Investigation of photophysical and charge transport properties of optical spacers and plasmonic nanostructures in organic photovoltaics

Than, Zaw Oo

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NANYANG
TECHNOLOGICAL
UNIVERSITY

**INVESTIGATION OF PHOTOPHYSICAL AND CHARGE
TRANSPORT PROPERTIES OF OPTICAL SPACERS AND
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PHOTOVOLTAICS**

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Doctor of Philosophy

2011

Abstract

Whilst organic photovoltaics (OPV) offer several opportunities such as easy-to-tailor molecular properties, low-cost fabrication and mechanical flexibility, an extensive boost of power conversion efficiency (PCE) is of fundamental necessity to realize the commercialization of OPV devices. This thesis focuses on two approaches, incorporation of (i) titanium suboxide (TiO_x) interfacial layer and (ii) plasmonic gold nanowires (Au-NWs), to improve the device efficiencies via modulation of optical and charge transporting properties in OPV devices. The PCE of $\sim 6\%$ was achieved in PCDTBT:PC₇₁BM and PTB7:PC₆₁BM devices.

The sol-gel derived TiO_x layer was integrated at the cathode interface of P3HT:PCBM, PCDTBT:PCBM and PTB7:PCBM devices. Firstly, the role of TiO_x optical spacer was investigated using the finite difference time domain (FDTD) optical simulation technique. The calculated and experimental absorption profiles show that optical spacer effect was more pronounced in the thinner active layer and diminished with increasing active layer thickness. The optical advantage of TiO_x interfacial layer was not achieved once the active layer thickness has been optimized. The enhanced current density (J_{sc}) with TiO_x interlayer was attributed to the combined effect of optical spacer and charge transport across cathode interface. The first part of the thesis highlights the decoupling of optical and electrical contributions of TiO_x to J_{sc} by using the optical reflectance and internal quantum efficiency (IQE) measurements. Decoupling of optical and electrical effects of interlayer would support further device optimization and designs including the evaluation of new interfacial layers.

The second part of thesis explores an implication of the modified contact properties (at polymer/ TiO_x /cathode interface), surface segregation of BHJ films, and V_{oc} enhancements in OPV devices. Next, the effect of TiO_x interlayer on charge transport and recombination across the cathode interface was studied by the dark current analysis. It was found that TiO_x interlayer increased the hole-blocking barrier and suppressed the charge recombination at polymer/cathode interface of P3HT:PC₆₁BM and PCDTBT:PC₇₁BM devices. Upon integrating TiO_x , V_{oc} increased in PCDTBT:PC₇₁BM device (PCBM-rich surface) while V_{oc} remained constant in P3HT:PC₆₁BM and PTB7:PC₆₁BM devices (polymer-rich surface). Thus, the electron transport at the PCBM/ TiO_x /cathode interface may have a stronger impact on the V_{oc} enhancement than the hole-blocking at the polymer/ TiO_x /cathode interface.

Solution processed zinc tin oxide (ZTO) film was also exploited as an efficient electron transporting layer in the P3HT:PCBM inverted solar cell and the PCE as high as 3.05% was achieved. Compared to the device with TiO_x , higher J_{sc} in the device with ZTO is attributed to the efficient electron transport via higher conductivity of ZTO layer. Finally, Au-NWs were used as plasmonic antennae in the P3HT:PCBM devices and the photocurrent J_{sc} was increased by 23.2 %. The physical origin of J_{sc} enhancement was examined by optical and time-resolved photoluminescence spectroscopy. The primary enhancement mechanism is an increased plasmon excitation field that enhances the active layer absorption, thereby increasing photocurrent in the Au-NWs integrated devices.

Finally, the integrations of Au-NWs as plasmonic antennae and TiO_x as optical spacer and electron transporting buffer are promising strategies for realization of the physically thin but optically thick organic photovoltaic devices.

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Chapter 1

Introduction

1.1 Background and Motivation

The development of renewable clean energy sources plays a crucial role in meeting the future energy demands of the world. Organic photovoltaics (OPV) are rapidly becoming attractive as the next generation solar cells due to its merits such as easy-to-tailor molecular properties, low-cost fabrication, versatility of production methods and mechanical flexibility enabled by solution processing at room temperatures [1-4]. A significant advance in the realization of efficient OPVs is represented by bulk heterojunction (BHJ) that comprise an interpenetrating network of electron-donor and electron-acceptor materials. The interpenetrating networks increase the interfacial surface area between blend components thereby enhancing interfacial charge separation. Theoretical studies suggest that performance can be maximized when phase separation is of the order of the diffusion length of excitons and a bicontinuous network is formed facilitating continuous percolation of the separated electrons and holes to the collecting electrodes [3, 5].

Organic photovoltaic devices are fabricated from polymers, small molecules or combination of both. To date, while the best polymer/polymer BHJs have power conversion efficiency (PCE) of up to 1.7% [6], the polymer/fullerene BHJs have already demonstrated PCE of 4-5% with poly-3-hexylthiophene: [6,6]-phenyl-C61 butyric acid methyl ester (P3HT:PCBM) blends [2, 7-8]. More recently, high performance BHJ solar cells using the carbazole based polymer (eg., PCDTBT) and the benzodithiophene based low band gap polymer (eg., PTB7)

have produced PCE of 6-7% [9-10]. Achieving higher PCE and improved device stability is a necessity for commercialization of OPV cells.

Two major approaches to maximize the efficiencies in OPV devices are (i) the optimization of photovoltaic bulk material properties and (ii) the modification of device architectures. First category includes the development of new donor polymer designs with small band gap and deeper HOMO without affecting the charge mobilities, the smart control over the morphology and phase distribution in the photoactive films via solvent-annealing and addition of a non-solvent, etc. Second category includes tandem configuration to gain the complementary absorption characteristics in active materials [11], inverted configuration for long-lived device stability, incorporation of optical spacer to maximize the electric field intensity distribution within active layer, introduction of interfacial layer at electrode interfaces to improve the charge transport properties as well as optical management strategy, etc. Ultimately, the combination of improved materials properties and modified device architecture would drive the efficiency of OPV cells beyond 10%.

In this thesis, we focus on the device architecture modification by integrating the interfacial buffers to modulate optical and charge transport properties in the OPV devices. The interfacial layers integrated at anode and/or cathode interface are the critical components to control the energetic barriers for enhanced charge transport/collection across the interfaces, thereby minimizing the interfacial losses [10, 12-13]. The interlayer between active layer and anode (typically ITO) is important not only for the hole extraction but also for the control over active layer morphology. Similarly, the interlayer between active layer and cathode (typically Al) not only serves as an electron extraction layer but also as an optical spacer to redistribute the optical electric field for enhanced light collection in the active layer. The optical spacer located near the reflective Al mirror has a more significant role because the

dead zone exists adjacent to cathode Al due to the optical interference effect. There are several types of interlayer materials including the conductive polymeric materials, self-assembled molecules and metal oxides.

The sol-gel derived titanium suboxide (TiO_x) is a promising n-type interfacial material which offers several important opportunities; specifically, ease of fabrication at room temperature, sensitive charge selectivity (inject electrons and block holes) and effective shield against oxygen and humidity. It has been demonstrated that the integration of TiO_x interfacial layer at cathode interfaces increased the short-circuit current density (J_{sc}) and fill factor (FF) in P3HT:PCBM and PCDTBT: PCBM BHJ devices [10, 14-15]. Since the TiO_x layer functions as an optical spacer and charge transport layer at the cathode interface, the enhanced J_{sc} is attributed to the combined effects of optical spacer and better electron collecting/hole blocking contact. The optical spacer is not a panacea for light collection in all OPV devices as its efficacy varies depending on the thickness, geometry and optical constants (refractive index and absorption coefficient) of constituent layers in the device.

In addition to the optical effect, the electrical effect of TiO_x as the electron transporting/hole blocking across the interface and associated charge recombination kinetics in these devices has not broadly been studied. Even though the influence of TiO_x on J_{sc} and FF has been fairly understood, its role on the V_{oc} modification is less reported. So far, the technique that can clearly separate the electrical and optical effects of TiO_x interlayer has not been developed. Decoupling the optical and electrical effects of TiO_x on the J_{sc} enhancement would be beneficial to the further device optimizations and designs. Additionally, the exploratory attempts with other promising metal oxides (eg., zinc tin oxide) in OPV cells yield the possibilities of achieving higher conversion efficiencies.

An additional optical management strategy is the application of metal nanostructures to modulate the optical absorption in the photovoltaic layer through the phenomenon of plasmonic resonance. These metal nanostructures including nanoparticles (NPs), nanorods and nanowires (NWs) act as an effective antenna for transducing the incoming light energy to a localized surface plasmon mode energy. Harnessing the localized plasmon excitation allows the use of optically thick, but physically thin photoactive layers, lowering materials cost and alleviating problems caused due to poor charge transport in the organic photoactive layer.[16] Presently, surface plasmon enhanced OPV devices with Au and Ag NPs have been demonstrated [17-21] where the variations in size, shape and density of plasmonic NPs have been optimized for increased photocurrent in the devices. However, the factors governing the enhancement including the role of the spacer layer as well as the thickness of the photovoltaic layer have not yet been well understood. In contrast to the studies on nanoparticles, the possibilities of integrating metallic nanorods/nanowires into organic solar cells for plasmonic enhancement have not been widely explored [22-23].

1.2 Objectives and Scope

To address the gaps mentioned above, the main objectives of this thesis are summarized as follows:

1.2.1 Studies of modified device architecture and their impact on device efficiencies

The conversion efficiency of OPV devices can be maximized by (i) optimizing the photovoltaic bulk material properties and/or (ii) modifying the device architecture. In this thesis, the second strategy of the device architecture modification is to be implemented. Under this scheme, the standard device structure would be modified by incorporation of the n-type titanium oxide (TiO_x) interfacial layer and plasmonic gold nanowires (Au-NWs).

Then, we would study their impacts on the optical, photophysical and charge transport properties in OPV devices. In this work, the three polymer/fullerene blends (P3HT:PCBM, PCDTBT:PCBM and PTB7:PCBM) are used as the photoactive materials.

1.2.2 Investigate the impact of metal oxide interfacial layer on optical and charge transport properties in OPV cells

Upon incorporating TiO_x interfacial layer, the optical spacer effect and better charge transport plays a concurrent role in increasing the J_{sc} of OPV devices. The optical spacer redistributes the optical electric field $|E|^2$ across all layers in the device, thereby increasing the optical absorption in photoactive layer. First, we would study the effect of TiO_x optical spacer on modulation of optical properties in OPV devices by using the finite difference time domain (FDTD) optical simulation technique, further experimentally confirmed by optical reflectance measurement. A convolution of optical absorption (1-reflectance) and internal quantum efficiency (IQE) of the devices would permit the decoupling of the optical and charge transport effects of TiO_x layer on the J_{sc} . The decoupling would be beneficial for further device optimization and designs.

The following study would be the effect of TiO_x on charge transport and recombination across the active layer/ TiO_x /cathode interfaces using dark current analysis. Being dark current, it eliminates the implications of light intensity dependent factors. The surface segregation of photoactive BHJ layer would play a role in determining the charge transport properties at the active layer/ TiO_x interface. We would explore a correlation among the surface segregation, the altered electrical contact properties and the V_{oc} of the devices. In addition, the built-in potential (V_{bi}) (estimated from the J_{ph} -V response of the devices) would provide the information about the energetic shifts at modified interface. We would also study

the effect of TiO_x layer on V_{BI} and its correlation to V_{oc} of the devices. Other than TiO_x, the high mobility zinc tin oxide (ZTO) is a promising n-type material. Thus, it would be exploited as electron extracting buffer layer in inverted OPV cells. Finally, we would compare the device performances (ZTO versus TiO_x).

1.2.3 Investigate the impact of plasmonic metal nanostructures on optical and photophysical properties in OPV cells

The application of plasmonic metal nanostructures is a promising strategy to modulate the optical and photophysical properties of adjacent photoactive materials. The solution processed gold nanowire (Au-NW) networks would be integrated as plasmonic antennae in OPV for enhanced device performance. The surface plasmon absorption band of Au-NWs in different dielectric environment and the absorption enhancement induced by Au-NWs would be investigated. Two possible origins for the improved photocurrent in the Au-NWs device are the strong surface plasmon excitation field strength (enhanced optical absorption) and/or the modulation of exciton relaxation dynamics (photophysical properties). These two origins would be distinguished via the optical and time-resolved photoluminescence (TRPL) spectroscopy. In addition, the role of PEDOT:PSS spacer between Au-NWs and photoactive molecules would also be stressed.

1.3 Thesis Organization

The thesis is organized as follows:

In chapter 2, the operating mechanisms, critical device parameters and bulk heterojunction (BHJ) concept in organic photovoltaics are briefly described. In addition, the role of interfacial layers in OPV devices, concentration of light by metal nanostructures, surface

plasmon enhanced OPV devices and finite difference time domain (FDTD) optical simulation technique are reviewed and discussed.

Chapter 3 presents the preparation of sol-gel derived titanium suboxide (TiO_x) and zinc-tin oxide (ZTO) interfacial layers and the fabrication of wet-chemistry-based Au-NWs on substrates. In addition, details of the optical, physical and chemical characterizations, the fabrication of OPV devices and the efficiency measurements are also mentioned.

Chapter 4 comprises four sections. The first section describes the effects of TiO_x interlayer on the absorption in photoactive layer studied by both optical simulation and experiments. Decoupling of optical and electrical effects of TiO_x layer is underlined. In the second section, the influence of TiO_x layer on V_{oc} was elucidated. The third section describes the demonstration of zinc-tin oxide (ZTO) layer as an electron selective layer in inverted OPV cells and the comparison of device performance with ZTO versus TiO_x . The fourth section presents the application of ultrafine Au-NW networks as plasmonic antennae in OPV. Highlighted in this section is the determination of physical origin of the Au-NWs induced photocurrent enhancement using the optical and time-resolved photoluminescence spectroscopy.

Chapter 5 brings the overall summary and conclusion. Along with the conclusion, future prospects addressing the combined approach of interfacial layer and plasmonic metal nanostructures in the inverted and tandem OPV cells are proposed.

1.4 Contributions of Thesis

The original contributions arising from my PhD work are listed as follows:

- (i) Decoupled the optical and electrical effects of TiO_x interlayer on J_{sc} enhancement in OPV cells.
- (ii) Explored the implication of the charge injection, surface segregation at cathode interface and V_{oc} enhancement upon integrating TiO_x in BHJ OPV cells.
- (iii) Exploited ZTO for the first time as an effective electron transport layer in inverted OPV cells.
- (iv) Successfully integrated Au-NWs for the first time as plasmonic antennae in OPV cells and achieved the J_{sc} enhancement via a careful reduction of PEDOT:PSS buffer layer thickness.
- (v) Resolved two possible origins of J_{sc} enhancement in Au-NWs integrated device via optical and photophysical properties of photoactive molecules near Au-NWs.

Chapter 2

Literature Overview

2.1 Organic photovoltaics

Organic photovoltaics (OPV) have the potential to provide the low-cost and large area devices on flexible substrates. The introduction of bulk heterojunction (BHJ) concept leads to a major breakthrough of power conversion efficiencies in OPV cells.

2.1.1 Operation principle and critical device parameters

The energy conversion processes involved in the operation of OPV cells are (i) exciton formation, (ii) exciton diffusion, (iii) exciton dissociation at the donor/acceptor interface (iv) charge transport in the blend materials and (v) charge collection at the electrodes. The operational schematic for an OPV cell is shown in *Figure 2.1*.

Figure 2.1 Schematic for the operative sequence of an organic photovoltaic cell.

- (i) **Exciton formation:** The photoexcitation in organic materials leads to the formation of coulombically bonded electron-hole pairs, called excitons. As the absorption coefficients of organic materials are of the order of 10^5cm^{-1} , a 100 nm thickness is enough to absorb most of the photons [1]. A wider spectral harvesting of the solar spectrum is achieved by utilizing low band gap polymers.
- (ii) **Exciton diffusion:** The excitons do not dissociate thermally because of the high exciton binding energy typically around 0.4 eV [24]. This is in contrast to inorganic semiconductors where the binding energy is of the same magnitude as the thermal energy. The excitons have to diffuse to the donor/acceptor interface where exciton dissociation can occur. The exciton diffusion length in conjugated polymers is typically 10-20 nm [25].
- (iii) **Exciton dissociation:** The nascent exciton dissociates into separated charge carriers. This is facilitated by the presence of an electron acceptor, which accepts the electron while the hole remains on the polymer chains. The efficient dissociation of excitons needs an electric field that is supplied via externally applied field or via energy offsets at the donor/acceptor interface.
- (iv) **Charge transport:** The separated charge carriers are then transported to the appropriate electrodes by an electric field created by the difference in work functions of the electrodes. Since the carrier mobility of organic semiconductors is usually very low, the thickness of the active layer has to be adjusted to balance the charge transport and the optical absorption.
- (v) **Charge collection:** The charge carriers are collected at the electrodes. The collection efficiency depends on the energy level matching at the metal/polymer.

The measurement of the current-voltage characteristics of a cell in the dark and under illumination permits an evaluation of its photovoltaic performances as well as its electrical behavior. The typical current-voltage curve of solar cell is depicted in *Figure 2.2*. The performance of the cell is commonly characterized by three parameters: open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and fill factor (FF).

Figure 2.2 Current-voltage (J-V) characteristics of a typical solar cell in the dark (black curve) and under illumination (red curve). The open circuit voltage (V_{oc}), short circuit current density (J_{sc}), the voltage and current density at maximum power point (V_{MPP} and J_{MPP}) are indicated in the J-V curve.

- (i) **Open-circuit voltage (V_{oc})** is the applied external bias at which the photocurrent in the solar cell is zero. The maximum V_{oc} is determined by the energy level difference between HOMO of donor and LUMO of acceptor.
- (ii) **Short-circuit current density (J_{sc})** is the current density under illumination at zero applied voltage. J_{sc} is determined by the photoinduced charge carrier density and carrier mobility within organic semiconductors.
- (iii) **Fill factor (FF)** is the ratio of the actual maximum obtainable power ($V_{MPP} \times J_{MPP}$) to the power determined by V_{oc} and J_{sc} ($V_{oc} \times J_{sc}$). It therefore describes the “squareness” of the solar cell’s current-voltage characteristics. It can be expressed as:

$$FF = \frac{V_{MPP} \times J_{MPP}}{V_{oc} \times J_{sc}} \dots\dots\dots (2.1)$$

where, V_{MPP} and J_{MPP} are the voltage and the current at maximum power point respectively.

Power conversion efficiency (PCE) is the ratio of the maximum obtainable electrical power to the incident radiant power.

$$PCE = \frac{P_{out}}{P_{in}} = \frac{V_{MPP} \cdot J_{MPP}}{P_{in}} = \frac{FF \cdot J_{sc} \cdot V_{oc}}{P_{in}} \dots\dots\dots (2.2)$$

External quantum efficiency (EQE) relates the number of electrons collected in an external circuit to the number of incident photons shining on the device. It is determined as a product of the absorbance efficiency in the photoactive region (η_A), exciton diffusion efficiency (η_{ED}), charge transfer efficiency (η_{CT}), and charge collection efficiency (η_{CC}).

$$EQE = \eta_A \cdot \eta_{ED} \cdot \eta_{CT} \cdot \eta_{CC} \dots\dots\dots (2.3)$$

Incident Photon to Current Efficiency (IPCE), the monochromatic version of EQE, is the yield of electrons generated per incident photon under monochromatic lightning at a certain wavelength (λ). In contrast to EQE, IPCE may be determined by measuring the monochromatic light power density, and can be calculated as a function of short circuit current density (J_{sc}), incident light power density (P_{in}), and wavelength (λ).

$$IPCE = \frac{1240 \times J_{sc}}{P_{in} \cdot \lambda} \dots\dots\dots (2.4)$$

2.1.2 Bulk heterojunction organic photovoltaic cells

Figure 2.3 (a) A typical organic BHJ solar cell. PEDOT:PSS is the hole transporting layer, ITO the anode and Al the cathode. (b) Molecular structures of three p-type polymers (P3HT, PCDTBT and PTB7) and n-type fullerene derivative (PCBM).

The best-performing organic photovoltaic device architecture uses the so-called bulk heterojunction (BHJ) configuration. A typical organic BHJ device is shown in *Figure 2.3(a)*. The essence of the BHJ is to intimately mix the donor and acceptor components in the bulk forming a nanoscale interpenetrating network in the active layer. The donor/acceptor phase separation length should be less than the exciton diffusion length in order to promote exciton dissociation prior to recombination. The typical exciton diffusion length in organic semiconductors is usually around 10-20 nm [25]. The bulk heterojunction concept increases the interfacial area between the donor and acceptor phases and results in improved efficiency in solar cells. In the last decade, the power conversion efficiency of organic BHJ solar cells was significantly progressed. Currently, the efficiencies exceeding 7% has been achieved using novel polymers such as P3HT, PCDTBT and PTB derivatives [2, 7-9, 26]. Since it is still inadequate for large-scale applications, tremendous efforts have been devoted to extensively boost the efficiency of organic BHJ devices.

In this attempt, it is crucial to realize the factors limiting the performance of organic solar cells as well as the challenging approaches for potential improvements. Two prime limitations for development of organic photovoltaics are (i) insufficient light trapping in organic materials and (2) poor charge extraction at the electrode contacts leading to recombination. The first limitation is optical in nature and can be improved by some strategies such as the integration of optical spacer to maximize the light intensity distribution in the organic photovoltaic layer, tandem architecture to harvest the photons with complimentary absorption characteristics and exploitation of surface plasmonics to concentrate light near metal nanostructures. The second limitation is electrical in nature and can be alleviated by introduction of the proper interfacial layer at electrodes to control the charge injection properties via a better energy level alignment. Thus, a combined optical and electrical approach would lead to a realization of high performance organic photovoltaic devices.

2.2 Interfacial layers for efficiency enhancement in organic photovoltaics

The interfacial layers play a crucial role in enhancing the efficiency of OPV cells due to their capabilities to improve the above mentioned limitations of insufficient light harvesting and poor charge extraction at electrodes. The interfacial layers serve as an optical spacer to modulate optical properties in photoactive layer. In addition, the interfacial layers can be exploited as selective charge transporting layers between photoactive layer and electrodes: p-type materials for hole and n-type for electron transports, respectively. Other than the hole and electron selectivity at the respective electrodes, p-type interlayers are important for controlling active layer morphology while n-type for preventing Al diffusion to active layer during vacuum evaporation and thermal annealing [27]. Different types of charge selective

materials have been reported that include conductive polymeric materials, self-assembled molecules, metal fluorides and metal oxides.

