described the effective bias dependent charge collection efficiencies of the devices,$^{117}$ were shown in Fig. 6.5. When the effective bias was less than 1.3 V, the bias dependent normalized photocurrent density was less than 1, which was attributed to carrier loss due to by bimolecular recombination and trap-assisted recombination.$^{118,119}$ As discussed in previous sections, trap-assisted recombination is the dominant loss process at the high effective bias, while the bimolecular recombination is the main loss process in OSCs at the low effective bias. From Fig. 6.5, the charge losses due to trap-assisted recombination in inverted OSCs with an optimal hybrid sMoO$_X$-PEDOT:PSS HTL and an eMoO$_X$ HTL were both negligible, while the trap-assisted recombination loss in inverted OSCs with a PEDOT:PSS anode interlayer was significant. With decrease in the effective bias, the charge collection efficiency decreased faster in inverted OSCs with a PEDOT:PSS anode interlayer than that did in inverted OSCs with a hybrid sMoO$_X$-PEDOT:PSS HTL and an eMoO$_X$ anode interlayer. That suggested the bimolecular recombination loss in inverted OSCs with a PEDOT:PSS anode interlayer was higher than that in inverted OSCs with a sMoO$_X$-PEDOT:PSS HTL and an eMoO$_X$ anode interlayer.
Fig. 6.5: Effective bias dependent charge collection efficiencies for inverted OSCs with different HTLs of sMoO\textsubscript{X}-PEDOT:PSS, eMoO\textsubscript{X} and PEDOT:PSS.

Light intensity-dependent photocurrent densities for the three devices under different effective biases were also studied. Light intensity-dependent $J$-$V$ characteristics of the three devices were shown in Fig. 6.6. As discussed in previous section, the empirical relationship between $J_{ph}$ and light intensity ($I$) is,

$$J_{ph} \propto I^\alpha,$$

(6.1)

where the exponent $\alpha$ is dependent on the recombination loss. Data in Fig. 6.6 also supported that charge loss due to trap-assisted recombination was negligible in inverted OSCs with sMoO\textsubscript{X}-PEDOT:PSS and eMoO\textsubscript{X} as anode interlayer under high effective bias, since the exponents $\alpha$ for the two devices were very close to 1. In the inverted OSCs with a PEDOT:PSS anode interlayer, the exponent $\alpha$ decreased from 0.97 to 0.94, when the effective bias across the organic active
layer changed from 0.8 V to 0.24 V. This suggested that the trap-assisted recombination loss in inverted OSCs with a PEDOT:PSS anode interlayer was significant. Since the organic blend layer and cathode interface in the three devices were exactly the same, the increase of trap states in OSCs with a PEDOT:PSS anode layer comes from the defects at the organic/electrode interface, caused by the deposition of hot metal particles onto PEDOT:PSS\textsuperscript{120}. The impact of bimolecular recombination (second order recombination) becomes significant at low effective bias. When the effective bias across the organic active layer was 0.12 V, the exponents $\alpha$ for the inverted OSCs with different anode interlayers of sMoO$_X$-PEDOT:PSS, eMoO$_X$ and PEDOT:PSS were 0.94, 0.89 and 0.60, respectively. The above results revealed that bimolecular recombination loss in the inverted OSCs with a PEDOT:PSS anode interlayer was more prominent than that in inverted OSCs with a hybrid sMoO$_X$-PEDOT:PSS HTL and an eMoO$_X$ anode interlayer.
Fig. 6.6: Light intensity-dependent photocurrent densities under different effective bias across the organic active layer in inverted OSCs with different anode interlayers of (a) sMoO$_X$-PEDOT:PSS, (b) eMoO$_X$ and (c) PEDOT:PSS.
For the three devices, organic active layer and ITO/ZnO cathode were the same. Therefore, the different organic/anode interfaces were the key factors that were responsible for the different performances and recombination characteristics in these devices. Better understanding of the charge transfer dynamics at organic/HTL/Ag interface is a prerequisite for analyzing the different recombination loss mechanisms in these devices.