2.2.1 Effect of optical spacer

One of the major requirements to increase power conversion efficiency is to maximize the light absorption in photoactive layer. In conventional device configuration, the optical electric field $|E|^2$ is zero in some fractions of photoactive layer adjacent to the reflective Al cathode due to optical interference between incident light and reflected light from cathode. Since the intensity of light directly scales with $|E|^2$, the collection of light in photoactive layer is reduced due to the existence of dead zone in this fraction of active layer. The optical interference effect is more important for thin photoactive layer which thickness is comparable to absorption depth and wavelength of the incident light [14]. Upon inserting an optical spacer, the light is spatially redistributed across all layers in the device and the light intensity maximum falls within the photoactive layer. Thus, the introduction of optical spacer enables better light absorption in photoactive layer.

Figure 2.4 Schematic representation of the spatial distribution of optical electric field $|E|^2$ in OPV devices with and without optical spacer. In the conventional device with no optical spacer (left), the maximum $|E|^2$ value is beyond the photoactive layer while in the device with optical spacer (right), the $|E|^2$ is maximized within the photoactive layer. [14]

Figure 2.4 shows schematic representation for the spatial distribution of optical electric field $|E|^2$ in conventional device and the redistribution of $|E|^2$ upon integrating optical spacer. It

was observed in OPV devices that the optical spacer effect on active layer absorption was significantly different when the optical spacer thickness was varied [10]. The optical spacer effect varies depending on layer thicknesses including the optical spacer thickness itself and multi-reflections at various interfaces. In addition, it depends on the wavelength of light [10, 28]. Figure 2.5 shows the calculated optical electric field distribution in P3HT:PCBM devices with and without ZnO optical spacer at different wavelengths of incoming light. Thus, optical spacer effect is not a panacea for enhanced light collection in all cases. Many works addressing the optical spacer effect have been implemented in the multilayer OPV devices with different photovoltaic materials and different layer-thicknesses.

Figure 2.5 Calculated optical electric field distribution in P3HT:PCBM solar cells with active layer thickness of 40 nm (a) without and (b) with optical spacer (39 nm) at different wavelengths of incoming light. In Figure b, optical spacer shifts the maximum light intensity into the active layer. [28]

2.2.1 P-type interfacial layers

The p-type interfacial layers can reduce hole extraction barrier at anode interface and improve contact properties, thereby enhancing the efficiency in OPV cells. The conductive PEDOT:PSS is commonly used as an anode buffer in OPV cells since its work function (5.0-5.2 eV) lies between the work function of anode ITO (~ 4.8 eV) and HOMO of most p-type polymers (~ 5.2 -5.5 eV). Chen-Yan Li et. al. demonstrated sulfonated poly(diphenylamine)

(SPDPA) as a novel hole-collecting layer in polymer solar cells.[29] The work function of SPDPA ($\sim 5.24\text{eV}$) is slightly higher than that of PEDOT:PSS (5.07eV) that favours hole extraction from ITO anode. The P3HT:PCBM device with SPDPA layer (10 nm) produced PCE of 4.2% higher than 3.6% in the device with PEDOT:PSS. Enhanced photocurrent density (J_{sc}) and fill factor (FF) of the devices with SPDPA layer was attributed to a better hole extraction at anode interface, high crystallinity and mobility of P3HT induced by SPDPA layer.

In addition to polymer-based PEDOT:PSS, transition metal oxides including vanadium oxide (V_2O_5), molybdenum oxide (MoO_3), tungsten oxide (WO_3) and nickel oxide (NiO) have been used as hole transporting/electron blocking layer to improve the interfacial properties between anode and active layer in OPV cells [30-32]. Since the large-band gap metal oxides are highly transparent in visible and infrared spectral regions, the incoming light is not absorbed in these layers before reaching the photoactive materials. Moreover, a sufficiently high conduction band minimum (CBM) of these p-type interlayer materials effectively blocks the electron leakage from both donor and acceptor materials while the valence band maximum (VBM) of these oxides aligns between Fermi level of anode and HOMO of donor polymer that favours effective hole transport with minimal contact resistance.

It was reported that the OPV cells with MoO_3 interlayer (10 nm) revealed a higher conversion efficiency than that with PEDOT:PSS layer and the enhanced efficiency was attributed to an increased FF and reduced series resistance [30]. Irwin et al reported p-type NiO interlayer as anode interfacial layer in polymer BHJ solar cells and demonstrated PCE as high as 5.2%. All device parameters (V_{oc} , J_{sc} and FF) were improved upon replacing PEDOT:PSS with NiO layer (10 nm). It was highlighted that the hole-transporting /electron-blocking NiO interfacial layer greatly suppressed the interfacial losses and

improved the stability of the device [33]. Recently, the sol-gel derived copper oxide (CuO_x) has shown as an effective hole transporting layer in inverted solar cell. The improved fill factor (FF) and reduced series resistance (R_s) in these devices are due to better contact properties at the hole collecting electrode with CuO_x interlayer [34].

2.2.2 N-type interfacial layers

Parallel to the development of p-type interlayers, several n-type materials have emerged for efficient electron extraction in OPV cells. As a result, the device performance and stability have been largely improved. A thin lithium fluoride (LiF) layer was typically used between Al and organic photoactive layer, resulting in an increase in V_{oc} . Improved device performance with LiF layer was suggested through the formation of favourable dipole moment across the junction and the modification of cathode work function which facilitates a better electron injection [35]. It was also reported that alternative metal fluorides (NaF, KF and CsF) interlayers yielded the improved device performance [36].

Other than metal fluorides, solution-processed poly(ethylene oxide) (PEO), spirobenzofluorene based phosphine oxide (SPPO21), alcohol-soluble polyfluorene derivatives (PF-EP) and conjugated polyelectrolytes (CPEs) layers have been demonstrated as efficient interfacial buffers [37-40]. Introduction of PEO layer at cathode interface increased V_{oc} and FF in organic solar cells. Improved FF was attributed to better charge transport by distribution of internal field while increased V_{oc} was attributed to higher built-in potential. Overall, the device performance with PEO was comparable to that with LiF [37]. Similar to PEO interlayer, SPPO21 interlayer increased V_{oc} and FF in the P3HT:PCBM solar cells. The dramatic increase in V_{oc} was ascribed to passivation of traps and interfacial band-bending induced by SPPO21 interfacial layer [38]. Chao He et. al. applied five distinct

conjugated polymers and electrolytes as cathode interlayers in three different polymer-fullerene BHJ systems. It was reported that V_{oc} was enhanced in the polyfluorene copolymer-based devices, whereas no significant V_{oc} enhancement occurs in typical P3HT:PCBM and MEH:PPV:PCBM devices [40]. Although the origin of V_{oc} enhancement in specific material system was examined by the dark currents, further investigations are still needed to fully understand the underpinning mechanisms.

Figure 2.6 (a) J-V characteristics of P3HT:PCBM solar cells with and without SPPO21 interlayer under AM 1.5G illumination. The V_{oc} was improved from 0.38 V to 0.61 V upon integrating SPPO21 (5 nm) [38]. (b) J-V characteristics of PFO-DBT35:PCBM, P3HT:PCBM and MEH-PPV:PCBM solar cells with and without PF-Br cathode interlayer under AM 1.5G illumination. The V_{oc} was improved from 0.92V to 1.07V in PFO-DBT35:PCBM system upon integrating PF-Br interfacial layer [40].

In addition to polymeric interlayers, the solution processed metal oxides including titanium suboxide (TiO_x) and zinc oxide (ZnO) are the well investigated n-type interfacial layers positioned between photoactive layer and cathode in OPV devices. J. Gilot et. al incorporated a solution processed ZnO nanoparticles as an electron transporting layer in P3HT:PCBM solar cells and an increase in photocurrent density with ZnO layer was realized [28]. As the conduction band maximum (CBM) of ZnO (4.3eV) facilitates a better energy level alignment between LUMO of PCBM and work function of Al, electron transfer from

active layer to electrode is more efficient. The low valence band of ZnO prevents the hole carriers in the active layer from reaching the electrode. The absorption enhancement in active layer is due to the redistribution of optical electric field by the ZnO optical spacer. The increased J_{sc} in the ZnO integrated device is attributed to the effects of optical spacer and better electron transport/hole blocking at modified cathode interface [28].

Figure 2.7 (a) Device structure with SAM modifier between ZnO and metal cathode. (b) Illustrative energy level diagram of ZnO/metal interface with and without SAM. Schottky and Ohmic contact are formed depending on the dipole direction and chemical bonding between the SAM and metal [41].

The electrical and electronic properties of ZnO can be easily modulated by modifying ZnO surface with self-assembled monolayers (SAM). Alex K.-Y. Jen et. al. demonstrated that the device performance was significantly altered upon applying carboxylic acid based SAM to ZnO/metal interface depending on the dipole direction and chemical bonding between the

SAM and metal [41]. *Figure 2.7* shows the device structure with SAM modifier between ZnO and metal cathode and illustrative energy level diagram of ZnO/metal interface with and without SAM. If the dipole across ZnO/metal contact is unfavourable, formation of Schottky contact leads to poorer device efficiency. With appropriate choice of SAM modifiers, Ohmic contact was formed and the organic solar cells showed dramatically improved device efficiency [41]. ZnO interfacial layer was exploited not only in conventional BHJ devices, but also in the devices with inverted configuration. The efficiencies of inverted cells with ZnO sol-gel and nanoparticles were improved as compared to the conventional device efficiency [42-43]. For device stability, the conventional device degraded within 5 days while the inverted cells with ZnO retained over 80% of its original efficiency after 40 days in ambient conditions [42]. Recently, Alan J. Heeger et. al. reported PCE of 6% in PCDTBT:PCBM inverted solar cells where sol-gel derived, low temperature treated ZnO film was used as electron transporting layer [44].

In parallel to showing a promising potential of ZnO as electron buffer layers in polymer solar cells, the sol-gel derived TiO_x emerged as a unique interlayer in OPV cells. Introduction of TiO_x interfacial layer in OPV has offered several promising opportunities for improving the performance of bulk heterojunction solar cells. It functions as (i) optical spacer that redistributes light intensity to maximize absorption in photoactive layer, (ii) electron transporting layer due to its conduction band minimum matched with Fermi level of Al, (iii) hole blocking layer due to its high valence band maximum of 8.1eV and (iv) oxygen barrier for improving the device stability. Alan. J. Heeger et. al. reported an approximately 50% increase in power conversion efficiency (PCE) upon integrating TiO_x interfacial layer in P3HT:PCBM devices [14]. Most of the increase in PCE was attributed to the J_{sc} enhancement in agreement with the incident photon to current efficiency (IPCE)

measurement. As seen in Figure 2.8, IPCE of 60% at 500 nm in conventional device was substantially increased to 90% in the TiO_x integrated device. The authors claimed that this effect was originated from the increased absorption in the P3HT:PCBM photoactive layer due to the effect of TiO_x as an optical spacer. However, the effect of TiO_x interlayer on charge transport at electron collecting electrode has not been clarified [14].

Figure 2.8 (a) Schematic of the device structure with TiO_x interfacial layer along with the preparation steps of TiO_x . (b) IPCE spectra of the device with and without TiO_x optical spacer. [14]

Christoph J. Brabec et. al. inserted TiO_x interfacial layer in inverted polymer-fullerene BHJ solar cells. The polyoxyethylene tridecyl ether (PTE) as an additional surface modification layer between ITO and TiO_x improved the electron collection efficiency at the bottom contact and increased FF in these devices [45]. In addition to improving the device performance, TiO_x layer integrated between active layer and Al electrode prevents the degradation of polymer solar cells. Akinobu Hayakawa et. al. showed that TiO_x layer is an efficient shield against physical damage and chemical degradation and the cell maintained its high performance with 94% durability under aerobic conditions for 100 hours [46].

Alan J. Heeger group reported high power conversion efficiency (PCE) of 6% when TiO_x layer was applied to PCDTBT:PCBM solar cells under AM 1.5 irradiation [10]. It was remarkable in OPV solar cells that internal quantum efficiency was close to 100% at 450 nm

indicating that nearly every absorbed photon converted to charge carriers and that all charge carriers were collected at the electrodes. The same group later clarified the role of TiO_x layer as an optical spacer in the same BHJ system using optical modelling and experiments. The optical modeling revealed that the efficacy of optical spacer (TiO_x) depends not only on its optical constants and thickness, but also on the optical constants and thickness of all other layers within the device. The TiO_x layer enhanced absorption in active layer for appropriate choice of active layer thickness [10]. J. H. Lee et. al analyzed the diode parameters for PCDTBT:PCBM organic solar cells and highlighted that the reverse saturation current density was decreased with TiO_x interfacial layer due to higher energy barrier for hole transport [47].

A more comprehensive understanding on modulation of charge transport and recombination kinetics at TiO_x modified cathode interface in OPV cells is still needed. Moreover, decoupling of optical and electrical effects of TiO_x interlayer on photocurrent density enhancement is important for further device optimizations and designs. It is exciting to exploit TiO_x interlayer in other high efficiency BHJ solar cells (eg., PTB7:PCBM) for enhanced device performances. In addition to interfacial layer approach, an alternative strategy to increase absorption in photoactive layer (i.e, application of metal nanostructures for surface plasmonics) will be described in the following section.

2.3 Surface plasmonics for organic photovoltaics

Surface plasmons (SP) are the coherent oscillation of surface conduction electrons excited by electromagnetic (EM) radiation. At resonance, the interaction of incident EM radiation with metal surface facilitates the electric field enhancement (light concentration) near the metal

surface. Surface plasmonics is thus a fascinating field that exploits the unique optical properties of metallic nanostructures and manipulates light at nanometer scales.

2.3.1 Optical manifestations of localized surface plasmon resonance

Figure 2.9 Schematic of the collective response of electrons on the surface of the metal to an optical field (localized surface plasmons).

Upon interaction of electromagnetic field on the metal nanostructures, the surface conduction electrons are shifted with respect to the lattice of positive ions. The redistribution of charges builds up a restoring local field on the displaced electrons that in turn enhances the oscillation of free electron relative to the ionic background. Localized surface plasmons (LSP) are the oscillation of surface conduction electrons confined to metal nanostructures including metal nanoparticles, nanowires, etc. At a specific optical frequency where localized surface plasmon resonance (LSPR) occurs, the coherent oscillation of LSPs with the electromagnetic excitation leads to the strong local light concentration around metal nanostructures that intensifies the SP absorption bands [48]. *Figure 2.9* illustrates the collective response of electrons on the surface of the metal to an optical field (localized surface plasmons).

The Au and Ag nanostructures are well known for plasmonics due to (i) their plasmonic frequency in visible region, (ii) negative real part of dielectric function and (iii) small imaginary part of dielectric function in visible region. The real part links the existence of SPR

while the imaginary part reflects the dielectric loss. The quasistatic approximation [49] can be used to derive a simple analytical equation for the dipole polarizability α of the small nanoparticles significantly smaller than the wavelength of exciting light.

$$\alpha = 4\pi a^3 \frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d} \dots\dots\dots(2.5)$$

where, ϵ_m and ϵ_d are the relative permittivities of metal and dielectric respectively. The dipolar LSPR of the metal nanoparticles (SP absorption band) is strongest at a frequency (ω) where the permittivity of metal satisfies

$$\text{Re} (\epsilon_m) \approx -2\epsilon_d \dots\dots\dots(2.6.a)$$

$$\text{Im} (\epsilon_m) \approx 0 \dots\dots\dots(2.6.b)$$

For metal nanoparticles on glass ($\epsilon_d = 2.25$), the ϵ_m of -4.5 is the necessary condition for the strong resonance of metal nanoparticle. For Au and Ag, this occurs at 520 nm and 420 nm respectively. Despite the more intense SP absorption peak of Ag nanoparticles (NPs) than Au-NPs, the Au-NPs have a better chemical stability due to its low oxidation rate.

According to the Drude model [50], the real part of ϵ_m can be expressed as a function of light frequency (ω) :

$$\text{Re} (\epsilon_m) = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2} \dots\dots\dots(2.7)$$

where, ω_p is the bulk plasma oscillation frequency associated with the free carriers and γ is their bulk collision frequency. From equations 2.6 (a) and 2.7, the LSPR frequency of metal nanoparticles is derived as

$$\omega_{SP} = \sqrt{\frac{\omega_p^2}{1+2\epsilon_d}} - \gamma^2.....(2.8)$$

The resonance frequency of the SP absorption band is thus sensitive to the dielectric environments. The metal nanoparticles in high dielectric environment give a red-shifted LSPR [49].

Figure 2.10 (a) Illustration of the effects of geometry and materials on SP resonances metal nanostructures. (b) Plot of resonant condition (ϵ_m/ϵ_d) against aspect-ratio parameter L for spheroidal particles.[51]

In addition, LSPR depends on the shape, size and size distribution of the metal nanoparticles [52]. The shape-dependent LSPR absorption band can be manifested by the surface plasmons unevenly distributed on the nonspherical nanostructures. Particularly, metal nanorods exhibit two resonance bands: transverse resonance (high energy band) corresponding to the electron oscillations perpendicular to the major axis and longitudinal resonance (low energy band) corresponding to the electron oscillations along the major axis. The longitudinal resonance band is red shifted with increasing the aspect ratio of nanorods [48]. *Figure 2.10* (a) shows the schematic of the effects of geometry and materials on the SP

resonance of metal nanostructures suggesting the red-shifted SP resonance as the metal nanoparticle is in high dielectric environment (left) and the aspect-ratio of nanorod is increased (right). The resonance condition (ϵ_m/ϵ_d) against the aspect-ratio for the spheroidal particles is depicted in *Figure 2.10* (b) [51].

2.3.2 Enhanced light absorption by plasmon-exciton coupling

An interesting phenomenon associated with the LSPR excitations is the local electromagnetic field enhancements. This intense local excitation of plasmons is coupled to the excitonic energy of adjacent semiconductors, thereby increasing light absorption in the surrounding semiconductor materials through the plasmon-exciton coupling. Thus, metallic nanoparticles can be exploited as the subwavelength plasmonic antennas that transduce the incoming light energy into the localized surface plasmon mode energy.

Figure 2.11 Light trapping by the excitation of LSPR. The strong local near-field enhances light absorption in semiconducting materials via plasmon-exciton coupling.

It particularly works well for the small nanoparticles (5-20 nm) for which scattering and reflection efficiency is low. It is a necessity that the absorption rate in the light absorbing materials must be higher than the reciprocal of the typical plasmon decay time (~ 10 -50fs). Otherwise, the absorbed energy is dissipated into ohmic damping in the metal. Most of the

organic semiconductors have such a high absorption rates. Thus these antennas are especially useful for the light absorbing organic materials with short carrier diffusion lengths that restrict the usage of thicker active layers in photovoltaic applications. *Figure 2.11* illustrates the light trapping in photoactive semiconductors by the excitation of localized surface plasmons in metal nanoparticles.

2.3.3 Plasmonic enhancement in organic photovoltaic cells

In order to improve absorption enhancement in thin active layers, applying plasmon active metal nanostructures near thin photovoltaic layer is one efficient route. Excitation of an SPR at metal nanoparticles interface can create strong near-field and far-field propagating waves that enhance light absorption and photocurrent in organic photovoltaic devices. The common fabrication schemes for metallic nanostructures include electron beam lithography, vacuum evaporation and chemical synthesis (wet chemistry). The plasmon enhanced performances of organic solar cells have not been systematically explored. The few reports that exist in this field are reviewed below in terms of the size of metal particles (Au and Ag), the fabrication method, their extinction properties, absorption enhancement in photoactive layer and device efficiency improvement.

Silver nanoparticles have been previously used to enhance absorption by plasmonic resonance in P3HT:PCBM devices[19, 21]. In the work by Kim et al [19], Ag nanoparticles (~13 nm) were produced via pulse-current electrodeposition while in the work by Morfa et al [53], island-like Ag nanostructures (thickness ~ 1-4 nm and median island diameter~ 10.5 nm) were fabricated by vapour-phase deposition. In both devices, the power conversion efficiency was increased from 3.05% to 3.69% and from 1.3% to 2.2% (non-annealed) respectively. This was attributed to an enhanced absorption in the photoactive polymer due

Figure 2.12 IPCE spectra of reference and Ag nanostructure incorporated cells; (a) annealed cell [19] and (b) non-annealed cell [53]. Inset: SEM image of (a) electrodeposited Ag nanoparticles and (b) vacuum evaporated Ag nanoparticles.

to the higher field strength in the vicinity of the excited surface plasmons. Additionally, IPCE was also improved uniformly at all spectral region (400-650 nm) for Kim et. Al [19] while a strong increase at longer wavelength (>500 nm) was observed in the work by another group [53]. As the annealed device has already a good red response, more red-shifted enhancement was not obtained. Utilizing gold rather than silver or annealing a thicker silver layer to form larger islands lead to plasmonic resonance at red wavelength region. The thickness of PEDOT:PSS layer is another important consideration for these devices as the enhanced electromagnetic field decays rapidly with distance. Depending on the Ag coverage on the transparent electrode, V_{oc} is slightly changed due to a decrease in the work function of electrode.

In addition to silver nanostructures, gold nanostructures also provide promising plasmonic enhancements in organic photovoltaics. Lee et al [20] fabricated gold nanorods on ITO by a layer-by-layer deposition, which were then transformed into nanodots (~30 nm) during thermal heating because of the structural instability of the nanorods. Accordingly, the two

distinct plasmonic bands of nanorods transformed to a single plasmonic band centered at 530 nm. The PCE also increased from 3.04% to 3.65% and an improved IPCE observed in the 500-600 nm region. The enhancement in PCE is mainly from an improved FF resulting from more efficient charge transfer in the blends due to the strong coupling between the organic excitons and plasmons of gold nanostructures.

Figure 2.13 (a) Current-voltage characteristics of the P3HT:PCBM devices incorporating PEDOT:PSS doped with various concentrations of Au-NP solutions. Inset: schematic device structure. (b) Corresponding IPCE spectra of these devices [54].