6.3 Interfacial Exciton Dissociation at Organic/Electrode Interfaces

*TPC* measurement was selected to study the charge transfer dynamics at organic/HTL/Ag interface. The basic operation processes of *TPC* and the measurement setup were elaborated in Chapter 3.

From the previous section, significant differences in the charge collection efficiencies in devices with different HTLs of PEDOT:PSS and sMoO$_X$-PEDOT:PSS were observed. To study the charge transfer dynamics at the organic/HTL/Ag interfaces in these OSCs, another two devices with structures of ITO/ZnO(15 nm)/PC$_{70}$BM(400 nm)/sMoO$_X$-PEDOT:PSS (15 nm)/Ag(30 nm) and ITO/ZnO (15 nm)/PC$_{70}$BM(400 nm)/PEDOT:PSS (15 nm)/Ag (30 nm) were fabricated and encapsulated in the glovebox. The thicknesses of photoactive layers in the devices were 400 nm, which were 4 times thicker than the actual active layer used in OSCs. The drift current generated in the active layer could be suppressed to very low level by applying external bias, which facilitated the observation of $I_{TPC}$ contributed by exciton dissociation at the organic/HTL/Ag interface. In the experiments, excitons in the organic active layer and the resulted $I_{TPC}$ were generated using a small optical perturbation, provided by a pulsed Nd:YAG laser from the 30 nm thick semitransparent Ag anode side. Due to the low transparency of 400 nm organic photoactive layer, the amount of excitons generated near the ITO/ZnO/organic
interface was negligible. Therefore, the $I_{TPC}$ generated by exciton dissociation at organic/HTL/Ag interface can be studied separately.

The $TPC$ characteristics for devices with structure of ITO/ZnO(15 nm)/ PC$_{70}$BM (400 nm)/ sMoO$_X$-PEDOT:PSS (15 nm)/Ag(30 nm) and ITO/ZnO (15 nm)/ PC$_{70}$BM (400 nm)/ PEDOT:PSS (15 nm)/Ag (30 nm) under different external biases were shown in Fig. 6.7. The transient photocurrent was an integrated signal composed of two parts: (a) drift current due to the difference in the work functions between anode and cathode, (b) transient current caused by exciton dissociation. The ITO and Ag sides of the device were connected to the anode and cathode of the oscilloscope, respectively. The drift current due to the difference in the work functions between anode and cathode was the main component of $I_{TPC}$, which had a direction from the ITO side to Ag side in an inverted structure. Therefore, the $I_{TPC}$ measured for the two cells under low external bias was negative. On the other hand, the contribution to the $I_{TPC}$ due to the exciton dissociation at the PC$_{70}$BM/HTL/Ag interface was hardly observed without external bias. When a negative bias was applied between the ITO cathode and Ag anode, the built-in potential inside the device was offset and the magnitude of drift current was suppressed significantly so that it was possible to distinguish between the transient current caused by exciton dissociation at the electrode/organic interfaces and the drift current due to the difference in the work functions between the anode and cathode.
Fig. 6.7: The transient current signal generated by incident light from the transparent Ag electrode side of the devices with a structure of (a) ITO/ ZnO/PC$_{70}$BM/sMoO$_X$-PEDOT:PSS/Ag (30 nm), (b) ITO/ZnO/PC$_{70}$BM/ PEDOT:PSS/Ag (30 nm)
As shown in Fig. 6.7(a), the transient current due to exciton dissociation and the drift current were integrated to form a very strong negative signal when 1 V bias was applied for device with structure of ITO/ ZnO/PC$_{70}$BM/ sMoO$_X$-PEDOT:PSS/Ag (30 nm). When the magnitude of the applied negative bias increased to about 1.1 V, it was clear that a fast negative signal was observed within a time frame of several ns after the optical perturbation. A slower positive signal was then appeared after a longer period of time (~100 ns). As known, exciton dissociation is an ultra-fast physical process and formation of drift current is a continuous process. Therefore, the signal due to exciton dissociation lasts for a very short period of time, while the drift current lasts for much longer time. With an external bias of 1.1 V, the fast negative current signal, as shown in Fig. 6.7(a), was attributed to the exciton dissociation at organic/sMoO$_X$-PEDOT:PSS interface. Under illumination, there were two electrical fields in the devices generated by the built-in potential across the active layer and the exciton dissociation at the organic/sMoO$_X$-PEDOT:PSS interface, respectively. The electrical field generated by exciton dissociation at the organic/sMoO$_X$-PEDOT:PSS interface was localized and confined to a very small space near the interface. The localized electrical field had little effects on the thick organic active layer. The drift current changed polarity with a negative bias of 1.1 V, suggesting that the built-in potential across the organic active layer was offset by the applied external bias. When the magnitude of the applied negative bias increased further to 1.2 V, the transient current due to exciton dissociation also changed polarity. Then the transient current due to exciton dissociation at organic/electrode interface and the drift current were integrated again to form a positive current signal. It was concluded that there existed exciton dissociation at the PC$_{70}$BM/sMoO$_X$-PEDOT:PSS interface and the resulted electrical field has the same direction with that of the drift current without external bias. Therefore, the exciton dissociation at the PC$_{70}$BM/sMoO$_X$-PEDOT:PSS interface and the resulted electrical field has the same direction with that of the drift current without external bias. Therefore, the exciton dissociation at the PC$_{70}$BM/sMoO$_X$-
PEDOT:PSS interface was favorable for charge transfer at the organic/electrode interface and the charge collection in the OSCs.