Chen et al [54] have also explored the effect of AuNP- induced surface plasmon resonance on the photocurrent generation in OPV device. In this approach, a AuNP solution was blended with PEDOT:PSS and used as an anodic buffer layer. The size of the AuNPs is approximately 30-40 nm so that their resonance peak is matched with the absorption of the photoactive layer. The enhanced IPCE is observed in the range 400 nm-600nm coinciding with the resonance band associated with AuNP embedded in PEDOT:PSS. In addition, PCE is increased from 3.48% to 4.19% mainly because of the increased J_{sc} and improved FF. It is attributed to an increased exciton generation rate and exciton dissociation probability approximated from an analytical approach initially reported by Mihailetchi et al [55-57].

2.4 Finite difference time domain (FDTD) optical simulation

In parallel to the experimental efforts, an analytical or numerical simulation is carried out to validate the surface plasmon properties of various metal nanostructures, to predict optimal nanostructures for specific applications and to explore new phenomena not evident from simple considerations.

2.4.1 Finite-difference time-domain (FDTD) method

The finite-difference time-domain (FDTD) method is a numerical method for solving the time-domain Maxwell's equations for spatio-temporal evolution of the electric (E) and magnetic (M) fields [58]. Figure 2.14 shows the main steps involved in FDTD simulation. An initial step would be the construction of a physical simulation structure including conductors, dielectrics and boundaries. Upon applying an input stimulus (pulse from source), the E and H fields are calculated at increment of time. After each increment, the input electric field amplitude is calculated followed by the recalculation of the E and H fields that moves forward in time in a leap-frog fashion. This continues until the E and H fields within the system decay to zero. The frequency information can be extracted from the transient response using the Fast Fourier Transform (FFT) technique. Thus, the information about a wide range of frequencies can be achieved by a single simulation run [58-59].

Figure 2.14 Finite difference time domain (FDTD) algorithm.

The starting point for the construction of the traditional FDTD algorithm is Maxwell's time-domain curl equations.

$$\mu \frac{\delta H}{\delta t} = -\nabla \times E \dots\dots\dots(2.9)$$

$$\varepsilon \frac{\delta E}{\delta t} = \nabla \times H \dots\dots\dots(2.10)$$

Applying appropriate boundary conditions on source, conductor and mesh walls gives a solution of these equations over a finite domain. Equation 2.9 in x direction can be rewritten as follow:

$$\mu \frac{\Delta H_x}{\Delta t} = \frac{\Delta E_y}{\Delta z} - \frac{\Delta E_z}{\Delta y} \dots\dots\dots(2.11)$$

The central difference approximation is then applied on both the time and space first-order partial differentiations to obtain discrete approximations [58]. This gives:

$$\mu \frac{H_{x\ i,j,k}^{n+1/2} - H_{x\ i,j,k}^{n-1/2}}{\Delta t} = \frac{E_{y\ i,j,k}^n - E_{y\ i,j,k-1}^n}{\Delta z} - \frac{E_{z\ i,j,k}^n - E_{z\ i,j-1,k}^n}{\Delta y} \dots\dots\dots(2.12)$$

Rearranging gives:

$$H_{x\ i,j,k}^{n+1/2} = H_{x\ i,j,k}^{n-1/2} + \frac{\Delta t}{\mu \Delta z} [E_{y\ i,j,k}^n - E_{y\ i,j,k-1}^n] - \frac{\Delta t}{\mu \Delta y} [E_{z\ i,j,k}^n - E_{z\ i,j-1,k}^n] \dots\dots(2.13\ a)$$

Similarly, the other E and H fields in the x, y and z directions can be written as follow.

$$H_{y\ i,j,k}^{n+1/2} = H_{y\ i,j,k}^{n-1/2} + \frac{\Delta t}{\mu \Delta x} [E_{z\ i,j,k}^n - E_{z\ i-1,j,k}^n] - \frac{\Delta t}{\mu \Delta z} [E_{x\ i,j,k}^n - E_{x\ i,j,k-1}^n] \dots\dots(2.13\ b)$$

$$H_{z\ i,j,k}^{n+1/2} = H_{z\ i,j,k}^{n-1/2} + \frac{\Delta t}{\mu \Delta y} [E_{x\ i,j,k}^n - E_{x\ i,j-1,k}^n] - \frac{\Delta t}{\mu \Delta x} [E_{y\ i,j,k}^n - E_{y\ i-1,j,k}^n] \dots\dots(2.13\ c)$$

$$E_{x\ i,j,k}^{n+1} = E_{x\ i,j,k}^n + \frac{\Delta t}{\varepsilon \Delta y} [H_{z\ i,j+1,k}^{n+1/2} - H_{z\ i,j,k}^{n+1/2}] - \frac{\Delta t}{\varepsilon \Delta z} [H_{y\ i,j,k+1}^{n+1/2} - H_{y\ i,j,k}^{n+1/2}] \dots\dots(2.13\ d)$$

$$E_{y\ i,j,k}^{n+1} = E_{y\ i,j,k}^n + \frac{\Delta t}{\varepsilon \Delta z} [H_{x\ i,j,k+1}^{n+1/2} - H_{x\ i,j,k}^{n+1/2}] - \frac{\Delta t}{\varepsilon \Delta x} [H_{z\ i+1,j,k}^{n+1/2} - H_{z\ i,j,k}^{n+1/2}] \dots\dots(2.13\ e)$$

$$E_{z\ i,j,k}^{n+1} = E_{z\ i,j,k}^n + \frac{\Delta t}{\varepsilon \Delta x} [H_{y\ i+1,j,k}^{n+1/2} - H_{y\ i,j,k}^{n+1/2}] - \frac{\Delta t}{\varepsilon \Delta y} [H_{x\ i,j+1,k}^{n+1/2} - H_{x\ i,j,k}^{n+1/2}] \dots\dots(2.13\ f)$$

The half time-steps indicate that the E and H are calculated alternately to obtain central differences for the time derivatives. The permittivity (ϵ) and the permeability (μ) values in these equations are set to approximate values depending on the location of each of the field components.

2.4.2 Modelling the optical systems

FDTD solution uses the electromagnetic simulation that accurately predicts the enhanced optical and photocurrent responses in the light absorbing semiconductor in the presence of metal nanostructures (eg. gold or silver nanoparticles) over the spectral range of interest. It gives the field solution for transient problems.

Figure 2.15 (a) Absorption profiles of a semiconductor (silicon) near a silver nanoparticle and bare silicon. (b) Absorption, scattering and extinction cross-sections of a gold nanoparticle of size 50 nm.

Figure 2.15 (a) shows absorption profiles of a semiconductor (silicon) near a silver nanoparticle and bare silicon. The increased absorption stems from the strong near-field enhancement or enhanced scattering cross-section (far-field) via the resonant interactions of the electronic charge density near the metal surface and incident light. The simulation allows identification of these two source mechanisms by calculating absorption, scattering and extinction cross-sections of metal nanoparticles at resonance. Figure 2.15 (b) shows the

absorption and scattering cross sections of Au nanoparticles of diameter 50 nm. The optimization of structural parameters such as sizes, densities and relative orientations of nanoparticles is an important part in designing a practical solar cell with a maximum absorption enhancement. The particle swarm optimization feature in FDTD is the most advanced optimization algorithm to run a large number of simulations simultaneously.

Figure 2.16 Calculated exciton generation profile as a function of CuPc and P3HT:PCBM layer thicknesses in the device (ITO/PEDOT:PSS/CuPc/P3HT:PCBM/Al). Line I: The exciton number variation with P3HT:PCBM layer thickness in absence of CuPc layer. Lines II and III: The exciton number variation with CuPc layer thicknesses at fixed P3HT:PCBM thicknesses of 80 and 208 nm, respectively [60].

For the multilayer organic solar cells, the optical optimization of the layer structure is important due to rather thin layers (1-100 nm) that is shorter than the coherence length of sunlight. As OPV is an optically coherence device, taking into account the optical interference effect, maximizing the light intensity distribution in photoactive layer via tuning the thicknesses of individual layer plays a key role in boosting the realistic device efficiency. For example, the thickness optimization of CuPc and P3HT:PCBM layers in the ITO/PEDOT:PSS/CuPc/P3HT:PCBM/Al device to achieve the maximum light absorption (increased number of exciton in active layer) is shown in *Figure 2.16*. The achieved PCE of 4.13% is due to enhanced light absorption contributed from the second optical interference

peak in this multilayer structure.[60] The theoretical and simulation studies not only provide fundamental understanding on the physics of multilayer organic solar cells but also yield a feasible way to further optimize the device performance.

Chapter 3

Experiment

First part of the chapter covers the preparation of n-type interfacial layers (sol-gel derived titanium suboxide and zinc tin oxide) and self-assembled gold nanowires (Au-NWs). Second part describes the optical, physical and chemical characterizations used in this work followed by the fabrication details of OPV devices and efficiency measurements.

3.1 Preparation of n-type interfacial layers

N-type titanium suboxide (TiO_x) was integrated between photoactive layer and metal cathode to modulate optical and charge transport properties in OPV devices with conventional structure. Zinc tin oxide (ZTO) was used as an electron selective layer in inverted OPV devices which have better device stability than conventional devices.

3.1.1 Sol-gel derived titanium suboxide (TiO_x)

The sol-gel TiO_x was prepared in a three-necked flask equipped with a water condenser and nitrogen gas inlet/outlet as shown in *Figure 3.1*. The flask was pre-heated to remove moisture and allowed the flow of N_2 throughout the synthesis. 20ml of 2-methoxyethanol (Sigma-Aldrich, 99.9 %) was injected into the 3 neck flask, followed by the injection of 5ml of titanium (IV) isopropoxide (Sigma-Aldrich, 99.999%) and 2ml of ethanolamine (Sigma-Aldrich, 99 %). The solution was stirred for 1 hr each at 80°C and 120°C and was cooled down to room temperature. The sol-gel TiO_x (yellow in colour) was formed and 10ml of isopropanol (IPA) was injected to dissolve the gel. The as-prepared TiO_x solution was diluted with ethanol (1:50) prior to the spin-coating of solution on substrates. The TiO_x precursor

solution was spin coated (1000 rpm for 10 s and 3000 rpm for 30 s) on the substrate to form the 10-12 nm thick film. The film thickness was measured by AFM step-height profile (inset of Figure S1) and ellipsometry. Subsequently, the resulting film was kept in air at room temperature for 30 min to convert the precursor to TiO_x by hydrolysis. The transmission (%), AFM topography image, XRD and EDX profiles of TiO_x film are presented in Appendix B (Figure S1-3).

Figure 3.1 Schematic for the synthesis of sol-gel TiO_x .

3.1.2 Zinc tin oxide (ZTO)

The precursor solution for fabrication of ZTO film was prepared by dissolving equal molar ratios of ZnCl_2 and SnCl_2 (0.07M) in acetonitrile solvent. The solution was then ultrasonicated for 10min at room temperature before spin-coating on substrates. The substrates were cleaned with detergent, de-ionized water and ethanol followed by oxygen plasma treatment for 10 min. They were then treated with 1M NaOH solution to make it hydrophilic. The solution was spin-coated on the substrates followed by annealing at 100°C for 1hr and at 500°C for 1 hr to form the ZTO films. The optical, morphological and

structural properties of ZTO film as well as its mobility/conductivity measurement are presented in Sections 4.4.1 and 4.4.2.

3.2 Wet chemistry based synthesis of gold nanowires (Au-NWs)

Figure 3.2 Schematic for the Au-NWs synthesis and the self-assembly of Au-NWs on substrates.

The Au-NWs were synthesized at room temperature by a simple one-step wet-chemistry approach using oleylamine (OA) as a stabilizer, one-dimensional growth template and triisopropylsilane (TIPS) as the reducing agent [61]. Schematic for synthesis of Au-NWs and self-assembly of Au-NWs on substrates is presented in *Figure 3.2*. The 3mg of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was dissolved in 2.5 ml of hexane followed by adding 100 μl of OA and 150 μl of TIPS resulting in the yellow solution. This solution was allowed to react for 9 hrs under slow stirring until it transforms into a dark-red solution. In the next step, the dark-red solution was washed with ethanol by centrifuging at 2500 rpm for 10 min followed by a redispersion in 2.5 ml of hexane. The as-prepared Au-NW solution was further diluted with hexane to a ratio of 1:15 ml/ml. The substrate was then immersed in the solution for 15 min allowing the

2D self-assembly of Au-NWs networks on the substrate. They are rinsed with ethanol and dried with nitrogen blow.

3.3 Optical and photophysical characterizations

Optical characterizations involved in this work are UV-vis absorption, steady-state photoluminescence and time-resolved photoluminescence (TRPL) spectroscopy and variable angle spectroscopic ellipsometry (VASE).

3.3.1 UV-vis absorption (UV-vis)

The absorption spectra of P3HT, PCDTBT and PTB7 films on quartz were recorded in the wavelength range of 200 to 800 nm using Shimadzu UV 3600 spectrophotometer in absorbance mode. The optical band gaps of the polymers were then estimated from the onset at higher wavelength end of each absorption spectrum. (Appendix B, Figure S4) The optical band gaps of polymers together with their HOMO (from CV measurement) were used to calculate LUMO of polymers.

The interfacial materials of TiO_x and ZTO were prepared on quartz and the transmission (T%) of TiO_x and ZTO films were measured using Shimadzu UV 3600 spectrophotometer in the scan range of 200-800 nm in the transmission mode.

The diffuse plus specular reflectance (R) from the OPV devices with and without optical spacer TiO_x were acquired in the spectral region (300 nm-800 nm) using Shimadzu UV 3600 spectrophotometer equipped with a 60 nm integrating sphere with a barium sulphate-coated inside (8° incidence angle). The reflectance (R) and the transmission (T) from this measurement allow calculation of absorption percentage (absorption efficiency) in the device which equals $(1-R-T)\%$. The schematic of the measurement is depicted in *Figure 3.3*. In order

to calibrate the measurement system, the baseline correction was done by positioning the BaSO₄ white plates at both reference and sample positions in the integrating sphere set-up. The reflection from the sample without absorber materials has been measured and the reflection is higher than 95% in the spectral region (300-800 nm).

The transmission through the device is usually zero as the penetration depth of the light in Al is much smaller than the thickness of Al cathode (100 nm) [62]. The transmission through the device has also been experimentally measured using the integrating sphere and is less than 0.05% in the same spectral region. Hence, other loss mechanisms (such as from scattering) that could be interpreted as absorption are negligibly small. The absorption efficiency combined with the external quantum efficiency EQE yields the calculation of internal quantum efficiency IQE of the devices. (Section 4.1.3)

Figure 3.3 Schematic for the measurement of diffuse plus specular reflectance from the OPV devices with and without TiO_x optical spacer.

The surface plasmon absorption band of Au-NWs on quartz was measured by UV-vis absorption spectrophotometer (Perkin-Elmer Lambda 900 UV-Vis-NIR). Measurement details: data interval 1 nm, scan range (300-700 nm), integration time 0.44 s, scan speed 125 nm/min and slit width 1 nm. The SP absorption band of Au-NWs deposited on ITO coated

with PEDOT:PSS was also measured to evaluate the effect of dielectric environment on SP band shift of Au-NWs. In this measurement, the ITO/PEDOT:PSS was used as a reference sample. The P3HT solution in DCB (concentration of 10mg/ml) was spin coated on the Au-NWs coated with PEDOT:PSS layer followed by the deposition of reflective Al jacket to simulate same condition in the OPV devices. Using the reflectance (R) measured from these samples, the absorption (%) in P3HT photoactive layer with and without Au-NWs was evaluated (Section 4.4.2).

3.3.2 Steady-state and time-resolved photoluminescence spectroscopy

Figure 3.4 Schematic for the time-resolved photoluminescence measurement set-up.

The radiative properties of P3HT in the proximity of Au-NWs was investigated by steady-state and time-resolved photoluminescence (TRPL) spectroscopy. *Figure 3.4* depicts the schematic for the TRPL measurement set-up. The samples for photoluminescence studies were prepared by spin-coating the P3HT solution (10mg/ml) on quartz substrate. Using the excitation wavelength 500 nm, the steady-state PL spectra were recorded by Horiba Jobin Yvon FL-1057 spectrofluorometer. For time-resolved PL measurement, the films were excited using 150fs laser pulses at 500 nm wavelength at a 1kHz repetition rate with an average excitation power of 0.004GWcm^{-2} . The luminescence signal was dispersed by a

DK240 1/4 m monochromator with 150 g/mm grating and was time-resolved by an Optronis Streak Camera which has an ultimate temporal resolution of 6 ps. The PL decay profiles of P3HT with and without Au-NWs were fitted by a single exponential function that is described as $I_{PL}(t) = A \exp(-t/\tau)$, where A is the normalized amplitude and τ is the lifetime of first component.

3.3.3 Ellipsometry

The simulation inputs for optical simulation are the refractive index $n(\lambda)$ and extinction coefficient $k(\lambda)$ that are normally measured by ellipsometry. The n , k values of P3HT:PCBM film were taken from the literature[63] while that of PCDTBT:PCBM and PTB7:PCBM films were measured at room temperature by using a variable angle spectroscopic ellipsometry (A. J. Woollam Co. VB-400) in the wavelength range of 300-900 nm with step 10 nm. The data were acquired at three different angles of incidence (65°, 70° and 75°). The ellipsometric ψ and Δ data for multiple wavelengths and angles were simultaneously fitted by the widely used Cauchy dispersion model to obtain the optical constants $n(\lambda)$ and $k(\lambda)$.

3.4 Physical/chemical characterizations

3.4.1 Atomic force microscopy (AFM)

The surface topography images of polymer/fullerene BHJ films (5 μ m $\times$ 5 μ m) from the devices were acquired by atomic force microscopy (AFM) in tapping mode (Asylum Research MFP-3D stand-alone). The root mean square (RMS) analysis over these dimension was carried out using WSxM software (version 5.0) giving the surface roughness of the films. The AFM images of thin TiO_x and ZTO films were also scanned over the area having a step height feature and their thicknesses were measured from the step height profiles.

The 2D self-assembly Au-NWs network on substrate ($2\mu\text{m} \times 2\mu\text{m}$) was visible by using a Pico LE scanning probe microscope (SPM) system in tapping mode. The height and width of Au-NWs were measured by the cross-section line profiles.

3.4.2 Transmission electron microscopy (TEM)

The as-prepared Au-NWs solution was dropped on copper grid and the high-resolution transmission electron microscopy (TEM) images of ultrathin Au-NWs were captured by a TEM (JEOL JEM-2000) operating at 200 kV.

3.4.3 Surface profilometry

The thicknesses of photoactive layers in OPV devices were measured by a surface profiler (Alpha step IQ) using a step height analysis. The scanning details are: scan length $500\mu\text{m}$, scan speed $50\mu\text{m/s}$, sampling rate 50Hz and sensor range $550\mu\text{m}/32.8\text{pm}$. The stylus force was manually adjusted to 3-4 mg for scanning of the soft polymer materials.

3.4.4 X ray diffraction (XRD)

The structural properties of TiO_x and ZTO films deposited on silicon substrates were characterized by X-ray Diffraction (XRD) Bruker D8 Advance. The XRD patterns in the 2θ range of (10° - 80°) were recorded using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature.

3.4.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was employed to determine the relative phase distribution of polymer and PCBM on the surface of BHJ blend films ($\text{P3HT:PC}_{61}\text{BM}$, $\text{PCDTBT:PC}_{71}\text{BM}$ and $\text{PTB7:PC}_{61}\text{BM}$) using an Omicron system attached with a hemispherical analyzer (EAC 2000-125). A monochromatic $\text{Al K}\alpha$ (1486.6 eV) x-ray source

was used for excitation. The samples were prepared on ITO coated with PEDOT:PSS in the same way as in device fabrication without Al cathode. The electrons were collected perpendicularly from the material surface, giving a probe depth of approximately 10 nm [64]. The sulfur $2p$ peak ($\sim 160\text{eV}$) from XPS spectra provides atomic information of polymers (P3HT, PCDTBT, PTB7) on the surface while the carbon $1s$ peak (284.7eV) for both polymers and PCBM. For all samples, the atomic % of S and C were directly calculated from the S and C peak intensities. Then the weight % of polymers and PCBM were evaluated using the corresponding atomic % of S and C.

3.4.6 Cyclic voltammetry (CV)

The E_{HOMO} of three p-type polymers (P3HT, PCDTBT and PTB7) were estimated by Cyclic voltammetry (CV) measurement (Autolab 302N Eco Chemie B.V.) using a three-electrode electrochemical cell with a scan rate of 100 mV/s under nitrogen atmosphere. A platinum (Pt) and gold button electrode were used as the working and counter electrode, respectively. The reference electrode used is a Ag/AgCl electrode with a porous Teflon tip filled with 1.0M KCl solution. The CV of polymer films was conducted in a supporting electrolyte solution of 0.1 M tetra-*n*-butylammonium hexafluorophosphate ($\text{n-Bu}_4\text{N}^+\text{PF}_6^-$) in anhydrous acetonitrile. The oxidation onset potentials (E_{ox}) were determined from the intersection of two tangents drawn at the rising current and base line charging current of CV traces. The oxidation potential of ferrocene was measured after every scan ($E_{\text{FC}} \sim 0.33\text{eV}$) and based on the assumption that Fc/Fc^+ is 4.8 eV below the vacuum level, E_{HOMO} can be readily calculated using the relation $E_{\text{HOMO}} = -[e(E_{\text{ox}} - E_{\text{FC}}) + 4.8]\text{ (eV)}$. The optical band gap E_g from UV-vis absorption together with the E_{HOMO} from CV gives an estimation of E_{LUMO} of the polymers. Calculation details and cyclic voltammograms of polymer films are presented in Appendix B (Figure S5).

3.5 Device fabrication and efficiency measurements

Device fabrication: The OPV devices were fabricated on ITO coated glass substrates ($7 \Omega/\text{square}$). The standard cleaning procedures were applied. The patterned ITO coated glasses were ultrasonicated in a detergent, deionized water, acetone and isopropyl alcohol for 10 min each. They were then dried with nitrogen and treated with oxygen plasma for 2 min prior to a device fabrication.

The TiO_x interlayer integrated devices have the configuration (ITO/PEDOT:PSS /photoactive layer/ TiO_x/Al). The reference devices without interlayers were also fabricated for comparison. The three different electron-donating polymers of the regioregular Poly(3-hexylthiophene) (P3HT) (Rieke Metals), poly[N-9''-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) (1-materials) and Poly[thiophene [3,4-b] thiophene and benzodithiophene] derivative (PTB7) (1-materials) and two different electron-accepting fullerene derivatives (PC_{61}BM and PC_{71}BM) (Nano-C) were used to obtain the three different BHJ solutions. The mixed solutions of P3HT: PCBM (1:0.8) in dichlorobenzene (DCB) with polymer concentration of 10mg/ml, PCDTBT: PCBM (1:4) in DCB (in some devices, chloroform) with concentration of 4mg/ml and PTB7: PCBM (1:1:5) in DCB with concentration of 4 mg/ml were spin-coated each on top of the PEDOT:PSS layer to form the photoactive films.

To study the optical spacer effect, the active layers of different thicknesses were prepared. The P3HT: PC_{61}BM film was annealed at 150°C for 15min, the PCDTBT: PC_{71}BM mild-annealed at 80°C for 10min and the PTB7: PC_{61}BM films kept non-annealed. In the next step, the TiO_x solution (synthesized as mentioned in section 3.1.1) was spin-coated on top of photoactive layer to form a thin interfacial layer (10 nm). Subsequently, the sample was

allowed to leave in air at room temperature for 30 min so that the precursor was converted to TiO_x by hydrolysis. The samples were then transferred to the evaporator in glove box for Al deposition, completing the devices with cell area of 0.071 cm^2 . The photographs of the OPV devices with P3HT:PCBM, PCDTBT:PCBM and PTB7:PCBM photovoltaic blend films are shown in *Figure 3.5*.

Figure 3.5 Photographs of the OPV devices with P3HT:PCBM, PCDTBT:PCBM and PTB7:PCBM photovoltaic blend films.

The inverted OPV cells with ZTO electron transporting layers were fabricated on FTO coated glass substrates. The ZTO films were prepared on the pre-cleaned FTO glasses treated with 1M NaOH solution under the annealing conditions mentioned in Section 3.1.2. The P3HT:PCBM (1:0.8) solution with polymer concentration of 20mg/ml was spin coated on ZTO layer (12-15 nm) to form an active layer of thickness 170 nm annealed at 150°C for 10 min. A hole transporting MoO_3 layer (10 nm) and a hole collecting electrode Ag (100 nm) were then deposited on the active layer by vacuum evaporation. The device with TiO_x electron transporting layer was also fabricated for comparison.

The Au-NWs integrated devices have the configuration (ITO/Au-NWs/PEDOT:PSS/photoactive layer/Al). The reference devices without Au-NWs were also fabricated for comparison. A bulk heterojunction (BHJ) blend of poly (3-hexylthiophene) (P3HT) and acceptor [6, 6]-phenyl-C61-butyric acid methyl ester (PCBM) was used as the photovoltaic

layer. The blend solution of P3HT (Rieke Metals) and PCBM (Nano-C) with weight ratio of (10:8) was prepared in 1,2 dichlorobenzene (DCB) forming a final concentration of 18mg/ml. The PEDOT:PSS (H. C. Starck) was used not only as a hole transporting layer but also as an effective buffer layer between the Au-NWs and active layer to prevent the quenching of excitons in the metal nanostructures [17, 63, 65]. The PEDOT:PSS layer should be as thin as possible and was optimized to ~15 nm sufficient to cover the Au-NWs of diameter 7-9 nm. Prior to the deposition of PEDOT:PSS, a surface treatment with a diluted PEDOT:PSS in an iso-propanol solution (1:20) was employed in order to improve the wettability of aqueous PEDOT:PSS towards the hydrophobic Au-NWs. The deposition of P3HT:PCBM photoactive layers (thickness 60 nm and 80 nm) were performed in a nitrogen glovebox. The devices were completed by deposition of cathode Al (100 nm) by evaporation followed by low temperature annealing at 60°C for 2.5 hours. High temperature annealing was avoided in order to keep the fabrication process compatible to plastic substrates. The effective cell area defined by the geometrical overlap between ITO and Al was 0.071 cm².

Efficiency measurements: The performance of photovoltaic cells is usually evaluated by two common efficiency measurements. Power conversion efficiency (PCE) is calculated from the photocurrent against the bias voltage (J-V characteristics) under white light while the incident photon to current efficiency (IPCE) is calculated from the spectral dependent photocurrent under zero bias voltage.

(i) Power conversion efficiency (PCE): The J-V curves of the devices were measured with a HP 4155 semiconductor analyzer by illuminating the cells with a light intensity of 100mW/cm² from a solar simulator (San-Ei XES-300, AAA rating) with an AM 1.5 filter in

nitrogen glove box. The light intensity of $100\text{mW}/\text{cm}^2$ was calibrated using a solarimeter with a reference silicon solar cell certified by National Renewable Energy Lab (NREL).

(ii) Incident photon to current efficiency (IPCE): IPCE spectra were recorded using 150 W Newport-Oriel Xenon light source, Cornerstone 260 1/4M monochromator, optical chopper set at 60 Hz and Merlin radiometry system. The light power-density was calibrated with Hamamatsu silicon photodiode.

Chapter 4

Results and Discussion

This chapter covers four sections. First section describes the effect of titanium suboxide (TiO_x) interlayer on the modulation of optical properties in OPV devices followed by the decoupling of optical and electrical effects of TiO_x on J_{sc} . Second section details the electrical effect of TiO_x in terms of charge transport and recombination across the cathode interface and the evaluation of V_{oc} in OPV devices. Third section describes the zinc-tin oxide (ZTO) as an electron transport layer in inverted OPV cells and the comparison of device performances (ZTO versus TiO_x). Fourth section presents the application of gold nanowires (Au-NWs) as plasmonic antennae in OPV and highlights the impact of Au-NWs on optical and photophysical properties in the device.

4.1 Decoupling optical and electrical effects of TiO_x interfacial layer on photocurrent density in organic solar cells

It has been demonstrated that the n-type titanium suboxide (TiO_x) layer integrated at the cathode interface increased the short circuit current density (J_{sc}) and fill factor (FF) in P3HT:PC₆₁BM and PCDTBT:PC₇₁BM devices [14, 26, 66]. *Figure 4.1* shows schematic of an OPV device with n-type TiO_x interfacial layer at the cathode interface. In these devices, the TiO_x interlayer serves as an electron transport layer (ETL) as well as an optical spacer. The better energy alignment at cathode interface promotes an efficient charge transport while the optical spacer allows an optimum light distribution in the photoactive layer. Thus, the general understanding in the literature attributes the increased J_{sc} induced by TiO_x interfacial layer as

collective contributions from both optical and electrical effects. In this section, we decoupled the optical and electrical effects of TiO_x interfacial layer on the J_{sc} in P3HT:PC₆₁BM, PCDTBT:PC₆₁BM and PTB7:PC₆₁BM devices by optical absorption and internal quantum efficiency (IQE) measurements.

Figure 4.1 Schematic of an OPV device integrated with n-type TiO_x as an electron transport layer as well as an optical spacer. The BHJ blends of P3HT:PC₆₁BM, PCDTBT:PC₆₁BM and PTB7:PC₆₁BM were used as photoactive layers.

4.1.1 Optical simulation in organic solar cells using FDTD method

Inefficient light absorption in photoactive layer is one of the major issues to achieve high device performance. The inclusion of optical spacer in the OPV devices enhances the optical absorption in photoactive layer by redistribution of light intensity inside the device. However, optical spacer effect could not provide an increased light absorption in all cases. It remarkably varies when the materials (optical constants) and thicknesses of constituent layers in the device are altered [66]. Thus, optical simulation using FDTD method was carried out as a first-hand optimization tool to investigate the role of optical spacer TiO_x in organic solar cells using different photoactive materials (P3HT:PC₆₁BM, PCDTBT:PC₆₁BM and PTB7:PC₆₁BM) with different thicknesses. The FDTD simulation structure for our devices is

shown in *Figure 4.2*. In this structure, two power monitors were mounted at the boundaries of photoactive layer to measure the power of the incoming light, thus allowing the calculation of theoretical light absorption in the photoactive layer.

Figure 4.2 FDTD simulation structure for optical modeling in OPV devices with and without TiO_x optical spacer.

The device configuration used is glass/ITO(200nm)/PEDOT:PSS(30nm)/active layer/TiO_x (10nm)/Al(100nm). Since the actual thickness of glass is 0.7mm, much larger than the wavelength of light, there is no interference effect from the glass [62]. In order to reduce the simulation time, glass thickness of 1μm was used and the interference effect in this thickness is negligible. The optical parameters, the refractive index (*n*) and absorption coefficient (*k*), of each layer in the device were used as the simulation inputs. The *n*, *k* values of glass, ITO, PEDOT:PSS, P3HT:PCBM, TiO_x and Al were taken from the literature [66] while that of PCDTBT:PCBM and PTB7:PCBM polymer blends were measured by ellipsometry and are shown in *Figure 4.3*.

Prior to running simulation, the model fitting (Experimental material dispersion vs. Multi-coefficient model MCM) was performed over the range of solar spectrum (400-900 nm). The fitting parameters mainly include (i) the tolerance which is the desired RMS error between the permittivity of the experimental data and the material fit, (ii) maximum coefficient with which a more accurate fit can be achieved, but making the simulation slower, (iii) wavelength range of the light source and (iv) imaginary weight, increasing which increases the importance of the imaginary part of the permittivity while fitting (A weight of 1 gives equal weight to the imaginary and real parts of the permittivity.) They were adjusted until a good fit is obtained (Appendix B, *Figure S7*). The details of fitting parameters are presented as follows: the tolerance (0.01), max coefficient (15), imaginary weight (1) and RMS error for the fit (0.021, 0.015 and 0.013 for the P3HT:PCBM, PCDTBT:PCBM and PTB7:PCBM blends respectively).

Figure 4.3 Refractive index (n) and absorption coefficient (k) spectra of PCDTBT:PCBM and PTB7:PCBM blends.

The FDTD method is applied to calculate the power dissipation per unit area $Q(x)$ at a particular thickness (x) in the device and at a particular wavelength (λ) .

$$Q(x) = \frac{2\pi c \epsilon_0 k n |E(x)|^2}{\lambda} \dots\dots\dots (4.1)$$

where c is the speed of light, ϵ_0 the permittivity of vacuum, λ the wavelength, n the refractive index, k the absorption coefficient and $E(x)$ the optical electric field at a particular thickness (x) . The active layer absorption $A(\lambda)$ is determined by integrating over the active layer thickness (x) .

$$A(\lambda) = \frac{\int_x Q(x) dx}{I(\lambda)} \dots\dots\dots (4.2)$$

where $I(\lambda)$ is the intensity of incident light. Then, the total number of absorbed photons N_{ph} is determined by convoluting the absorption $A(\lambda)$ and the irradiance of AM 1.5 solar spectrum over the selected spectral range.

$$N_{ph} = \int \frac{\lambda}{hc} A(\lambda). I_{AM1.5}(\lambda) d\lambda \dots\dots\dots (4.3)$$

Assuming that all absorbed photons are converted into charge carriers (100% internal quantum efficiency) and there are no multielectron generation from high energy photons, the upper limit for short circuit current density (J_{sc}) is described as

$$J_{sc} = e \int \frac{\lambda}{hc} A(\lambda). I_{AM1.5}(\lambda) d\lambda \dots\dots\dots (4.4)$$

where e is the electronic charge and h is the Planck constant.

Figure 4.4 Plots of the upper limit short current density (J_{sc}) against the active layer thicknesses in P3HT:PC₆₁BM, PCDTBT:PC₆₁BM and PTB7:PC₆₁BM devices.

Based on these theoretical basis, the FDTD calculation was carried out to determine the N_{ph} and upper limit J_{sc} in three different BHJ reference devices (P3HT:PC₆₁BM, PCDTBT:PC₆₁BM and PTB7:PC₆₁BM) with different active layer thicknesses (50-250 nm). The N_{ph} and J_{sc} values in these devices as a function of active layer thickness are shown in *Figure 4.4*. This simulation results suggest that the optimal active layer thickness for maximum absorption (corresponds to first optical interference peak) in P3HT:PC₆₁BM, PCDTBT:PC₆₁BM, PTB7:PC₆₁BM devices (without TiO_x) was 90, 80 and 120 nm respectively and the respective upper-limit J_{sc} are 11.15, 11.90 and 12.73 mA/cm². In the two former devices, the number of absorbed photons N_{ph} decreased at the thicknesses beyond the optimal thickness while in the latter one, the N_{ph} saturated at the optimum level till thickness $\sim$ 160 nm.

Following this, the optical spacer TiO_x was incorporated in the non-optimum devices (active layer is thinner than optimum thickness) and the spacer induced optical properties in the

photoactive layer were studied. Since the absorption in the photoactive layer (exciton generation in the device) is proportional to $|E|^2$, the optical spacer induced $|E|^2$ redistribution across all layers in the device was monitored. *Figure 4.5* reveals the calculated $|E|^2$ distribution profiles at 550 nm light illumination for P3HT:PC₆₁BM devices (active layer thicknesses of 60 nm, 70 nm and 80 nm) with and without TiO_x optical spacer. For 60 nm thick active layer, the $|E|^2$ maximum was situated out of the photoactive layer due to the presence of dead zone in an immediate vicinity of Al reflective cathode. The inclusion of TiO_x optical spacer (10 nm) shifted the $|E|^2$ peak into the active layer, thereby increased exciton generation inside the TiO_x integrated device. The optical spacer effect is significantly less in the 80 nm thick devices where the $|E|^2$ distribution is already maximized inside the photoactive layer. A similar effects of TiO_x optical spacer were observed in the PCDTBT:PC₆₁BM and PTB7: PC₆₁BM devices and their $|E|^2$ distribution profiles are shown in Appendix B (*Figure S10-11*).

It is more rational to study the optical spacer effect on the absorption distribution $A(\lambda)$ in photoactive layers throughout all visible wavelengths other than at a specific wavelength since the device is usually illuminated by AM1.5 white light. Using FDTD optical simulation, the modulation of absorption properties induced by optical spacer was recorded over the spectral region (400-700 nm) for the P3HT:PC₆₁BM and PCDTBT:PC₆₁BM devices with active layer thicknesses of 60 nm, 70 nm and 80 nm. As the absorption of low band gap polymer PTB7 extends beyond 700 nm, $A(\lambda)$ was measured over the spectral region (400-800 nm) in PTB7:PC₆₁BM devices with active layer thicknesses of 80 nm, 100 nm and 120 nm. The calculated absorption spectra of all devices with and without TiO_x spacer are shown in *Figure 4.6*.

Figure 4.5 Calculated optical electric field energy $|E|^2$ distribution profiles at 550 nm incident light in the P3HT:PC₆₁BM devices with active layer thicknesses of 60 nm, 70 nm and 80 nm. The black and red curves represent $|E|^2$ in reference devices and TiO_x integrated devices respectively.

In all 60 nm-thick devices, the absorption $A(\lambda)$ was significantly increased over the wavelengths upon inserting the TiO_x spacer (*Figure 4.6*). The reason is the same as what we observed in the $|E|^2$ profiles indicating that the presence of dead zone in the 60 nm-thick active layers was effectively reduced by inclusion of optical spacer. Increasing active layer thicknesses, the optical spacer shows less improvement in the light absorption and no improvements were observed in the 80 nm-thick P3HT:PC₆₁BM, the 70 nm-thick PCDTBT:PC₆₁BM and the 100 nm-thick PTB7:PC₆₁BM devices. Obviously, the optical spacer only facilitates absorption enhancements in the non-optimum active layer thicknesses and no optical benefit was achieved by optical spacer once the photoactive layer thickness has been optimized.

Having studied the optical modulation in photoactive layer with different thicknesses induced by a 10 nm-thick TiO_x optical spacer, the optical modulation against the spacer thickness (varied from 10 nm to 50 nm) for a specific active layer thickness was also studied by FDTD calculation. The calculated maximum J_{sc} against the TiO_x layer thickness in the P3HT:PC₆₁BM, PCDTBT:PC₆₁BM and PTB7:PC₆₁BM devices are shown in *Figure 4.7*. The J_{sc} values of reference devices (without TiO_x layer) are also included in the plots for comparison. The thicker TiO_x spacer gives a more enhanced optical absorption at some active layer thicknesses as seen in *Figure 4.7*. Despite better optical advantages with thicker spacers, there are some electrical restrictions such as a higher series resistance with thicker layers. Hence, only the 10 nm-thick TiO_x optical spacer was used in the experiments (Section 4.1.2).

Figure 4.6 Calculated total absorption in photoactive layer of the P3HT:PC₆₁BM, PCDTBT: PC₆₁BM and PTB7: PC₆₁BM devices with and without TiO_x interfacial layer using FDTD optical simulation.

Figure 4.7 Calculated maximum current density (J_{sc}) as a function of optical spacer TiO_x thickness in P3HT:PC₆₁BM, PCDTBT:PC₆₁BM and PTB7:PC₆₁BM devices with different active layer thicknesses. The J_{sc} of the devices without optical spacer is also included for comparison.

4.1.2 Effect of TiO_x interfacial layer on OPV device performance

The current-voltage (J-V) characteristics of P3HT:PC₆₁BM, PCDTBT:PC₆₁BM and PTB7:PC₆₁BM devices with and without TiO_x spacer were measured under simulated AM1.5 solar light illumination. The effect of TiO_x interfacial layer on the power conversion efficiencies (PCE) of the devices was observed in general. Highlighted in this section is an evaluation of changes in short-circuit current density (J_{sc}) as the optical and electrical effects of TiO_x interlayer. Since TiO_x layer as an optical spacer would not affect V_{oc} and FF, the pure electrical effect (charge transport and recombination) of TiO_x interlayer on V_{oc} and FF will be discussed in the next section 4.2.

P3HT:PC₆₁BM devices

The J-V characteristics under illumination of the P3HT:PC₆₁BM devices (60-80 nm) with and without TiO_x interlayer are depicted in *Figure 4.8* and the device parameters (PCE, V_{oc} , J_{sc} and FF) are listed in *Table 4.1*. Upon integrating TiO_x interlayer (10 nm) in P3HT:PC₆₁BM devices, the efficiency increased from 2.65% to 3.56% in the 60 nm-thick devices, from 2.98% to 3.63% in the 70 nm-thick devices and from 3.69% to 4.14% in the 80 nm-thick devices. The V_{oc} almost unchanged and the FF increased upon TiO_x incorporation. In the TiO_x integrated devices, the J_{sc} increased by 19.88%, 11.54% and 2.53% in the active layer thickness of 60 nm, 70 nm and 80 nm respectively. Obviously, the J_{sc} enhancement is more pronounced in the thinner devices (60 nm).

PCDTBT:PC₆₁BM devices

The J-V characteristics under illumination of the PCDTBT:PC₆₁BM devices (60-80 nm) with and without TiO_x interlayer (10 nm) are depicted in *Figure 4.9* and the device parameters (PCE, V_{oc} , J_{sc} and FF) are listed in *Table 4.2*. Upon integrating a 10 nm TiO_x interlayer, the

efficiency increased from 2.78% to 3.44% in the 60 nm-thick devices, from 2.97% to 3.48% in the 70 nm-thick devices and from 2.93% to 3.65% in the 80 nm-thick devices. Although V_{oc} in P3HT:PC₆₁BM devices remained unchanged, the V_{oc} of the TiO_x integrated PCDTBT:P C₆₁BM devices increased from 0.83-0.85V to 0.92V that will be discussed in Section 4.2. As observed in Table 4.2, the introduction of TiO_x layer also increased J_{sc} and FF of the devices. Upon integrating TiO_x layer, the J_{sc} of PCDTBT:PC₆₁BM devices increased by 8.06%, 0.41% and -1.02% in the active layer thicknesses of 60 nm, 70 nm and 80 nm respectively. Likewise in P3HT:PC₆₁BM devices, the TiO_x induced J_{sc} enhancement was more pronounced in the thinner PCDTBT:PC₆₁BM devices (60 nm). However, as compared to J_{sc} enhancement (19.88%) in the P3HT:PC₆₁BM devices, the lesser J_{sc} enhancement (8.06%) is due to lesser absorption enhancement in PCDTBT:PC₆₁BM devices of same thickness 60 nm. The J_{sc} enhancement in the 70 nm-thick PCDTBT:PC₆₁BM device was even lesser (0.41%) and was degraded in 80 nm-thick devices. The trend of increasing J_{sc} (experimental) upon increasing thickness is qualitatively consistent with that of increasing J_{sc} obtained by FDTD simulation data in Figure 4.7. The calculated J_{sc} is usually higher than the experimental J_{sc} (from the device) because FDTD is only optical simulation technique and the electrical restrictions in the device were not taken in account.

PTB7:PC₆₁BM devices

The current-voltage characteristics under illumination of the PTB7:PC₆₁BM devices (80-120 nm) with and without TiO_x interlayer (10 nm) are depicted in Figure 4.10 and the device parameters (PCE, V_{oc} , J_{sc} and FF) are listed in Table 4.3. Upon integrating a 10 nm TiO_x interlayer, the efficiency was increased from 4.19% to 4.83% in the 80 nm-thick devices while it was decreased from 5.58% to 4.77% in the 100 nm-thick devices and from 5.96% to 3.20% in the 120 nm-thick devices. The V_{oc} remained almost unchanged at 0.75-0.77V in all

Figure 4.8 Current-voltage (J-V) characteristics of the P3HT:PC₆₁BM devices with and without TiO_x interfacial layer under illumination of 100mW/cm². The active layer thicknesses are 60 nm, 70 nm and 80 nm.

Table 4.1 Device parameters of P3HT:PC₆₁BM devices with and without TiO_x interfacial layer.

P3HT:PC ₆₁ BM	PCE (%)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	J _{sc} enhancement
Reference (60 nm)	2.65	-6.84	0.64	0.60	19.88%
With TiO _x (60 nm)	3.56	-8.20	0.65	0.67	
Reference (70 nm)	2.98	-8.4	0.63	0.56	11.54%
With TiO _x (70 nm)	3.63	-9.37	0.64	0.61	
Reference (80 nm)	3.69	-9.46	0.61	0.64	2.53%
With TiO _x (80 nm)	4.14	-9.70	0.63	0.68	

Figure 4.9 Current-voltage characteristics of the PCDTBT:PC₆₁BM devices with and without TiO_x interfacial layer under illumination of 100mW/cm². The active layer thicknesses are 60nm, 70nm and 80nm.

Table 4.2 Device parameters of P3HT:PC₆₁BM devices with and without TiO_x interfacial layer.