The transient photocurrent characteristics for the device with structure of ITO/ZnO(15 nm)/PC$_{70}$BM (400 nm)/PEDOT:PSS(15 nm)/Ag(30 nm) were shown in Fig. 6.7(b). The polarity of the transient current was changed from negative to positive when the external bias increased from 0.8 V to 0.9 V. It was difficult to observe two distinguishable components of the transient photocurrent when the external bias was between 0.8 V and 0.9 V. On the other hand, the transient current was too small to be observed at an external bias of 0.85 V. With an external bias of 0.85 V, the built-in potential due to the difference in the work functions between anode and cathode was completely offset and effective electrical field in the organic active layer was zero. The current signal due to the interfacial exciton dissociation at organic/PEDOT:PSS interface was not observed when the drift current signal was completely suppressed. The above results suggested that the effect of the interfacial exciton dissociation at organic/PEDOT:PSS interface was too weak to be observed through the TPC measurement.

Based on the working principles discussed in Chapter 2, the photovoltaic effect in the devices with a structure of ITO/ZnO/PC$_{70}$BM/HTL/Ag should be magnified significantly if favorable exciton dissociation exists at the PC$_{70}$BM/HTL interface. Three OSCs with device structures of ITO/ZnO/PC$_{70}$BM/ sMoO$_X$-PEDOT:PSS(15 nm)/Ag, ITO/ZnO/ PC$_{70}$BM/ PEDOT:PSS (15 nm)/Ag and ITO/ZnO/ PC$_{70}$BM/eMoO$_X$ (2 nm)/Ag were fabricated. J-V characteristics for these three devices were shown in Fig. 6.8. The $J_{SC}$ and $V_{OC}$ in the OSC with structure of ITO/ZnO/PC$_{70}$BM/ sMoO$_X$-PEDOT:PSS(15 nm)/Ag were much higher than those in OSCs with structure of ITO/ZnO/ PC$_{70}$BM/ PEDOT:PSS (15 nm)/Ag. The higher photovoltaic performance
of OSC with structure of ITO/ZnO/PC$_{70}$BM/ sMoO$_X$-PEDOT:PSS(15 nm)/Ag was attributed to the favorable exciton dissociation at the PC$_{70}$BM/ sMoO$_X$-PEDOT:PSS interface.