PCDTBT:PC ₆₁ BM	PCE (%)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	J _{sc} enhancement
Reference (60 nm)	2.78	-6.57	0.85	0.50	8.06%
With TiOx (60 nm)	3.44	-7.10	0.92	0.53	
Reference (70 nm)	2.97	-7.31	0.83	0.49	0.41%
With TiOx (70 nm)	3.48	-7.34	0.92	0.52	
Reference (80 nm)	2.93	-7.87	0.83	0.45	-1.02%
With TiOx (80 nm)	3.65	-7.79	0.92	0.51	

Figure 4.10 Current-voltage characteristics of the PTB7:PC₆₁BM devices with and without TiO_x interfacial layer under illumination of 100mW/cm². The active layer thicknesses are 80 nm, 100 nm and 120 nm.

Table 4.3 Device parameters of PTB7:PC₆₁BM devices with and without TiO_x interfacial layer.

PCDTBT:PCBM	PCE (%)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	J _{sc} enhancement
Reference (80 nm)	4.19	-9.64	0.75	0.58	12.13%
With TiO _x (80 nm)	4.83	-10.81	0.77	0.58	
Reference (100 nm)	5.58	-12.68	0.76	0.58	-6.07%
With TiO _x (100 nm)	4.77	-11.91	0.77	0.52	
Reference (120 nm)	5.96	-12.89	0.77	0.60	-7.99%
With TiO _x (120 nm)	3.20	-11.86	0.77	0.35	

devices. With TiO_x layer, a small decrease in efficiencies of 100 nm-thick devices is due to the slightly decreased J_{sc} and FF. For 120 nm-thick devices, the slight decrease in J_{sc} and huge decrease in FF result in the dramatically lower efficiency of the device with TiO_x layer.

In all devices, the TiO_x interlayer induced J_{sc} modulations are attributed to the combination of optical spacer and charge transport effects. These combined effect (optical plus electrical) of TiO_x interlayer on the photocurrent ($\Delta J_{sc}\%$) will be decoupled in the immediate section 4.1.3. Decoupling of optical and electrical effects will be useful for further device optimization and designs.

4.1.3 Decoupling the optical and electrical effects of TiO_x interlayer on J_{sc}

As mentioned earlier, the photocurrent enhancement by the TiO_x interfacial layer in these devices was attributed to the combination of (i) an enhanced absorption by maximizing light intensity within the photoactive layer (optical spacer effect) and (ii) a better electron transport due to a matched energy alignment at cathode interfaces. In order to decouple the combined optical and electrical effects, we determined the weight contributions against optical and charge transport effects of TiO_x interlayer to the photocurrent in the devices. First, the total absorption (1-reflectance) % from the devices with and without TiO_x layer were measured using integrating sphere in order to investigate the role of optical spacer (TiO_x) in the devices. Second, the internal quantum efficiency (IQE) of the devices were determined from total absorption (1-reflectance) % and external quantum efficiency (EQE) of the devices [$\text{IQE} = \text{EQE} / (1-R-T)$ where, R is the reflectance and T the transmittance] in order to evaluate how TiO_x interlayer improves charge transport and collection at cathode interface.

Figure 4.11 (a) Total absorption spectra, (b) external quantum efficiency (EQE) spectra and (c) internal quantum efficiency (IQE) spectra of the P3HT:PC₆₁BM device (60 nm) with and without TiO_x. From this plots, the percentage changes in absorption ($\Delta A\%$) and internal quantum efficiency ($\Delta IQE\%$) upon TiO_x integration are evaluated and listed in Table 4.4. $\Delta A\%$ is solely due to the optical spacer effect while $\Delta IQE\%$ solely due to the better charge transport/collection at the active layer/TiO_x/cathode interface.

Figure 4.11(a) shows the spectral dependent total absorption $A(\lambda)$ from the P3HT:PC₆₁BM device (60 nm) with and without TiO_x layer (10 nm). The absorption from the devices was calculated from $(A = 1-R-T)$ where the reflectance R from the device was measured using the integrating sphere and the transmittance T through Al is usually zero. The TiO_x induced absorption enhancement ($\Delta A\%$) calculated over spectral range (400-700 nm) was 9.16% that is solely ascribed to the optical spacer effect. Next, the EQE of P3HT:PC₆₁BM devices (60 nm) with and without TiO_x layer (10 nm) were also measured (Figure 4.11(b)). Using $A(\lambda)$ and $EQE(\lambda)$, the $IQE(\lambda)$ of the devices with and without TiO_x layer were calculated and shown in Figure 4.11(c). IQE represents the combined efficiencies of exciton dissociation, charge transport and collection.

Since TiO_x interlayer does not affect the exciton dissociation efficiency in the bulk material, the difference in IQE (ΔIQE of 7.94%) is solely attributed to the charge transport/collection at the cathode interface induced by TiO_x layer. For P3HT:PC₆₁BM devices (60 nm), the convolution of $\Delta A = 9.16\%$ and $\Delta IQE = 7.94\%$ gives an overall J_{sc} enhancement ($\Delta J_{sc} = 19.88\%$). With the same manner, $\Delta A(\%)$ and $\Delta IQE(\%)$ for all other devices were calculated and tabulated in Table 4.4. Figures 4.12-4.14 show the (1-R), EQE and IQE spectra of P3HT:PC₆₁BM (70 nm and 80 nm), PCDTBT:PC₆₁BM (60 nm, 70 nm and 80 nm) and PTB7:PC₆₁BM (80 nm, 100 nm and 120 nm) devices with and without TiO_x layer.

Figure 4.12 Total absorption spectra (red), external quantum efficiency (EQE) spectra (blue) and internal quantum efficiency (IQE) spectra (green) of the P3HT:PC₆₁BM device [(a) 70 nm and (b) 80 nm] with and without TiO_x. From this plots, the percentage changes in absorption ($\Delta A\%$) and internal quantum efficiency ($\Delta IQE\%$) upon TiO_x integration are evaluated and listed in Table 4.4.

Figure 4.13 Total absorption spectra (red), external quantum efficiency (EQE) spectra (blue) and internal quantum efficiency (IQE) spectra (green) of the PCDTBT:PC₆₁BM device [(a) 60 nm, (b) 70 nm and (c) 80 nm] with and without TiO_x. From these plots, the percentage changes in absorption ($\Delta A\%$) and internal quantum efficiency ($\Delta IQE\%$) upon TiO_x integration are evaluated and listed in Table 4.4.

Figure 4.14 Total absorption spectra (red), external quantum efficiency (EQE) spectra (blue) and internal quantum efficiency (IQE) spectra (green) of the PTB7:PC₆₁BM device [(a) 80 nm, (b) 100 nm and (c) 120 nm] with and without TiO_x. From this plots, the percentage changes in absorption ($\Delta A\%$) and internal quantum efficiency ($\Delta IQE\%$) upon TiO_x integration are evaluated and listed in Table 4.4.

Table 4.4 The changes in absorption ($\Delta A\%$), internal quantum efficiency ($\Delta IQE\%$) and short-circuit current density ($\Delta J_{sc}\%$) upon TiO_x integration in P3HT:PC₆₁BM, PCDTBT:PC₆₁BM and PTB7:PC₆₁BM devices.

	Thickness (nm)	ΔA (%)	ΔIQE (%)	$\Delta A + \Delta IQE$ (%)	ΔJ_{sc} (%)
P3HT:PC ₆₁ BM	60	9.16	7.94	17.10	19.88
	70	5.93	6.19	12.12	11.54
	80	0.62	1.41	2.03	2.53
PCDTBT:PC ₇₁ BM	60	3.86	5.98	9.84	8.06
	70	-0.21	0.52	0.31	0.41
	80	-3.51	0.45	-3.06	-1.02
PTB7:PC ₆₁ BM	80	4.36	8.25	12.61	12.13
	100	-0.38	-5.61	-5.99	-6.07
	120	-3.80	-3.83	-7.63	-7.99

Table 4.4 summarizes the effects of optical spacer ($\Delta A\%$) and charge transport/collection ($\Delta IQE\%$) induced by TiO_x interlayer for all devices that have been correlated to the photocurrent enhancement ($\Delta J_{sc}\%$). Obviously, the $\Delta A\%$ decreased with increasing active layer thicknesses for all the devices. For the active layer thickness of 80 nm for P3HT:PCBM, 70 nm for PCDTBT:PCBM and 100 nm for PTB7:PCBM devices, the $\Delta A\%$ were almost invariant indicating that optical spacer effect was insignificant at the respective critical thickness for each system as predicted by FDTD optical simulation. Similarly, the $\Delta IQE\%$ also decreased with increasing active layer thickness and this electrical effect of TiO_x will be discussed in detail in next section 4.2. Since $\Delta A\%$ and $\Delta IQE\%$ were related to $\Delta J_{sc}\%$ in a convoluted manner, they cannot be simply added up to yield $\Delta J_{sc}\%$. In short, the

convolution of $\Delta A\%$ and $\Delta IQE\%$ gives an overall J_{sc} enhancement ($\Delta J_{sc}\%$) in all devices with different heterojunctions.

4.1.4 Summary

The optimum active layer thicknesses corresponding to the first optical interference peaks in the P3HT:PC₆₁BM, PCDTBT:PC₆₁BM and PTB7:PC₆₁BM devices were determined using FDTD optical simulation. The TiO_x interfacial layer was integrated to the devices with non-optimum active layer thicknesses and the optical spacer induced absorption enhancement was more pronounced at active layer thickness of 60 nm in three different BHJ systems. The optical advantage was not achieved from optical spacer once the active layer thickness was already optimized. The absorption in the devices were measured from the optical reflectance (1-R)% using the integrating sphere attached to UV-vis spectrophotometer. The experimentally measured absorption profiles were consistent with the calculated ones using FDTD simulation. Generally, the shape and intensity of the experimental and calculated absorption spectra are almost the same in the spectral region where the blend materials absorb. The TiO_x interlayer induced absorption enhancement ($\Delta A\%$) is solely attributed to the optical spacer effect.

Power conversion efficiencies (PCE) and external quantum efficiencies (EQE) spectra were recorded from the devices with and without TiO_x interfacial layer. In addition, their corresponding internal quantum efficiencies (IQE) spectra were also obtained by convoluting the absorption and EQE spectra. The TiO_x interlayer induced IQE enhancement is solely attributed to charge transport effect at cathode interface. As a consequence, the $\Delta A\%$ and $\Delta IQE\%$ collectively contribute to the $\Delta J_{sc}\%$ in the devices. The optical and electrical contributions of interlayer vary between different heterojunction

materials. Judging these weight contributions in each system, the optimizations can be implemented separately to improve the optical and electrical effects of interlayer, leading to an improved overall efficiency of the device. The optical spacer induced absorption in the device can be improved by optimizing not only the thicknesses but also the materials of optical spacer and BHJ layer. On the other hand, to improve the electrical characteristics at modified electrode interface, some attempts include the energy level matching of interlayer with its adjacent layers, increased conductivity (mobility) of interlayer and wettability of interlayer towards active layer. Thus, it is highlighted that the decoupling of optical and electrical effects of TiO_x interlayer on J_{sc} in OPV devices would support the further optimization of the devices. In addition, the decoupling method can be applicable to other interfacial layers and BHJ systems.

4.2 Electrical effects of TiO_x interfacial layer: Evaluation of open circuit voltage (V_{oc})

In section 4.1, the optical and electrical effects of TiO_x interlayer on the current density (J_{sc}) in OPV cells have been addressed. The electrical effect of interfacial layer influences not only the current density (J_{sc}) but also the open circuit voltage (V_{oc}) of the devices. This sub-chapter aims to understand the effect of TiO_x interlayer on the open circuit voltage (V_{oc}) which is important in optimizing and enhancing the device performance. In particular, the effects of TiO_x interlayer on charge transport and recombination kinetics at the cathode interfaces as well as the donor/acceptor phase-segregation on the surface of BHJ films were investigated.

4.2.1 High performance organic solar cells with TiO_x interfacial layer

N-type TiO_x interfacial layer was integrated between active layer and cathode in organic solar cells comprising three different polymer-fullerene BHJ blends (P3HT:PC₆₁BM, PCDTBT:PC₇₁BM and PTB7:PC₆₁BM). Upon cathode modification by TiO_x (10 nm), the device efficiency was improved from 2.65% to 3.55% in P3HT:PC₆₁BM devices and from 4.85% to 5.91% in PCDTBT:PC₇₁BM devices while it was decreased from 5.58% to 4.77% in PTB7:PC₆₁BM devices (Table 4.5). The J-V characteristics under illumination of these devices with and without TiO_x are presented in *Figure 4.15* (a). The device parameters were averaged over ten cells and the maximum error was calculated as $(\Delta x_{\text{max}} = (x_{\text{max}} - x_{\text{min}})/2)$. The device parameters together with maximum errors for all devices are listed in *Table 4.5*. The energy level diagrams of the constituent materials used in the photovoltaic devices are shown in *Figure 4.15* (b). In this study, the modulation of V_{oc} upon integrating TiO_x layer in these devices is highlighted.

It is well recognized that the maximum attainable V_{oc} in organic solar cells is governed by the effective band gap of donor-acceptor polaron pair state after exciton dissociation which corresponds to the difference between the highest occupied molecular orbital (HOMO) of the electron donor and the lowest unoccupied molecular orbital (LUMO) of the electron acceptor. The relation is expressed as:

$$V_{oc}(\text{max}) = \frac{1}{e} (HOMO_{\text{donor}} - LUMO_{\text{acceptor}}) \dots\dots\dots(4.5.a)$$

While the maximum attainable V_{oc} estimated from the HOMO-LUMO offsets are 1.21V, 1.50V and 1.45V respectively for the P3HT:PC₆₁BM, PCDTBT:PC₇₁BM and PTB7:PC₆₁BM devices, the V_{oc} obtained from experiments are 0.64V, 0.88V and 0.76V respectively.

Figure 4.15 (a) Linear J-V characteristics of P3HT: PC₆₁BM, PCDTBT: PC₇₁BM and PTB7: PC₆₁BM devices with and without TiO_x interlayer under illumination of light intensity 100 mW/cm². (b) Energy level diagram of constituent materials in the device in which the value described on top and in bottom of the blocks are LUMO and HOMO of the corresponding materials respectively. The HOMO and LUMO of polymers (P3HT, PCDTBT and PTB7) were determined by cyclic voltammetry and UV-vis absorption. (Appendix B, Figure S4-5)

Scharber et al. [67-68] demonstrated that using -4.3 eV for LUMO of the fullerene PCBM, the V_{oc} of the polymer-fullerene BHJ solar cells can be estimated by

$$V_{oc} = \frac{1}{e}(HOMO_{donor} - LUMO_{acceptor}) - 0.3 V .....(4.5.b)$$

The value of 0.3 V in Equation 4.5.b is an empirical factor. In our case, the offset value is higher than 0.3 eV because we used -3.92 eV for LUMO of PCBM obtained from our cyclic voltammetry measurement. In the literature, it varies between -3.7 eV and -4.3 eV [69-72]. If we used the LUMO of PCBM as -4.3 eV, our offset value was consistent with Scharber’s estimation (0.3 eV). In short, the actual V_{oc} of the polymer-fullerene solar cells are lower than their theoretical limits (maximum attainable V_{oc}).

Table 4.5 Device parameters for P3HT:PC₆₁BM, PCDTBT:PC₇₁BM and PTB7:PC₆₁BM devices with and without TiO_x interlayer. The device parameters were averaged over ten cells and the maximum error was calculated as ($\Delta x_{max} = (x_{max} - x_{min})/2$). In PCDTBT:PC₇₁BM device, the V_{oc} increased by 4.54% upon TiO_x integration.

		PCE (%)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	V _{oc} enhancement
P3HT:PC ₆₁ BM	Reference	2.65±0.12	-6.84±0.23	0.64±0.01	0.60±0.01	-
	(60 nm) With TiO _x	3.55±0.12	-8.36±0.17	0.65±0.01	0.66±0.01	
PCDTBT:PC ₇₁ BM	Reference	4.85±0.10	-9.29±0.18	0.88±0.00	0.59±0.01	4.54%
	(60 nm) With TiO _x	5.91±0.13	-10.14±0.20	0.92±0.01	0.64±0.01	
PTB7:PC ₆₁ BM	Reference	5.58±0.11	-12.68±0.29	0.76±0.00	0.58±0.01	-
	(100 nm) With TiO _x	4.77±0.16	-11.91±0.35	0.77±0.00	0.52±0.02	

One of the major losses affecting the experimental V_{oc} is the interfacial losses at electrode interfaces. Typically, the standard hole transporting interlayer (PEDOT:PSS) is inserted at ITO (anode) interface to improve hole transport and block electrons, thereby eliminating the interfacial losses at anode interface. However, in typical OPV device configuration, there is no electron transport layer at cathode interface that leads to the possibility of interfacial loss at cathode interface. Here, the TiO_x interlayer was integrated at the cathode interface of OPV devices to study whether the interlayer is able to compensate the losses at the cathode interface of the devices. Upon inserting TiO_x interfacial layer, the V_{oc} increases from 0.88V to 0.92V in the PCDTBT: PC₇₁BM devices while it is almost the same at 0.64-0.65V in P3HT: PC₆₁BM devices and at 0.76-0.77V in PTB7:PC₆₁BM devices. The increased V_{oc} in the PCDTBT: PC₇₁BM device was exclusively attributed to the modified cathode interface with TiO_x layer that offsets the interfacial losses. Obviously, TiO_x interlayer selectively improves V_{oc} only in the PCDTBT:PCBM system. Hence it is of vital importance to investigate the effect of TiO_x layer on the electrical characteristics at the modified cathode interface of OPV devices with different BHJ materials and eventually to elucidate the modulation of open circuit voltage (V_{oc}) in the devices.

In the metal-insulator(semiconductor)/metal (MIM) solar cells, the V_{oc} was influenced by the interface parameters such as ideality factor (n), reverse saturation current density (J_o) and barrier potential (ϕ_B). The commonly used expressions for V_{oc} in terms of J_o and ϕ_B are expressed in equation 4.6.

$$V_{oc} = \frac{kT}{q} \ln\left(\frac{J_{sc}}{J_o} + 1\right) \dots\dots\dots(4.6.a)$$

$$V_{oc} = n \left[\phi_B + \frac{kT}{q} \ln\left(\frac{J_{sc}}{A^{**}T^2}\right) \right] \dots\dots\dots(4.6.b)$$

These interfacial parameters provide information about carrier injection and recombination behaviour inside the device and the parameters can be deduced from the dark J-V characteristics fitted with Shockley equation. The Shockley equation was originally derived for inorganic p-n junction where the optical excitation produces free carriers directly. In organic p-n junction, the nature of excited state is different because the free charge carriers are generated after exciton dissociation at p-n interfaces. Thus, the organic p-n layer was modeled as a virtual material with an effective band gap equal to HOMO(D)-LUMO(A) difference [73]. In addition, the J-V approach using Shockley equation has been extended to the bilayer and BHJ organic solar cells [73-79].

A simple and typical model to represent the electronic structure of organic solar cell is that the electron donor is adjacent to anode while the electron acceptor to cathode so that the charge carriers move to the respective electrodes (holes to anode and electrons to cathode) (Figure 4.16 a) [80-81]. However, in BHJ solar cells comprising the nanoscale donor/acceptor interpenetration network, both the donor and acceptor domains can be in intimate contact with anode as well as cathode. Thus, in addition to the donor/acceptor interface (p-n junction) in the bulk, there are four interfaces with electrodes (donor/anode, acceptor/anode, donor/cathode and acceptor/cathode). As a hole transporting layer (PEDOT:PSS) is typically used at anode side (Ohmic contact for hole transport), the current work emphasizes on the cathode interfaces (donor/cathode and acceptor/cathode) where the Schottky-like junctions may exist due to an energy difference between LUMO of D/A materials and work function of Al. At these interfaces, the electron transporting/hole blocking layer (TiO_x) was incorporated. The model presented in Figure 4.16 illustrates the donor/cathode and acceptor/cathode interfaces where we studied the role of TiO_x layer in two aspects: (i) electron-transporting at acceptor/cathode interface and (ii) hole-blocking at

donor/cathode interface. Indeed, the organic BHJ solar cell is an even more complicated system. To gain full insights into understanding, we also examined the donor/acceptor surface phase segregation (ratio of donor to acceptor) of BHJ layer and correlated with the electrical characteristics across the interfaces between TiO_x and BHJ layer. Finally, even though this model may simplify the real physical mechanism, to our knowledge, this is currently the best representation of the electronic structure of BHJ organic solar cell.

Figure 4.16 Illustration of several interfaces in organic bulk heterojunction (BHJ) solar cells. (a) Donor/acceptor interface (p-n junction) in BHJ materials, (b) donor/cathode and acceptor/cathode interfaces (Schottky-like junctions) and (c) TiO_x interfacial layer integrated at donor/cathode and acceptor/cathode interfaces. Active-layer/PEDOT:PSS/ITO interfaces (Ohmic contacts) are not shown here.

4.2.2 Effect of TiO_x interlayer on charge transport and recombination at cathode interface

The charge transport across the junction barriers can be described by the thermionic-emission theory or the diffusion theory [82]. Equation 4.7 is the general diode equation describing the J-V characteristics of both p-n junction and Schottky diodes.

$$J = J_o \left[\exp\left(\frac{qV}{nkT}\right) - 1 \right] \dots\dots\dots(4.7)$$

where, J_o is the reverse saturation current density, q the electronic charge, V the applied voltage, n the ideality factor, k the Boltzmann constant and T the absolute temperature. The thermionic-emission theory is commonly applied to describe the charge transport for inorganic semiconductors with high mobility.[82-83] According to the thermionic-emission theory, J_o is given by

$$J_o = A^*T^2 \exp\left(-\frac{q\phi_B}{kT}\right) \dots\dots\dots(4.8)$$

where, A* is the Richardson constant and ϕ_B the barrier potential. The diffusion theory is based on the assumption that the barrier height is much larger than kT and it is applicable for low mobility materials with short carrier mean free path.[82-83] According to the diffusion theory, J_o is given by

$$J_o = J_D = q\mu N_c E \exp\left(-\frac{q\phi_B}{kT}\right) \dots\dots\dots(4.9)$$

where, μ is the carrier mobility, E the electric field at metal/semiconductor interface and N_c the effective density of states in conduction band.

The J_0 expressions in the diffusion and thermionic-emission theories are basically similar, except that the J_0 in diffusion theory is dependent on the bias and is less sensitive to temperature [82]. Since the thermionic emission is not applicable to organic materials with low carrier mobility [84], the diffusion theory tends to be more appropriate for the charge transport in organic solar cells. As there is no accurate model for BHJ solar cells, under the frame work of metal/ insulator (semiconductor)/ metal structure, the dark J-V characteristics of BHJ solar cells can be described by equation 4.7 [73, 78-79].

Figure 4.17 Typical J-V characteristics in dark of a solar cell where three regions are identified. Inset: equivalent circuit of solar cell modelled as a diode taking into account the series resistance R_s and shunt resistance R_{sh} . V is the applied bias and J_{ph} is the source for photocurrent.

As with conventional p-n junction cells, the series and shunt resistances (R_s and R_{sh}) have been taken into account in the simple equivalent model of a diode for an organic solar cell (inset of Figure 4.17). According to this model, the J-V characteristics for a solar cell can be analytically described by

$$J = J_o \left[\exp \left(\frac{q(V - JAR_s)}{nkT} \right) - 1 \right] + \frac{V - JAR_s}{AR_{sh}} - J_{ph}(V) \dots\dots\dots(4.10)$$

where, A is the effective diode area, R_s the series resistance and R_{sh} the shunt resistance, V is the applied bias and J_{ph} (V) the voltage dependent photocurrent density which is zero in dark.

Figure 4.17 reveals the typical dark J-V characteristics of a solar cell where the three regions can be identified. Region I is a linear region at reverse bias and small forward bias where current is limited by shunt resistance R_{sh} (leakage current). Region II exhibits an exponential behavior at intermediate forward bias where current is controlled by a diode behavior (diffusion current dominated at open circuit point). Region III is a linear region at high forward bias where the current is limited by series resistance R_s (space charge limited current) [85]. Obviously, the R_s and R_{sh} can be extracted from the region I and III respectively. The slope and the extrapolation of region II to $V=0$ give the ideality factor (n) and J_o respectively. Using the extracted parameters, the experimental dark J-V curves were fitted with equation (4.11) for all devices. In order to judge the accuracy of fitting, the root mean square (RMS) error was calculated by equation (4.11).

$$RMS\ error = \sqrt{\frac{\sum (J_{exp} - J_{fit})^2}{J_{exp} \cdot n_{data}}} \dots\dots\dots(4.11)$$

where, J_{exp} and J_{fit} is the experimental and fitted current density respectively and n_{data} is the number of data points. The extracted parameters were adjusted until the RMS error converges to the smallest value. In our fittings, the RMS errors are in the range of 0.05-0.08.

Figure 4.18 depicts the experimental and fitted curves for P3HT:PC₆₁BM, PCDTBT:PC₇₁BM and PTB7: PC₆₁BM devices with and without TiO_x interlayer. The extracted parameters (n,

Figure 4.18 Experimental J-V characteristics (black ● and red ◆) in dark of the (a) P3HT:PC₆₁BM, (b) PCDTBT:PC₇₁BM and (c) PTB7:PC₆₁BM devices with and without TiO_x. Using the extracted parameters (n , J_0 , R_s and R_{sh}), experimental J-V were fitted with the equation (4.10). The fitted J-V curves are shown as the black and red lines. The error bars indicate the standard deviations, $\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - \mu)^2}$, where $\mu = \frac{1}{N} \sum_{i=1}^N x_i$. For fitting of all curves, RMS errors were within 0.05 and 0.08.

J_o , R_s and R_{sh}) of all devices are listed in *Table 4.6*. Based on the parameters extracted from the dark J-V characteristics, the effect of TiO_x interlayer on the charge transport and recombination at cathode interface was examined.

Table 4.6 Extracted parameters (n , J_o , R_s and R_{sh}) from the dark J-V curves of P3HT: PC₆₁BM, PCDTBT: PC₇₁BM and PTB7: PC₆₁BM devices with and without TiO_x interlayer. Calculated RMS errors for the fittings are presented in the right-most column. Relative changes upon TiO_x integration, $\Delta n/n$ (%) and $\Delta\phi_B$, are also presented.

		n	$\Delta n/n$ (%)	J_o (mA/cm ²)	$\Delta\phi_B$ (meV)	R_s (Ω cm ²)	R_{sh} (k Ω cm ²)	RMS error
P3HT:PC ₆₁ BM	Reference	2.10		4.0x10 ⁻⁵		4.8	300	0.069
	With TiO_x	1.52	-27.6	1.3x10 ⁻⁶	88.6	2.9	880	0.055
PCDTBT: PC ₇₁ BM	Reference	1.70		8.0x10 ⁻⁹		4.5	83	0.053
	With TiO_x	1.51	-11.2	6.0x10 ⁻¹⁰	67.0	3.5	136	0.078
PTB7:PC ₆₁ BM	Reference	1.51		2.0x10 ⁻⁸		7.4	170	0.073
	With TiO_x	1.54	1.98	2.0x10 ⁻⁸	-	27	160	0.072

On the ideality factor, n

The ideality factor (n) is a powerful tool for examining the recombination kinetics at the interface , therefore can be correlated with the morphology and the quality of the interface [73, 86-87]. Typically, the ideality factor n varies between 1 and 2. As per the Sah-Noyce-Shockley theory, $n= 1$ implies the band-to-band recombination in the bulk semiconductor materials while the $n= 2$ suggests the gap-state recombination of carriers in the space charge regions. (at interfaces in the device) [88-90]. In the case of organic semiconductors, it is sensible to term the monomolecular and bimolecular recombination for $n=1$ and $n =2$ respectively. Indeed a mixture of these two mechanisms would happen within a real device.

The dominant mechanism depends on the band-gap energy and density of interface states. In polymer/fullerene blends, the dominant mechanism is the interface state recombination ($n=2$) [90]. It is also applicable to our polymer/fullerene BHJ devices since the measured ideality factors are around 2 and close to 2 (2.10 for P3HT:PC₆₁BM, 1.73 for PCDTBT:PC₇₁BM and 1.51 for PTB7:PC₆₁BM devices).

When TiO_x interfacial layer is inserted at cathode interface, the ideality factor reduces from 2.10 to 1.52 (27.6%) in P3HT:PC₆₁BM devices and from 1.70 to 1.51 (11.2%) in PCDTBT:PC₇₁BM devices. In contrast, it is almost invariant at $n = 1.51$ -1.54 in PTB7:PC₆₁BM devices. As the ideality factor was extracted externally from the output dark J-V curve of our real BHJ device with several interfaces, it would represent the combined effect of all individual rectifying junctions inside the device. However in our case, since TiO_x interlayer only affects the active layer/cathode interface, the modulated n -value is exclusively originated from this modified cathode interface where two recombination mechanisms mentioned above are involved.

Figure 4.19 (a) Schematic of the monomolecular recombination ($n=1$) in the bulk and the bimolecular recombination ($n=2$) at the interface between donor polymer and cathode. (b) Possible effects of TiO_x interlayer on recombination kinetics: the bimolecular recombination can be reduced while the monomolecular recombination can be increased. In the P3HT:PC₆₁BM and PCDTBT:PC₇₁BM devices, the reduced ideality factors with TiO_x layer may reflect these changes in recombination at the donor/cathode interface.

Figure 4.19 illustrates two recombination mechanisms at the interface between donor polymer and cathode and the possible effect of TiO_x interfacial layer on these recombination mechanisms. In this proposed schematic, the TiO_x interlayer blocks holes and passivates the interface traps, reducing the bimolecular recombination ($n=2$) of electrons and holes at cathode interface. As a consequence of hole blocking, the accumulation of holes in the bulk promotes the monomolecular recombination. As a result, the overall recombination at the cathode interface was reduced by TiO_x interlayer in P3HT:PC₆₁BM and PCDTBT:PC₇₁BM devices. However, the invariant ideality factors in PTB7:PC₆₁BM devices suggest that the interface recombination could not be altered upon TiO_x integration.

On the J_0 and ϕ_B

The reverse saturation current density (J_0) in the device is the minority charge carrier density (holes in this case) overcoming the energetic barrier towards the Al electrode. In P3HT:PC₆₁BM and PCDTBT:PC₇₁BM devices, when the TiO_x interfacial layer were inserted, J_0 decreased from 4.0×10^{-5} to 1.3×10^{-6} mA/cm² and from 8.0×10^{-9} to 6.0×10^{-10} mA/cm² respectively. The reduced J_0 indicates that TiO_x interfacial layer blocks the hole-flow to the cathode in the P3HT:PC₆₁BM and PCDTBT:PC₇₁BM devices. Similar to the effect of TiO_x on the ideality factor, there was no effect of TiO_x on J_0 in PTB7:PCBM devices. The physical origin has not been known yet.

Equation (4.9) shows a relationship between J_0 and barrier potential ϕ_B . The ϕ_B represents the energetic barrier to the minority carriers at both electrode interfaces (holes at cathode interface and electrons at anode interface) of the device. However, since only the cathode interface was modified with TiO_x interlayer, only the barrier height ϕ_B that blocks holes at cathode interface was focused. Figure 4.20 shows schematics of the energetic barrier

blocking the holes (in the donor polymer) and the effect of TiO_x on the hole-blocking barrier height at donor/cathode interface. Since the absolute value of ϕ_B could not be obtained in this work, the change in ϕ_B ($\Delta\phi_B$) upon TiO_x integration was evaluated. In P3HT:PC₆₁BM and PCDTBT:PC₇₁BM devices with TiO_x , the ϕ_B were increased by 88.6 meV and 67.0 meV respectively while ϕ_B remained unchanged in PTB7:PCB₆₁M devices. It indicates that TiO_x interlayer increased the hole-blocking barrier in P3HT:PC₆₁BM and PCDTBT:PC₇₁BM devices. Thus, the effect of TiO_x on the n , J_o and ϕ_B followed the same trend in all devices.

Figure 4.20 (a) Schematic of the energetic barrier at donor/cathode interface that blocks holes in the donor polymer towards cathode. (b) Effect of TiO_x layer on the hole-blocking barrier height at donor/cathode interface. The reduced J_o with TiO_x layer suggests a higher hole-blocking barrier.

On R_s and R_{sh}

The extracted series and shunt resistances (R_s and R_{sh}) of the devices with and without TiO_x layer are presented in Table 4.6. The series resistance (R_s) of the device is the total resistance of the bulk and electrode materials as well as contact resistance while the shunt resistance (R_{sh}) represents the local shunts between two electrodes that favour the additional current paths circumventing the diode. Upon integrating TiO_x interlayer, R_s was reduced from 4.8 to 2.9 Ωcm^2 in P3HT:PC₆₁BM devices and from 4.5 to 3.5 Ωcm^2 in PCDTBT:PC₇₁BM devices.

The series resistance and morphology of the active film usually determine the fill factor (FF) of the devices.[91-93] The FF was improved from 60% to 66% in P3HT:PC₆₁BM devices and from 59% to 64% in PCDTBT:PC₇₁BM devices. AFM topography images (*Figure 4.23.a-c*) show the similar active layer morphologies in these devices (RMS roughness 1.1-1.2 nm). Thus, the improved FF in these devices are attributed reduced R_s . Unlike the P3HT:PC₆₁BM and PCDTBT:PC₇₁BM devices, R_s was dramatically increased from 7.4 to 27 Ωcm^2 and FF was degraded from 58% to 52% in PTB7:PC₆₁BM devices with TiO_x layer. As previously observed, the charge transport across the cathode interface was not improved by TiO_x interlayer in PTB7:PC₆₁BM devices, thus the series resistance of TiO_x layer increased the series resistance (R_s) of these devices.

4.2.3 Surface segregation at active layer/TiO_x interface: Evaluation of V_{oc}

The interfacial layer induced V_{oc} enhancement has been explained by several mechanisms including the formation of dipole moment across the junction [94], band-bending at the interface [37-38], the superposition of the built-in field with the interfacial dipole of the interlayer [95] and smaller reverse saturation current density in dark [76, 96-98]. As observed in previous section, in P3HT:PC₆₁BM and PCDTBT:PC₇₁BM devices, TiO_x interlayer reduces the hole current density and recombination, thereby reducing the leakage losses at donor/cathode interface. Consequently, it is expected in these devices that V_{oc} can be enhanced by cutting contact losses. However, V_{oc} was increased by 40mV only in PCDTBT:PC₇₁BM devices. It remained unchanged at 0.64-0.65V in P3HT:PC₆₁BM devices and at 0.76-0.77V in PTB7:PC₆₁BM devices.

It is thus speculated that the TiO_x induced V_{oc} modulation can be influenced by the acceptor/cathode interface as well since both donor and acceptor phases are in contact with

cathode in BHJ devices. It implies that the donor and acceptor surface distribution adjacent to TiO_x interlayer plays a key role. It was reported in literature that a larger fraction of p-type P3HT-rich domains is accumulated at the surface of P3HT:PC₆₁BM blend film [99-102] while the surface of the PCDTBT:PC₇₁BM film is relatively richer with PCBM phase [103]. The schematic illustrations of the vertical phase segregation patterns of P3HT:PC₆₁BM and PCDTBT:PC₇₁BM blend films are depicted in *Figure 4.21*. According to this phase segregation pattern in P3HT:PC₆₁BM devices, there is a very small area of interfaces between the n-type PCBM phase and n-type TiO_x layer for electron transport, resulting in the vanishing effect on V_{oc} enhancement (0.64-0.65V) despite having a hole-blocking and reduced recombination at donor/cathode interface by TiO_x layer.

Figure 4.21 Schematic illustration of donor/acceptor phase segregation patterns in P3HT:PC₆₁BM and PCDTBT:PC₇₁BM BHJ blends.

This view was supported by the prior reports demonstrating that V_{oc} was invariant at 0.60-0.61V with n-type interlayer (polyelectrolyte) located between cathode and P3HT:PCBM BHJ film in which the majority domains are P3HT-rich on the surface [40] while V_{oc} increased from 0.61 V to 0.73 V with p-type interlayer (thin pentacene) in the same BHJ system [104]. Since the phase segregation pattern in PCDTBT:PC₇₁BM blends is opposite to that in P3HT:PCBM blends, the effective electron transport at the large PCBM/ TiO_x interfaces increased the V_{oc} of PCDTBT:PC₇₁BM devices from 0.88 V to 0.92 V. So far, the

surface segregation for the PTB7:PC₆₁BM blend has not been reported in literature. Thus, the X-ray photoelectron spectroscopy (XPS) measurement was employed to examine the surface compositions of PTB7:PC₆₁BM BHJ film as well as to confirm the previously reported surface segregation pictures of P3HT:PC₆₁BM and PCDTBT:PC₇₁BM BHJ films.

XPS is widely used for surface analysis due to its relative simplicity in use and data interpretation. X-ray photoelectron signals of sulfur S2p and carbon C1s in the blend films were detected and the resulting XPS profiles are shown in *Figure 4.22*. The peaks at around 165eV and 285eV binding energies are assigned to S2p and C1s. The atom % of S2p and C1s were calculated from the integrated area of the XPS profiles and their sensitivity factors (taken from the reference [105]). In the polymer/PCBM blends, the S2p peaks are from the polymers and C1s is contributed from both polymers and PCBM. Based on this information and the atomic % (S2p and C1s), the weight % of polymer (P3HT, PCDTBT and PTB7) and PCBM in each blend was calculated and tabulated in *Table 4.7*.

The weight fraction of P3HT is 60.4% (P3HT-rich on the surface) in the P3HT:PC₆₁BM blend film that is consistent with prior XPS reports.[101, 106] In contrast, the weight fraction of PCDTBT is only 32.8% in PCDTBT:PC₇₁BM blend film suggesting an abundance of PCBM phases at the active layer/TiO_x interface. For PTB7:PC₆₁BM blend film, the weight fraction of PTB7 is as high as 90.8% indicating that polymer PTB7 phases mostly occupied the surface of PTB7:PC₆₁BM film. In addition to XPS, AFM phase images of the P3HT:PC₆₁BM, PCDTBT:PC₇₁BM and PTB7:PC₆₁BM blend films were also acquired to study the surface segregation patterns. (*Figure 4.23. d-f*) Although AFM phase image could not identify the correct domains, it reveals two domains of different materials. Based on the chemical composition of the XPS results, the donor-acceptor segregation

Figure 4.22 X-ray photoelectron spectroscopy (XPS) profiles of sulfur (S 2p) and carbon (C 1s) obtained from the surface of P3HT:PC₆₁BM, PCDTBT:PC₇₁BM and PTB7:PC₆₁BM blend films.

Figure 4.23 AFM topography images of (a) P3HT:PC₆₁BM blend film (RMS roughness 1.16 nm), (b) PCDTBT:PC₇₁BM blend film (RMS roughness 1.20) and (c) PTB7:PC₆₁BM blend film (RMS roughness 1.11 nm). AFM phase image of (d) P3HT:PC₆₁BM blend film, (e) PCDTBT:PC₇₁BM blend film and (f) PTB7:PC₆₁BM blend film. The colour coding relates the donor (green) and acceptor (red) phases.

patterns in nanoscale can also be better visualized in the AFM phase images of the two BHJ blend films (Figure 4.23 d-f).

Table 4.7 Atomic (%) and weight (%) of surface compositions in P3HT:PC₆₁BM, PCDTBT:PC₇₁BM and PTB7:PC₆₁BM blend films.

	Atom (%)		Weight (%)	
	S2p	C1s		
P3HT:PC ₆₁ BM			P3HT	PCBM
	5.1	94.9	60.44	39.6
PCDTBT:PC ₇₁ BM			PCDTBT	PCBM
	1.87	98.13	32.79	67.21
PTB7:PC ₆₁ BM			PTB7	PCBM
	7.84	92.16	90.85	9.15

4.2.4 Effect of TiO_x interlayer on built-in potential (V_{BI}): Evaluation of V_{oc}

In the previous section 4.2.2, the effect of TiO_x interfacial layer on charge transport and recombination phenomena at cathode interface has been discussed by using the dark J-V analysis. In this section, the effect of TiO_x layer on the built-in potential (V_{BI}) was investigated using the photocurrent (J_{ph}) - voltage (V) response of the devices. The photocurrent ($J_{ph} = J_{light} - J_{dark}$) is independent of the dark injection mechanisms and thus, is solely due to the flux of incident photons. In the illuminated BHJ devices, the V_{BI} associated with built-in field drives the separated charge carriers to respective collecting electrodes, resulting in V_{oc}. It provides critical information about the energetic position of p-type and n-type semiconductors and associated physical process governing the device operation.

At zero applied voltage (V) in the device, the diffusion current is induced by V_{BI} , at $(V - V_{BI})$ the diffusion and drift currents compete and at $(V = V_{BI})$, which is also referred as compensation voltage (V_o), the diffusion is compensated by the drift ($\Delta J=0$). So, V_o is a good estimate of V_{BI} [107-109]. Ooi et al deduced V_{BI} of 0.58V from the point-of-optimal symmetry of J_{ph} - V curve in P3HT:PC₆₁BM BHJ device [110]. Limpinsel et. al. later identified it as the quasi flat band voltage considerably smaller than V_{BI} (0.9V at $J_{ph}=0$) [111]. In the devices with zero contact loss (Fermi level pinning at electrode interfaces), V_{BI} is V_{oc} while in the real device with non-ohmic contact loss, it is described as an upper limit to V_{oc} [67].

The V_{BI} of the P3HT:PC₆₁BM, PCDTBT:PC₇₁BM and PTB7:PC₆₁BM devices with and without TiO_x layer were deduced from their J_{ph} - V plots (*Figure 4.24 b-d*). The resulting V_{BI} values are listed in *Table 4.8* along with the corresponding V_{oc} of the devices. The V_{BI} is increased from 0.78 V to 0.81V, from 0.93V to 0.98V and from 0.83 V to 0.85V upon TiO_x integration in P3HT:PC₆₁BM, PCDTBT:PC₇₁BM and PTB7:PC₆₁BM devices. The increased V_{BI} in the TiO_x integrated device signifies a higher internal field across the device and is attributed to band-bending [37-38] at the contact interfaces. Jeon et. al demonstrated that the incorporation of polymeric interlayer in P3HT:PCBM cells increased the build-in potential attributable to the band bending at the interlayer/Al interface, thereby improving V_{oc} in the interlayer integrated devices [38]. *Figure 4.24.a* illustrates schematic of the band bending at modified interface of an OPV device. According to the quantitative analysis, the TiO_x interlayer increased V_{BI} by 3.84% in P3HT:PC₆₁BM, 5.37% in PCDTBT:PC₇₁BM and 2.41% in PTB7:PC₆₁BM devices that were correlated to the corresponding V_{oc} enhancement (ΔV_{oc} of 1.56% for P3HT:PC₆₁BM, 4.54% for PCDTBT:PC₇₁BM and 1.31% for PTB7:PC₆₁BM devices). Obviously, there is a consistency between ΔV_{BI} (%) and ΔV_{oc} (%) in all devices.

Figure 4.24 (a) Schematic of illustrating the band-bending at modified cathode interface. Plots of photocurrent (J_{ph}) against voltage (V) in (b) P3HT:PC₆₁BM, (c) PCDTBT:PC₇₁BM and (d) PTB7:PC₆₁BM devices with and without TiO_x. The compensation voltages (V_o) were deduced from the J_{ph} -V plots.

Table 4.8 The built-in potential (V_{BI}) (lower limit) deduced from the photocurrent-voltage (J_{ph} -V) response of OPV devices with and without TiO_x interlayer. The changes in V_{BI} and V_{oc} ($\Delta V_{BI}\%$ and $\Delta V_{oc}\%$) upon TiO_x integration are also described.

		V_{BI} (V) (Lower limit)	$\Delta V_{BI} / V_{BI}$ (%)	V_{oc} (V)	$\Delta V_{oc} / V_{oc}$ (%)
P3HT:PC ₆₁ BM (60 nm)	Reference	0.78	3.84	0.64	1.56%
	With TiO _x	0.81		0.65	
PCDTBT:PC ₇₁ BM (60 nm)	Reference	0.93	5.37	0.88	4.54%
	With TiO _x	0.98		0.92	
PTB7:PC ₆₁ BM (100 nm)	Reference	0.83	2.41	0.76	1.31%
	With TiO _x	0.85		0.77	

4.2.5 Summary

The effects of TiO_x interfacial layer on the charge transport and recombination at cathode interfaces were studied in the P3HT:PC₆₁BM, PCDTBT:PC₇₁BM and PTB7:PC₆₁BM BHJ solar cells using dark current analysis. Subsequently, the V_{oc} enhancement upon integrating TiO_x interlayer was investigated. In P3HT:PC₆₁BM and PCDTBT:PC₇₁BM devices, TiO_x interlayer decreased the ideality factor (n) that suggests a suppressed recombination of holes (residing in the donor polymers) and electrons (reaching the cathode). In addition, TiO_x interlayer increased the hole-blocking barrier at cathode interface, thereby reducing the minority carrier (holes) density (J_o). In PTB7:PC₆₁BM devices, the TiO_x interlayer could not modulate the charge transport/recombination at cathode interface, but significantly increased the series resistance (R_s) of the device. Its physical origin has not been known yet.