![Fig. 6.8: J-V characteristics for devices with structure of ITO/ZnO(15 nm)/PC$_{70}$BM (100 nm)/HTL(sMoO$_X$-PEDOT:PSS, eMoO$_X$, PEDOT:PSS)/Ag (100 nm).](image)

As shown in Fig. 6.5, the charge collection efficiency in inverted OSCs with a 2 nm thick eMoO$_X$ anode interlayer was lower than that in inverted OSCs having a 15 nm thick hybrid sMoO$_X$-PEDOT:PSS anode interlayer. To explain the above difference, charge transfer dynamics at the PC$_{70}$BM/eMoO$_X$ interface were also studied through the $TPC$ measurement. Two devices with an identical structure but a different HTL, e.g., ITO/ZnO/PC$_{70}$BM(400 nm)/eMoO$_X$(2 nm, and 20 nm)/Ag(30 nm), were fabricated for $TPC$ measurements. A 2 nm thick eMoO$_X$ HTL was optimized for the performance of inverted OSCs. However, the surface of the organic active layer in OSCs cannot be completely covered by a 2 nm thick eMoO$_X$ HTL. Therefore, the charge transfer dynamics at organic/anode interface in devices with a 2 nm thick eMoO$_X$ HTL were
affected by the two interfaces, i.e. PC$_{70}$BM/eMoO$_X$ and PC$_{70}$BM/Ag. On the other hand, the charge transfer dynamics at organic/anode interface in devices with a 20 nm thick eMoO$_X$ were solely determined by the PC$_{70}$BM/eMoO$_X$ interface. The above difference was responsible for the different transient photocurrent characteristics for the two devices, as shown in Fig. 6.9.

![Fig. 6.9: The TPC characteristics generated by incident light from semitransparent Ag side in devices with structure of ITO/ZnO(15 nm)/PC$_{71}$BM(400 nm)/HTL/Ag (30 nm) with (a) a 2 nm thick eMoO$_X$ HTL and (b) a 20 nm thick eMoO$_X$ HTL.](image_url)
From Fig. 6.9, favorable exciton dissociation at the organic/eMoO$_X$ interfaces in both devices was observed. As shown in Fig. 6.7(a) and Fig. 6.9(b), the TPC characteristics in device with a 20 nm thick eMoO$_X$ anode interlayer was the same with that in device with a 15 nm tick sMoO$_X$-PEDOT:PSS anode interlayer. It implies that the effects of exciton dissociation at organic/electrode interface on the charge collection efficiency were the same in inverted OSCs with a 15 nm thick sMoO$_X$-PEDOT:PSS HTL and a 20 nm thick eMoO$_X$ HTL. However, the polarity of the transient photocurrent due to the interfacial exciton dissociation in the device with a 2 nm thick eMoO$_X$ anode interlayer changed under a lower external bias (~1 V), compared to that in devices with a 15 nm thick sMoO$_X$-PEDOT:PSS HTL or a 20 nm thick eMoO$_X$ anode interlayer (~1.2 V). This suggested that the amount of the free carriers generated due to the interfacial exciton dissociation in device with a 2 nm thick eMoO$_X$ anode interlayer was less than that in devices with a 15 nm thick sMoO$_X$-PEDOT:PSS anode interlayer. The above difference was attributed to the uncompleted coverage of the organic active layer by a 2 nm thick eMoO$_X$ layer. Though the amount of the free carriers generated by the exciton dissociation at the organic/eMoO$_X$ in devices with a 20 nm thick eMoO$_X$ HTL was about the same as compared to that in devices with a 15 nm thick sMoO$_X$-PEDOT:PSS HTL, the high resistivity of a 20 nm thick eMoO$_X$ interlayer increased the series resistance, therefore, decreasing the PCE of the OSCs.