Despite being observed an increased hole-blocking barrier at donor/cathode interface of P3HT:PC₆₁BM and PCDTBT:PC₇₁BM devices, the V_{oc} was only improved in PCDTBT:PC₇₁BM devices. It was speculated that V_{oc} modulation would be influenced by the electron transport across acceptor/cathode interface. X-ray photoelectron spectroscopy (XPS) measurement and atomic force microscopy (AFM) phase images revealed that the surface of P3HT:PC₆₁BM and PTB7:PC₆₁BM blend films are polymer-rich while that of PCDTBT:PC₇₁BM film is enriched with PCBM phase. Thus in PCDTBT:PC₇₁BM devices, an efficient electron transport across the larger interfaces between acceptor (PCBM) and TiO_x reduced the contact loss, thereby increasing V_{oc} . This comes to conclusion that the efficient electron transport at the PCBM/ TiO_x /cathode interface has a stronger impact on the V_{oc} enhancement than the effect of hole-blocking in the polymer/ TiO_x /cathode interface.

Alternatively, the effect of TiO_x interlayer on built-in potentials (V_{BI}) was also studied and correlated to V_{oc} of the devices. The V_{BI} 's were estimated from the $J_{\text{ph}}-V$ responses. The pronounced increased V_{BI} with TiO_x interlayer in PCDTBT:PC₇₁BM device may be attributed to the band-bending at modified cathode interface. Upon integrating TiO_x , the changes in V_{BI} (ΔV_{BI} %) were consistent with the changes in V_{oc} (ΔV_{oc} %) for all devices.

4.3 Zinc Tin Oxide (ZTO) as the electron transporting layer in inverted organic solar cells

For organic solar cells, the improved power conversion efficiencies and inherent device stability are of great potential for their commercialization. However, the standard device architecture (ITO/PEDOT:PSS/active-layer/Al) suffers from an inherent device instability due to the oxidization of low work function electrodes (Al and Ca/Al) and the degradation of ITO by the strong acidity of PEDOT:PSS [112]. This instability can be improved by alternative device geometry, the so called inverted devices with reversed electrode polarities and additional anodic/cathodic metal oxide buffers. The titanium and zinc oxides (TiO_2 , TiO_x and ZnO) have been widely utilized as efficient electron transporting buffers in inverted OPV cells. The amorphous Zinc Tin Oxide (ZTO) has emerged as a promising channel material in thin film transistor due to its high electron mobility. In addition, its solution processability would be of interest for low-cost and flexible electronics and photovoltaic devices. This section describes the optical, morphological and structural properties as well as the field effect mobility of ZTO film. The device performances of inverted P3HT:PCBM cells with ZTO and TiO_x electron transport layers are compared.

4.3.1 Optical, morphological and structural properties of ZTO film

In the device structure where light is illuminated from the electron collecting electrode, the transmission of electron transporting layer should be high in the visible region so that the incoming light can effectively reach the photoactive layer without losses. *Figure 4.25* shows the transmission spectra of ZTO film on quartz indicating that the ZTO film is highly transparent with T% of $\sim 95\%$ in the visible region (400-800 nm). The band gap calculated from the plot of $(\alpha h\nu)^2$ versus $h\nu$ is 3.6 eV (Appendix B *Figure S6*), consistent with previous reports on the ZTO band gap of 3.35-3.89 eV [113-114]. The AFM height image profile (inset of *Figure 4.25.a*) shows that the thickness of ZTO film is 12-15 nm. The surface topography image of ZTO film on quartz substrate (inset of *Figure 4.25.a*) reveals that the surface of the film is smooth and RMS roughness of 1.16 nm. The X-ray diffraction (XRD) profile (*Figure 4.25.b*) confirms the amorphous nature of the ZTO film.

4.3.2 Field effect mobility and electrical conductivity of ZTO film

The field effect mobility of a material reflects the current driving capacity that in turn is determined by the charge transport properties of that material. Thus, the field effect mobility of ZTO film was evaluated by fabricating field effect transistors (FET) with ZTO as channel material. Here, we fabricated the ZTO FET using a bottom-gate test structure (Inset of *Figure 2.a*). The ZTO film was deposited on the Si_3N_4 dielectric (200 nm) coated Si substrate followed by optimized annealing at 100°C for 1 hr and 500°C for 1 hr. The aluminium was deposited through patterned mask on top to ZTO as source and drain electrodes. The channel mobility of ZTO was extracted from slope of $\sqrt{I_{ds}}$ versus V_{gs} in the transfer characteristics (*Figure 4.26 a-b*) and was as high as 3.21 $\text{cm}^2/\text{V s}$, when measured in vacuum and 2.55 $\text{cm}^2/\text{V s}$ in air. The drain current ON/OFF ratio was 10^6 in the V_{gs} range of -10V to

Figure 4.25 (a) Transmission spectrum of ZTO film on quartz. Inset: AFM Surface topography image and its step height profile of ZTO film on quartz substrate. (b) X-ray diffraction (XRD) pattern of ZTO on silicon.

Figure 4.26 (a) Drain current versus gate voltage ($I_D - V_G$) and the square root of the drain current versus gate voltage ($I_D^{1/2} - V_G$) transfer characteristics of the ZTO thin film transistor. (b) Drain current versus drain-to-source voltage ($I_D - V_{GS}$) output characteristics of the ZTO thin film transistor. (c) Current-voltage characteristics of ZTO and TiO_x films obtained from two-terminal diode configuration.

60V. The mobility of ZTO is found to be significantly higher than that of TiO_x ($1.7 \times 10^{-4} \text{ cm}^2/\text{Vs}$) [14, 115]. The high mobility displayed by amorphous ZTO is due to its high ionicity. The conduction band minimum (CBM) and valance band maximum (VBM) are formed from different ionic states. The CBM of oxides made up of spherically expanded s-orbitals which overlap with s-orbitals of neighbouring metals. So electronic levels of CBM are not altered by strained bonds and the electron transport is not affected significantly [116].

It is noteworthy that charge mobility of ZTO in FET geometry is in the direction parallel to the substrate while it is across the thickness of ZTO film in solar cell geometry. Thus, the electrical conductivities of ZTO as well as TiO_x films were also measured by two-terminal configuration (FTO/ZTO or TiO_x/Al) (inset of Figure 4.26 c). The films were spun-coat on FTO followed by Al deposition, the same condition as in the solar cell structure. Figure 4.26 c shows the current-voltage (I-V) characteristics of ZTO and TiO_x films. The electrical conductivities of ZTO and TiO_x determined from their I-V curves at the bias voltage region (0-1V) are $1.02 \times 10^{-4} \text{ Sm}^{-1}$ and $2.03 \times 10^{-6} \text{ Sm}^{-1}$ respectively. The conductivity of ZTO is two-order of magnitude higher than that of TiO_x . In short, the better electron transport properties of the ZTO film allow its application as an effective electron transport layer in inverted solar cells.

4.3.3 Device performance with ZTO electron transporting layer

In inverted device configuration, cathodic buffer layers (eg., TiO_2 and ZnO) and anodic buffers (eg., MoO_3 and WO_3) are integrated for improved electron and hole transports respectively [112, 117-121]. In addition, higher workfunction metals (Ag, Au) are chosen as hole collecting electrodes since the polarity of charge collection is opposite in inverted cells and these higher workfunction metals offer better stability in ambient environment. A

transparent conducting ITO is still used on the light-illuminated side, but in cases which demand high temperature annealing, the transmission and workfunction of ITO can fluctuate, affecting device performance. Rather, fluorine-doped tin oxide (FTO) can be utilized because it is thermally and chemically more stable than ITO [122]. In this work, a solution processed, high electron mobility and highly transparent ZTO film was exploited as an electron transporting buffer layer in an inverted OPV cell. As the ZTO film preparation still needs a high temperature treatment, the inverted cells were fabricated on FTO substrates with device configuration: FTO/ZTO/P3HT:PCBM/ WO_3 /Ag as shown in *Figure 4.27*.

Figure 4.27 Schematic structure of inverted solar cell with photoactive layer (P3HT:PCBM), electron selective layer (ZTO or TiO_x) and hole selective layer (WO_3).

The current-voltage characteristics in dark and under illumination of the devices with ZTO and TiO_x electron transport layers are depicted in *Figure 4.28* along with the corresponding device parameters. The power conversion efficiencies of 3.04% and 2.71% were achieved in the devices with ZTO and TiO_x respectively. A similar device configuration

(FTO/TiO_x/P3HT:PCBM/PEDOT:PSS/Au) was reported by Kuwabara et. al. with a PCE of 2.13% (J_{sc} 6.95mA/cm², V_{oc} 0.55, FF 0.56).[120] Although our devices showed the same V_{oc} and FF as Kuwabara et. al, our TiO_x devices displayed higher J_{sc} . An increased J_{sc} in our device is likely due to better electron and hole transport properties with spin-coated sol-gel based TiO_x and WO₃ rather than electrodeposited TiO_x and PEDOT:PSS. Thus an enhanced device performance can be achieved through careful selection of electron and hole transporting layers in the devices. With ZTO layer, further enhanced device efficiency was obtained that mainly derives from increased V_{oc} and J_{sc} . In contrast, FF is higher in the device with TiO_x.

Figure 4.28 Current-voltage characteristics of the inverted cells with ZTO and TiO_x as electron transporting layers along with the corresponding the device parameters.

The inverted solar cell with ZTO layer gives open circuit voltage (V_{oc}) of 0.61V that is higher than V_{oc} of 0.56V with TiO_x layer. It is well recognized that the V_{oc} is mostly governed by the HOMO-LUMO offset of donor and acceptor materials if ohmic contact is established between both electrodes and active materials via electron and hole extracting layers [108]. At

present, it is difficult to judge whether the electrode contacts are ohmic or not. Thus, not only HOMO-LUMO energetics but also contact properties are responsible for modulation of V_{oc} . Although the inverted cells typically give low V_{oc} and FF, the V_{oc} of 0.61V in inverted cell with ZTO is comparable to that of conventional device. The higher V_{oc} obtained with ZTO can be attributed to smaller voltage loss favoured by better energy alignment between the CB of ZTO and the LUMO of the acceptor material. As ZTO and TiO_x materials act as both electron transporting and hole blocking layers between photoactive materials and FTO electrode, they should completely cover the FTO substrate. However, it is hard to have a complete coverage on FTO because FTO roughness is very high (RMS roughness 14.34 nm). The statistical evaluation on AFM height images (*Figure 4.29.a*) shows that RMS roughness of ZTO and TiO_x on FTO are 10.44 nm and 14.29 nm respectively. This better coverage of ZTO on FTO substrate may suppress the recombination of electrons collected in ZTO layer and residual holes in the photoactive blend film. Hence, a better energy alignment and reduced recombination at cathode interface are possible reasons for relatively enhanced V_{oc} with ZTO layer.

The device with ZTO generated a short circuit current density (J_{sc}) of 11.0mA/cm² that is significantly larger than the J_{sc} of the device with TiO_x (8.74mA/cm²). The J_{sc} depends on light absorption efficiency, the charge carrier density and mobility within organic materials for ideal devices with no contact loss.[1] Since the absorption efficiencies of both ZTO and TiO_x films (transmission $\geq 95\%$ in the range of 400-800 nm) are similar, its contribution to J_{sc} is negligible. The charge carrier density depends on the exciton dissociation efficiency at the donor/acceptor interface that in turn depends on interpenetrating network morphology of photoactive film. The lower J_{sc} in the TiO_x device is probably due to unfavourable morphology of the photoactive film close to underlying rougher TiO_x /FTO interface. When

contact losses are not negligible, the J_{sc} also depends on the charge transport at the contact interfaces which is influenced by the mobility/conductivity of charge transporting layers at the contacts. In the device with ZTO, the higher mobility/conductivity of ZTO allows efficient collection of photogenerated electrons at electrode with reduced charge recombination and current leakage, thereby increased photocurrent density.

Figure 4.29 (a) AFM topography images ($5 \times 5 \mu m$) of ZTO and TiO_x on FTO substrate having RMS roughness of 10.44 nm and 14.29 nm. (Note: RMS roughness of FTO is 14.34 nm). (b) AFM topography images ($5 \times 5 \mu m$) of P3HT:PCBM film on top of ZTO and TiO_x having RMS roughness of 1.35 nm and 1.15 nm respectively.

Despite the increased V_{oc} and J_{sc} in the devices with ZTO layer, the FF was lower (0.46 with ZTO and 0.55 with TiO_x). The fill factor (FF) of the device is sensitive to the series resistance of the device and the morphology of the photoactive film [93, 123-124]. The series resistances of the devices were extracted from the inverse derivative of current with respect

to voltage in current-voltage curve around the open-circuit point. The calculated R_s of the devices with ZTO and TiO_x are $19.68 \Omega cm^2$ and $11.92 \Omega cm^2$ respectively. Since the only difference between these two devices is the interlayer materials (ZTO vs. TiO_x), the changes in R_s solely stem from the electrical and physical properties at the active layer/interlayer/FTO interface. A surface analysis on AFM topography images ($5 \times 5 \mu m$) (Figure 4.29 a) using Igor Pro 6.12A software provides the surface areas of $25.9 \mu m^2$ and $27.0 \mu m^2$ and the corresponding area percents of 3.77% and 8.02% respectively for ZTO and TiO_x interlayer on FTO substrates. A smaller area of intimate contact between ZTO and its adjacent layers, despite higher conductivity of ZTO, increased the electrical resistance of ZTO interlayer, thereby increasing the R_s of ZTO device.

Additionally, the wettability of ZTO and TiO_x underlying layers towards subsequent deposition of P3HT:PCBM blend film were studied by the contact angle measurement as the surfaces of polar hydrophilic oxides are often chemically incompatible with non-polar organic films leading to delamination of organic film[125] and increasing the contact resistance. A marginal difference in contact angles (11.5° with ZTO and 9.8° with TiO_x) indicates that the adhesion between active and interlayers would not significantly contribute to the R_s changes in the devices. Figure 4.29 (b) displays the AFM surface topography images of P3HT:PCBM film on ZTO and TiO_x and their RMS roughness are 1.35 nm and 1.15 nm respectively. The surface roughness of P3HT:PCBM with ZTO is even slightly higher facilitating uneven interfacial contact leading to higher R_s of the device. As the interfaces are fundamentally different, it is possible that these interfaces are also different electronically which could also affect J_{sc} . As such, it is a possible that there are also differences in these interfaces electronically (i.e. different interface states), which could also affect J_{sc} . As the conduction and valence band maxima of TiO_x and ZTO are not significantly different, it is

not ascertain that the surface states at these interfaces are different electronically. However, the conductivity measurements of ZTO and TiO_x exhibited a significant difference between these two bulk materials. Thus, the J_{sc} enhancement our devices can be due to a higher conductivity of ZTO (difference in bulk material properties) rather than surface properties.

4.3.4 Summary

We demonstrated an inverted organic solar cell with ZTO film as an efficient electron extracting layer and power conversion efficiency as high as 3.05%. The n-type ZTO films were prepared by a solution-processed method. It is amorphous in nature and its transmission is higher than 95% in visible region. The field effect mobility and electrical conductivity of ZTO are as high as $3.21 \text{ cm}^2/\text{Vs}$ and $1.02 \times 10^{-4} \text{ Sm}^{-1}$ - significantly higher than those of TiO_x . As compared to the device with TiO_x layer, the enhanced device efficiency with ZTO mainly derives from higher J_{sc} and V_{oc} which is attributed to an efficient electron collection and a suppressed recombination. The observed changes in the devices are due to the differences in mobility/conductivity of interlayer as well as surface properties at polymer/interlayer interface. A good electron transport and transparency of the ZTO layer demonstrates its potential as electron buffer layer in organic solar cells.

4.4 Ultrafine Au-NW networks as plasmonic antennae in organic photovoltaics

As another optical management strategy, the ultrafine gold nanowires (Au-NWs) were integrated in OPV devices comprising thin P3HT:PCBM photoactive layers for surface plasmon enhanced device performance. The fabrication process is completely solution compatible and does not involve the use of high temperature processes. The plasmonic

effect on the optical and photophysical properties (absorption and emission) of conjugated polymer (P3HT) as well as on the photocurrent generation in OPV devices was investigated. The spacer effect on the relaxation dynamics of excited P3HT molecules near Au-NWs was also explored.

4.4.1 Surface plasmon resonance of Au-NWs

In *Figure 4.30* (a), TEM image of the as-synthesized Au-NWs typically reveals that the ultrathin Au-NWs are parallel and closely packed to form a two-dimensional network structure. This packing structure is preserved when transferred on to substrates dipped in the solution. This self-assembled Au-NW network is visible with an average diameter of 7-9 nm as shown in *Figure 4.30* (b). Since the physical origin of light absorption by metal nanostructures is the coherent oscillation of conduction electrons upon interaction with incoming electromagnetic field, the surface plasmon resonance (SPR) of Au-NWs deposited on various substrates is evaluated by optical absorption [126]. In 2D nanostructures, both transverse or longitudinal resonance can be excited, depending on the oscillation of electrons perpendicular or parallel to the long axis of the structures [126-127].

Figure 4.30 (a) High-resolution TEM image of ultrafine Au-NWs and (b) AFM image of self-assembled Au-NW networks on silicon substrate.

As shown in *Figure 4.31*, the absorption peak for the NWs on quartz at 516 nm is assigned to the transverse resonance of Au-NWs. The longitudinal resonance which typically occurs at higher wavelengths depending on the aspect ratio of nanorods/nanowires is difficult to estimate due to the micron lengths of the Au-NWs. The SPR peak of metallic nanostructures depends strongly on their dielectric environment and is tuned by changing the surrounding media. In a high k environment, the SPR of metal nanostructure is typically red-shifted following the relation: $\omega_{sp} = \omega_p / \sqrt{1 + 2\epsilon_m}$ where ω_{sp} is the SP frequency, ω_p is the plasma frequency of the electrons in the metal and ϵ_m is the average permittivity of the surrounding medium [128-129]. In order to simulate the dielectric environment of OPV devices, the Au-NWs were deposited on ITO and coated with PEDOT:PSS layer. Since the refractive index

Figure 4.31 Optical absorption bands of Au-NWs on quartz, on ITO and sandwiched between ITO and PEDOT:PSS layer. The baselines for the measurement are quartz, ITO and ITO/PEDOT:PSS respectively.

Inset: The transverse mode surface plasmon resonance of Au-NWs.

of PEDOT: PSS is greater than that of air, it results in an additional red shift of the SPR band to around 625 nm (Figure 4.31). In addition, the absorption cross-sections of Au-NWs in different dielectric environments were also calculated using FDTD simulation (Appendix B, Figure S13). The SPR of Au-NWs on glass and in ITO/PEDOT:PSS environment were observed at around 520 nm and 630 nm respectively which are in agreement with the experimental results.

4.4.2 Au-NWs induced absorption enhancement

Since the photoexcitation in polymer-fullerene photovoltaic cells preferentially occurs in the polymer domain, optical absorption in P3HT near Au-NWs was studied. In order to simulate the conditions within a solar cell created by reflection from the cathode, a blanket Al layer (100 nm) was deposited on the photoactive P3HT layer. *Figure 4.32* illustrates the absorption (%) in P3HT photoactive layer with and without Au-NWs measured in reflection geometry. The increased absorption in photoactive layer can be attributed either to plasmon near-field enhancement or to enhanced scattering (far-field effect). However, for Au nanostructures smaller than 25 nm, the scattering efficiency is very low and is negligible [126, 130]. The absorption and scattering cross sections of Au-NWs with diameters of 10 nm and 50 nm were calculated using FDTD simulations (Lumerical). (Appendix B *Figure S12*)

For 10 nm diameter Au-NWs, only absorption contributes to the extinction while for 50 nm diameter Au-NWs, the contribution from scattering becomes significant. Thus, in our case, the absorption enhancement in P3HT molecules is attributed to an increased local electric field in the photoactive P3HT excited by the SPR of Au-NWs. The interaction between localized surface plasmons in metal nanostructures and incident photons creates a high density of photons at the near-field distance and a strong local electromagnetic field builds

up [65, 131-132]. When this resonant frequency matches the absorption band of photoactive molecules, the absorption in the molecules is effectively enhanced - essential for increased photogeneration of charge carriers.

Figure 4.32 Absorption (%) of P3HT on PEDOT:PSS coated quartz measured in reflection geometry with blanket Al layer to simulate reflections induced by the cathode in solar cells.

4.4.3 Increased photocurrent in the Au-NWs integrated devices

Taking the advantage of increased absorption occurring in the photoactive layer, the Au-NWs integrated photovoltaic devices comprising the P3HT:PCBM photoactive layer of thickness 60 nm and 80 nm were fabricated. The schematic of the device structure is depicted in *Figure 4.33*. *Figure 4.34* displays J-V characteristics of the 80 nm thick devices with and without Au-NWs in dark and under illumination. The device parameters are tabulated in *Table 4.11*. Upon integrating Au-NWs, the short circuit current (J_{sc}) increased from 7.87 to 9.02 mA/cm² in the 80 nm devices and from 6.38 to 7.86 mA/cm² in the 60

nm devices. The photocurrent is thus enhanced by 14.6% and 23.2% in the 80 nm and 60 nm devices respectively.

Figure 4.33 Schematic of the Au-NWs integrated OPV device.

Figure 4.34 J-V characteristics of the 80 nm thick cell with and without Au-NWs under illumination (100mW/cm²). Inset: J-V curves of the same device in dark on a semi- logarithmic scale.

It is noted here that the device efficiencies of reference P3HT:PCBM devices in this section 4.4 (with Au-NWs) were slightly lower than those with the same active layer thickness in section 4.1-4.2 (with TiO_x). It is because of the different thickness of PEDOT:PSS layer and different annealing conditions. The PEDOT:PSS thickness (spacer) was reduced to 15 nm in Au-NW device (taking the evanescent SP excitation field of Au-NWs into account) while an optimized thickness of (30-40nm) was used in the TiO_x devices. In addition, an optimum annealing temperatures for active layer (150 °C for 10 min) and for PEDOT:PSS layer (140 °C for 10 min) were applied in the TiO_x devices while a mild annealing for active layer (60 °C for 2.5 hr) and for PEDOT:PSS (60 °C for 30 min) was treated in the Au-NW devices where high temperature annealing was avoided in order to keep the morphology of self-assembled Au-NWs undisturbed as well as the fabrication process compatible to plastic substrates.