The higher charge collection efficiency under low effective bias across the organic active layer in inverted OSCs with a 15 nm thick hybrid sMoO$_X$-PEDOT:PSS HTL is closely related to the exciton dissociation at the organic/anode interface. When the magnitude of the reverse external bias is close to $V_{OC}$, the built-in potential is offset, resulting in a weak electrical field in the organic active layer. Therefore, the photocurrent formed by the photo-generated carriers in
the active layer is small under low effective bias. On the other hand, a reverse external bias, larger than the built-in potential, is needed to change the polarity of the photocurrent formed by the free carriers generated by the exciton dissociation at the organic/electrode interface. When the photocurrent generated by the free carriers in the active layer is suppressed at low effective bias, the free carriers generated by exciton dissociation at organic/electrode interface still contribute additional photocurrent. The difference in charge transfer dynamics at the organic/electrode interfaces in inverted OSCs with different anode interlayers is one of the important factors that result in the difference in the charge collection efficiencies of the three devices as shown in Fig. 6.5.

6.4 Summary

In summary, inverted OSCs using solution-processed hybrid sMoO$_{x}$-PEDOT:PSS HTL have been fabricated, achieving excellent performance with good performance repeatability. The solution-processed hybrid sMoO$_{x}$-PEDOT:PSS anode interlayer does not require an additional post-annealing treatment, making it very attractive for application in large scale fabrication of OSCs at low costs. It is the first time that favorable exciton dissociation at the interface between organic active materials and MoO$_{x}$/Ag electrode was observed and studied. The favorable interfacial exciton dissociation is crucial to enhance the charge collection efficiency and suppresses the bimolecular recombination at the organic/electrode in inverted OSCs. For inverted OSCs with an eMoO$_{x}$ anode interlayer, it is difficult to realize simultaneously a large amount of the free carriers generated from the favorable exciton dissociation at organic/electrode interface and excellent hole transport due to the low hole mobility in eMoO$_{x}$. Combined with the excellent hole transport capability of PEDOT:PSS and the high work function nature of the transitional metal oxides, the advantages of the hybrid sMoO$_{x}$-PEDOT:PSS HTL in inverted OSCs were
demonstrated, attaining high photocurrent generated and efficient charge collection due to the favorable interfacial exciton dissociation at organic/MoO$_X$ interface. PCE of $\sim$7.4% was achieved for inverted OSCs with an optimal hybrid sMoO$_X$-PEDOT:PSS HTL, which was 10% higher than that of the inverted OSCs having an optimized eMoO$_X$ HTL.
Chapter 7

Summary and Future Outlook

7.1 Summary

The relationship between the charge recombination dynamics and light intensity-dependent $J$-$V$ characteristics in OSCs was developed. Charge collection efficiency and charge recombination dynamics in OSCs were systematically studied by analyzing light intensity-dependent $J$-$V$ characteristics and $TPC$ characteristics. The effect of a thin ZnO cathode interlayer on light absorption and charge collection efficiency in conventional OSCs were studied by optical admittance analysis and the measurement of light intensity-dependent $J$-$V$ characteristics, respectively. A mixed solution composed of sMoO$_X$ and PEDOT:PSS was used as the anode interlayer in inverted OSCs without post-annealing treatment. The charge transfer dynamics at the organic/anode interfaces in inverted OSCs with different anode interlayers of sMoO$_X$-PEDOT:PSS, PEDOT:PSS and eMoO$_X$ were studied by the measurement of $TPC$ characteristics.

The charge collection efficiency of an OSC is described by the effective bias dependent normalized photocurrent density. Charge collection efficiency of OSCs is affected by bimolecular recombination and trap-assisted recombination in the organic active layer and at organic/electrode interfaces. The charge recombination dynamics were studied by the measurement of light intensity-dependent $J$-$V$ characteristics. $J_{ph}$ and $I$ follow a power law relationship under different effective bias across the active layer. The power law relationship is characterized by the exponent $\alpha$, which describes the total recombination loss in the OSCs. $V_{OC}$ and $\ln(I)$ follow a linear relationship. The bimolecular recombination or trap-assisted
recombination dominated the recombination loss process in the cells can be identified according to the slope of $d[V_{OC}]$ and $d[\ln(I)]$. The $FF-I$ characteristics of OSCs were adopted to assess the dominant recombination loss which occurred in the organic active layer or at the organic/electrode interfaces. It is found that the bimolecular recombination at the organic/electrode interface is one of the main factors that limits the performance of PTB7:PC$_{70}$BM, PTB7-Th:PC$_{70}$BM and PNB4:PC$_{70}$BM based OSCs.

A comprehensive discussion of the effect of ZnO cathode interlayer on the performance of PTB7:PC$_{70}$BM based OSCs was conducted. OSCs with a mismatch between optical absorption length and charge transport scale in conjugated polymers, such as PTB7:PC$_{70}$BM based OSCs, can benefit from ZnO cathode interlayer in two ways. First, it can enhance the optical absorption in OSCs with a thinner active layer. The thinner organic active layer increases the internal electric field for reducing the recombination loss of the photo-generated charges. Second, it can also reduce the bimolecular recombination among photo-generated charges at the cathode/organic interface. The lower bimolecular recombination rate in OSCs with a thin ZnO cathode interlayer under low effective bias is mainly responsible for the enhancement in $FF$. TPC results reveal that the interfacial exciton dissociation at the metal/organic interface of regular OSCs hinders the electron collection. The unfavorable interfacial exciton dissociation can be removed by interposing a ZnO interlayer at the Al/organic interface, thus bimolecular recombination at the electrode/active layer interface can be reduced for improving the charge collection efficiency. This simple yet effective implementation of ZnO interlayer can improve the device performance in all aspects including $J_{SC}$, $V_{OC}$ and $FF$ and the total device $PCE$ by 20%. 

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Solution-processed anode interlayer, a mixture of MoO$_X$ and PEDOT:PSS, was adopted for application in inverted PTB7:PC$_{70}$BM-based OSCs. The ratio of MoO$_X$ to PEDOT:PSS in the mixed solution was optimized for achieving the best performance in inverted OSCs. A PCE of 7.4% was obtained for OSCs with an optimal MoO$_X$-PEDOT:PSS-based interlayer, interposed between the BHJ active layer and Ag anode, which is 10% higher than that of the control cell made with an evaporated MoO$_X$ interlayer. The solution-processed sMoO$_X$-PEDOT:PSS anode interlayer does not require a post-annealing process, making it suitable for application in large scale fabrication of OSCs at low costs. Favorable interfacial exciton dissociation at the interface between organic photoactive materials and MoO$_X$/Ag electrode was observed and studied. The favorable interfacial exciton dissociation is crucial to suppress the bimolecular recombination and enhances the charge collection efficiency in inverted OSCs. For inverted OSCs with a conventional thin eMoO$_X$ anode interlayer, it is difficult to realize simultaneously a large amount of free carriers generated from the favorable exciton dissociation at organic/electrode interface and an excellent hole transport due to the low hole mobility in eMoO$_X$. Combined with the excellent hole transport capability of PEDOT:PSS and the high work function nature of transition metal oxides, the advantages of the use of solution-processable hybrid sMoO$_X$-PEDOT:PSS anode interlayer in inverted OSCs were clearly demonstrated, improving photocurrent generation and charge collection efficiency by favorable interfacial exciton dissociation at the organic/sMoO$_X$-PEDOT:PSS interface.

7.2 Future Outlook

Charge recombination processes in the active layer and at the organic/electrode interfaces are essential for the performance of photovoltaic devices. Typical factors affecting the charge
recombination dynamics in OSCs include the physical and chemical properties of organic active materials, the functional interlayers between the organic active layer and electrodes. Study of the charge recombination dynamics through the measurements of light intensity-dependent $J$-$V$ characteristics of OSCs based on new organic materials is helpful in investigating the fundamental principles in the design of new organic semiconducting materials for high efficiency OSCs. By studying the charge transfer dynamics through the measurement of $TPC$ characteristics in OSCs with appropriate interfacial modification at the organic/electrode interfaces is helpful in understanding the performance of OSCs. On the other hand, the analyses of $J$-$V$ characteristics and $TPC$ characteristics can also be applied to study the charge recombination dynamics in perovskite solar cells. Through the study of charge collection and recombination processes, the factors limiting the performance of perovskite solar cells can be better understood, and the guidance to achieving better performance can be identified.
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