Table 4.9 Device parameters of the control and Au-NWs incorporated devices under AM 1.5 solar illumination with intensity of 100mW/cm². The device parameters were averaged over ten cells and the maximum error was calculated as ($\Delta x_{\max} = (x_{\max} - x_{\min})/2$).

	PCE (%)	J _{sc} (mA/cm ²)	ΔJ _{sc} (%)	V _{oc} (V)	FF	R _s (Ωcm ²)
Control (80 nm)	2.44±0.12	-7.87±0.37	14.61	0.65±0.00	0.48±0.00	19.75
Au-NWs (80 nm)	2.72±0.10	-9.02±0.35		0.65±0.01	0.46±0.01	20.73
Control (60 nm)	2.31±0.19	-6.38±0.39	23.19	0.65±0.01	0.56±0.03	19.45
Au-NWs (60 nm)	2.45±0.06	-7.86±0.24		0.65±0.01	0.48±0.01	23.65

In all devices, the open circuit voltage (V_{oc}) remained constant at 0.65V suggesting that the PEDOT: PSS completely covers the Au-NWs and does not act as a recombination centre for the photocarriers [17]. The modification of contact properties such as injection barriers can lead to changes in series resistance R_s of the device. The examination of J-V curve in dark at

higher positive bias where current is limited by R_s (inset of *Figure 4.34*) reveals that R_s is not changed significantly in Au-NWs incorporated device. The R_s of the devices are obtained by linearly fitting the J-V curve under illumination around the point ($J = 0$). Besides, AFM topography images (Appendix B, *Figure S14-15*) show that the morphology of the P3HT-PCBM layer is unchanged in the devices with and without Au-NWs indicating that the Au-NWs below the PEDOT:PSS results in a minimal perturbation to the active layer morphology. No changes in bulk active layer morphology and series resistance in the devices results in an unchanged fill factor (FF) for the 80 nm thick devices. These factors indicate that the enhancement in solar cell efficiencies is not electrical in nature.

Figure 4.35 IPCE enhancement (%) in 400-700 nm spectral range for the Au-NWs integrated device with thickness 80 nm. Inset: IPCE spectra of the control and Au-NWs incorporated devices.

In order to examine the wavelength dependence of the photocurrent enhancement, we recorded the IPCE spectra for the 80 nm and 60 nm thick devices. It was found that the IPCE of both devices were enhanced in the spectral region from 400 nm to 650 nm (insets

of Figure 4.35). In addition, the calculated relative enhancement (%) $[100 \times (\text{IPCE}_{\text{Au-NW}} - \text{IPCE}_{\text{control}}) / \text{IPCE}_{\text{control}}]$ against wavelength is plotted in Figure 4.35. It is significantly enhanced around 620 nm coinciding with the SPR band of Au-NWs in the ITO-PEDOT:PSS environment (Figure 4.31).

4.4.4 Exciton relaxation dynamics of P3HT in the vicinity of Au-NWs

Having confirmed the increased absorption of the photons in the Au-NWs integrated devices translates to improved PV efficiencies, the exact nature of the plasmon excitation effect of the Au-NWs on the photoactive P3HT molecules was explored. Accordingly, we have performed steady state and time resolved photoluminescence (TRPL) measurements to elucidate the extent of the local electric field enhancement and recombination dynamics (photophysical properties) of P3HT molecules near Au-NWs. Time resolved photoluminescence spectroscopy is a powerful technique to study the energy and charge transfer mechanisms in molecular systems [93]. The temporal information from the photoluminescence decay provides a measure of the exciton lifetimes within the photoactive layers (i.e. $(1/\tau_{\text{PL}}) = (1/\tau_{\text{R}}) + (1/\tau_{\text{NR}})$, where τ_{PL} , τ_{R} and τ_{NR} refers to the PL, radiative and non-radiative lifetimes respectively. The excited state properties of emitting molecules can be significantly modified by the proximity of a metal nanostructure through interactions between the excitons and surface plasmons, which may lead to three phenomena:

- (i) non-radiative metallic quenching (i.e. increased $k_{\text{NR}} = (1/\tau_{\text{NR}})$ contribution where k_{NR} is the non-radiative rate constant),
- (ii) an increase in the local excitation field strength and
- (iii) an increase in radiative recombination rate (i.e. $k_{\text{R}} = (1/\tau_{\text{R}})$) [133-134].

Such phenomena are often described in the weak coupling regime – i.e. coupling between the exciton dipole and the electromagnetic (EM) field of the surface plasmon, where the wavefunctions and EM modes of the excitons and surface plasmons are unperturbed [135].

Metallic quenching of fluorescent molecules is associated with energy and/or charge transfer processes. When the excited molecules are close to the metal surface (typically < 5 nm), the excitons in the fluorescent materials can be quenched by the metal via non-radiative Forster-like energy transfer [133] or through charge transfer at the metal-semiconductor interface by exciton splitting. A quenched PL intensity and an increased PL decay rate constant (i.e. $k_{\text{PL}} = (1/\tau_{\text{PL}})$) are signatures of metallic quenching [133, 136]. The other two phenomena—increased local excitation field and faster PL decay rate—gives rise to increased PL intensity due to increased quantum yield (Y) expressed as $Y = |L(\omega_{\text{ex}})|^2 Z(\omega_{\text{em}})$ where L is the excitation field intensity and Z is the radiative decay efficiency [133]. Thus, the implications of the above-mentioned first and third phenomena are a faster PL decay rate while that of the second and third phenomena are an increased steady-state PL intensity. In order to elucidate the effects of the integrated Au-NWs, we compared four different sets of samples prepared on quartz substrates. The material combinations are P3HT, P3HT /PEDOT: PSS, P3HT/Au-NWs and P3HT/PEDOT: PSS/Au-NWs. The P3HT film thickness is 40 nm and the PEDOT: PSS is 15 nm.

P3HT molecules in direct proximity to Au-NWs produced a 2.5 fold enhancement in the steady-state PL intensity (*Figure 4.36*). It may be ascribed to arise from a coupling between the emitting P3HT molecules and surface plasmons in Au-NWs at resonance frequency [20, 65]. TRPL spectra in *Figure 4.37* indicate that the lifetime of pristine P3HT molecules 550 ± 50 ps (consistent with literature values [23]) reduces to 410 ± 50 ps when directly in contact

Figure 4.36 Steady-state photoluminescence of P3HT with and without Au-NWs and the modulation of the PL profiles upon inserting PEDOT:PSS spacer layer. Excitation wavelength is 500 nm.

Figure 4.37 Time-resolved photoluminescence (TRPL) lifetime profile of P3HT with and without Au-NWs. Excitation wavelength is 500 nm. TRPL decay profiles are monitored at 650 nm and time resolution of streak camera is approximately 50 ps. The extracted lifetime are 550 ± 50 ps, 410 ± 50 ps, 490 ± 50 ps and 500 ± 50 ps for pristine P3HT, Au-NW/P3HT, PEDOT:PSS/P3HT and Au-NW/PEDOT:PSS/P3HT respectively.

with Au-NWs. A faster PL decay rate would dramatically increase the number of emitting photons from P3HT molecules leading to enhanced PL intensity. Thus, the increase in excitation field intensity and faster PL decay rate that maximizes PL intensity competes with the metallic quenching that suppresses PL intensity. Exciton splitting effects at the Au-NW/P3HT interface are unlikely due to the presence of an insulating oleylamine layer on the Au-NWs. The faster PL recombination rate of the excitons is commensurate with a shorter exciton diffusion length in the P3HT domain, which leads to undesirable losses in organic photovoltaics.

The effect of PEDOT: PSS spacer layer on the plasmonic field strength and exciton relaxation dynamics was also investigated. In relation to pristine P3HT samples, the decay rate in PEDOT: PSS/P3HT system is faster and PL intensity is slightly quenched, attributable to losses due to exciton splitting at the PEDOT: PSS/P3HT interface. In the presence of plasmonic nanostructures, it was reported that the decay rate is altered by insertion of the spacer layer or by varying the spacer thickness (metal nanostructure-emitter distance) [133, 136-138]. The PL enhancement induced by the Au-NWs is still present after integration of the 15 nm PEDOT: PSS spacer- clear evidence that the plasmon-exciton coupling is still effective. As mentioned previously, the PL enhancement could arise from

- (i) an increase in the local excitation field and/or
- (ii) an increased radiative recombination rate.

The radiative decay profiles of the PEDOT:PSS/P3HT and Au-NW/PEDOT:PSS/P3HT remain invariant (within experimental precision: 490 ± 50 ps and 500 ± 50 ps respectively) (See Figure 4.37.b), indicating that the exciton splitting rates are not significantly affected. Thus, the increase in steady state photoluminescence stems from the enhanced local excitation field arising from light concentration and accumulation from hot points at the Au

nanowires, rather than from a concentration of the local density of photon states at the emission wavelengths due to the invariance of the radiative decay rate. These findings are in agreement with the absorption enhancement (Figure 4.32).

4.4.5 Analysis of exciton generation rate and dissociation probability

In the previous sections, the investigation on the absorption and emission properties of P3HT near Au-NWs indicates that the increased photocurrent in the Au-NWs integrated devices is due to plasmon excitation field enhancement. The conclusion was also supported by calculations of the maximum exciton generation rate ($G_{\max}$) and exciton dissociation probability based on the analysis reported by Mihailetschi et al. [57]. In this analysis, the photocurrent J_{ph} is plotted as a function of effective voltage ($V_o - V$) for the 60 nm and 80 nm-thick devices. (Figure 4.38) The J_{ph} is the difference between the dark current (J_D) and the current under illumination (J_L) while V_o is defined as the compensation voltage applied when J_L equals J_D . At higher effective voltages, all free charge carriers are extracted (zero recombination) and J_{ph} saturates to qGL where G is the maximum exciton generation rate and L is the thickness of photoactive layer. In this regime, all bound electron-hole pairs are separated into free carriers and consequently the maximum exciton generation rate $G_{\max}$ is determined only by the amount of absorbed photons. For the devices in this work, the maximum exciton generation rates increased by 10-17% after incorporating Au-NWs, with 60 nm devices showing higher increment than 80 nm thick ones. This correlates well with increased absorption in the Au-NWs integrated devices. In addition, the exciton dissociation probability at the short circuit condition was calculated. The dissociation probability for 80 nm thick films shows only a slight increase from 77.36% to 80.58% in Au-NW incorporated devices indicating that the primary enhancement mechanism is due to the increase in the excitation field intensity.

Figure 4.38 Photocurrent (J_{ph}) versus effective applied voltage (V_{eff}) for the control and Au-NWs incorporated devices with active layer thicknesses of (a) 80 nm and (b) 60 nm.

4.4.6 Summary

In this work, the optically thick, but physically thin organic photovoltaic devices were successfully fabricated by utilizing the solution processed ultrafine Au-NWs as plasmonic antennae. The effective coupling between local plasmon excitation field of Au-NWs and excitation energy of organic molecules (P3HT) leads to the absorption enhancement in P3HT:PCBM photoactive layer. The careful reduction of the PEDOT:PSS buffer layer thickness allows the evanescent field to be extended into the photoactive layer of the solar cell, resulting in the short circuit current density to be enhanced by 23.2 %. The photocurrent enhancement (%) is maximized at 620 nm, matching the plasmon resonance band of Au-NWs in ITO-PEDOT:PSS environment.

We have further investigated the mechanism behind this improved photocurrent density. The two possible origins for the increased photocurrent are the Au-NWs induced strong surface plasmon excitation field strength (enhanced absorption) and/or modulation of the exciton relaxation dynamics (longer exciton lifetime) by Au-NWs. These two origins were distinguished by investigating the optical and photophysical properties (time-resolved photoluminescence) of photoactive P3HT molecules near Au-NWs. The primary enhancement mechanism in our devices is due to an increased plasmon excitation field that leads to an enhanced absorption in photoactive layer thereby increasing photocurrent in the Au-NWs integrated devices. Our conclusion was supported by calculations which showed an increase in the maximum exciton generation rate (G_{max}) and an invariant exciton dissociation probability.

Chapter 5

Conclusion and Prospects

5.1 Overall summary and Conclusion

The sol-gel processed titanium suboxide (TiO_x) interfacial layer was integrated at cathode interface of the organic BHJ solar cells comprising P3HT:PCBM, PCDTBT:PCBM and PTB7:PCBM photoactive layers. The power conversion efficiencies (PCE) of $\sim 6\%$ was achieved in PCDTBT:PC₇₁BM device with TiO_x interlayer. As the TiO_x interfacial layer functions as an optical spacer and charge transporting layer, the impacts of TiO_x layer on optical and electrical properties in OPV cells was investigated. The FDTD simulation and optical reflectance measurements showed that the optical spacer effect is more pronounced in the thinner active layer and diminished with increasing active layer thickness for all devices. The optical spacer effect is not significant once the active layer thickness approaches its optimum value in each system (90 nm for P3HT:PCBM, 80 nm for PCDTBT:PCBM and 120 nm for PTB7:PCBM devices).

The enhanced photocurrent in TiO_x integrated device is attributed to the combined effect of optical spacer and charge transport at modified cathode interface. The optical reflectance combined with the internal quantum efficiency of the device is a simple methodology to decouple the optical and electrical contributions of TiO_x interlayer to photocurrent which vary between different heterojunctions. Judging these weight contributions in each system, the optimizations can be implemented separately to improve the optical and electrical effects of interlayer, leading to an improved overall efficiency of the device. Decoupling of optical and electrical effects of interlayer would support further device optimization and designs including the evaluation of new interfacial layers.

As an electrical effect, TiO_x interlayer increased the hole-blocking barrier and suppressed the recombination at polymer/cathode interface of P3HT:PC₆₁BM and PCDTBT:PC₇₁BM devices. A higher V_{oc} results upon modifying the cathode interface with TiO_x in PCDTBT:PC₇₁BM device (from 0.88V to 0.92V) as compared to P3HT:PC₆₁BM (V_{oc} is almost invariant at 0.64-0.65V). The blend morphology of BHJ system where both donor and acceptor phases can be in contact with the TiO_x /cathode plays a crucial role in controlling the V_{oc} induced by TiO_x interlayer. An increased surface segregation of PCBM promotes the increased in electron density at PCBM/cathode interface, enhancing electron extraction through TiO_x and thus increases the quasi-Fermi level splitting of electrons and holes which results in a higher V_{oc} in PCDTBT:PCBM device. Thus, TiO_x induced electron transport at PCBM/cathode interface may have a stronger impact on the V_{oc} enhancement than the hole-blocking at polymer/cathode interface.

Solution processed zinc tin oxide (ZTO) film was exploited as an efficient electron transporting layer in the P3HT:PCBM inverted solar cell and power conversion efficiency as high as 3.05% was achieved. The transmission of amorphous ZTO is higher than 95% in visible region and its electrical conductivity is as high as $1.02 \times 10^{-4} \text{ Sm}^{-1}$. As compared to the device with TiO_x layer, the enhanced device efficiency with ZTO mainly derives from a higher J_{sc} and V_{oc} that is attributed to the better electron collection and suppressed recombination at active layer/ZTO interface. The better electron transport properties of the ZTO allow its application as an effective electron transport layer in inverted solar cells.

As an additional optical management strategy, the plasmonic gold nanowires (Au-NWs) were incorporated in organic P3HT:PCBM devices. The effective coupling between local plasmon excitation field of metal nanostructures and excitation energy of organic molecules leads to an enhanced absorption within photovoltaic materials, thereby increasing photocurrent by

23.2% in our Au-NWs integrated devices. The observed optical and photophysical properties indicate that the primary enhancement mechanism is due to an increased plasmon excitation field of Au-NWs, rather than a longer life-time of excited state P3HT molecules. The solution processed, geometrically favorable arrangement of ultrafine Au-NWs induces the plasmonic advantages in photoactive materials with minimal perturbation to the photoactive layer morphology, thereby achieving the easy and successful fabrication of thin organic photovoltaic devices.

In conclusion, the integrations of Au-NWs (as plasmonic antennae) and TiO_x (as optical spacer and electron transporting buffer) are the promising strategies for realization of the physically thin but optically thick organic photovoltaic devices. In comparing these two strategies, the Au-NW approach offers a relatively higher absorption enhancement in P3HT:PCBM devices than the TiO_x one. However, there are several merits of TiO_x integration over Au-NWs:

- (i) easy to tune the optical spacer thickness,
- (ii) flexible to integrate TiO_x layer at both cathode and anode interfaces (in conventional and inverted configurations),
- (iii) non-perturbation to active layer morphology,
- (iv) affect both optical and electrical aspects and
- (v) shield against penetration of oxygen and water moisture into photoactive layer.

5.2 Future recommendations

In the present work, two optical management strategies [metal oxide interlayer (TiO_x) and plasmonic metal nanostructure (Au-NWs)] were applied separately in OPV cells in order to evaluate their individual effects on the device performance in terms of optical and electrical aspects. It is proposed that the OPV power conversion efficiency can be further increased by utilizing both metal oxide interlayer and Au nanostructures at each electrode interface of conventional and inverted OPV cells. An additional proposed structure is the surface plasmon enhanced tandem organic solar cells with Au nanorods (Au-NRs) and low band gap polymer (PTB7).

5.2.1 Combined approach in OPV cells with standard and inverted configurations

The proposed OPV cells with standard and inverted structures are depicted in *Figure 5.1*. Despite the same buffers incorporated at electrode interfaces, the electron and hole transport characteristics across the electrodes would be different as the polarities are opposite in standard and inverted configurations. The efficiencies in each configuration can be maximized by optimizing the charge transport and recombination across the interfaces. In addition, the surface plasmon resonance (SPR) induced by the metal nanostructures would vary as the Au-nanostructures are situated in different environments (PEDOT:PSS and TiO_x in standard and inverted configurations). Other types of Au and Ag nanostructures exhibits the plasmonic activities, with a stronger effect demonstrated by Ag nanostructures. However, if the Ag nanostructures are integrated at the ITO electrode, the work function mismatch between ITO and Ag would be encountered. It can be avoided by alternatively integrating Ag nanostructures at the Al or Ag electrodes.

Figure 5.1 Schematics of OPV devices with incorporation of both Au-NWs and TiO_x interlayer in (a) standard and (b) inverted configurations.

5.2.2 Surface plasmon enhanced tandem organic solar cells

In tandem configuration, two photoactive layers with complementary absorption characteristics are stacked through the interconnecting layers. This interconnecting layer functions as a charge recombination centre where the holes from bottom cell through a hole transporting interlayer (eg., PEDOT:PSS) and electrons from top cell through an electron transporting layer (eg., TiO_x) recombine. The top cell normally suffers from weak absorption due to the attenuation of incoming light. Thus unbalanced current generation limits the efficiency of tandem cells. Introduction of metal nanostructures in the interlayer system can increase the absorption in top cell via the phenomenon of surface plasmon resonance. A photoactive layer comprising low band gap polymer is typically used in top cell. *Figure 5.2* (a) shows the proposed tandem organic solar cell where the low band gap polymer blend layer (PTB7:PCBM) is used in top cell and Au nanorods are embedded inside the PEDOT:PSS or between TiO_x and PEDOT:PSS of the interlayer system. Au nanorods (Au-NRs) described in *Figure 5.2* (b) have diameter of 15 nm and aspect ratio of 3 showing two resonance peaks at 520 nm and 680 nm [139]. The absorption spectra of PTB7 polymer and PTB7:PCBM

BHJ blend are shown in *Figure 5.2* (c). The coincidence of the second resonance peak (~ 680 nm) and the absorption maximum of low band gap polymer PTB7 (~ 700 nm) [9] would offer a plasmonic advantage to the absorption enhancement in top cell where the light absorption is weak.

Figure 5.2 (a) Proposed organic tandem cells with Au nanorods (Au-NRs) embedded in interlayer system. (b) Au-NRs with diameter of 15 nm and aspect ratio of 3 shows two plasmon absorption bands peaked at 520 nm and 680 nm [139]. (c) Absorption spectra of PTB7 polymer and PTB7:PCBM BHJ blend [9].

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Appendix A

List of Abbreviations

OPV	Organic Photovoltaics
BHJ	Bulk Heterojunction
PCE	Power Conversion Efficiency
J _{sc}	Short-circuit current density
V _{oc}	Open-circuit voltage
FF	Fill factor
J-V	Current-voltage
P3HT	Poly-3-hexylthiophene
PCDTBT	Poly[N-9''-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'- benzothiadiazole)]
PTB7	Poly[thieono [3,4-b] thiophene and benzodithiophene] derivative
PC ₆₁ BM	[6,6]-phenyl-C61 butyric acid methyl ester
PC ₇₁ BM	[6,6]-phenyl-C71 butyric acid methyl ester
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate)
LUMO	Lowest Unoccupied Molecular Orbital
HOMO	Highest Occupied Molecular Orbital
TiO _x	Titanium suboxide
ZTO	Zinc-tin oxide
ZnO	Zinc oxide
Au-NPs	Gold nanoparticles
Au-NWs	Gold nanowires
NRs	Nanorods
FDTD	Finite Difference Time Domain

EQE	External Quantum Efficiency
IQE	Internal Quantum Efficiency
IPCE	Incident photon to current efficiency
P_{in}	Incident light power density
η_A	Absorption efficiency
η_{ED}	Exciton diffusion efficiency
η_{CT}	Charge transfer efficiency
η_{CC}	Charge collection efficiency
AFM	Atomic Force Microscopy
XPS	X-ray Photoelectron Spectroscopy
EDX	Energy Dispersive X-ray
XRD	X-Ray Diffraction
TEM	Transmission Electron Microscopy
PL	PhotoLuminescence
TRPL	Time-Resolved Photoluminescence
UV-vis	Ultraviolet-visible
CV	Cyclic voltammetry
ITO	Indium tin oxide
FTO	Fluorine doped tin oxide
LSPR	Localized surface plasmon resonance
EM	Electromagnetic
ϵ_d	Permittivity of dielectric
ϵ_m	Permittivity of metal
IPA	Isopropanol
rpm	revolution per minute
OA	Oleylamine

TIPS	Triisopropylsilane
DCB	Dichlorobenzene
R	Reflectance
T	Transmittance
A	Absorbance
$n(\lambda)$	Refractive index
$k(\lambda)$	Absorption coefficient
N_{ph}	Total number of absorbed photons
V_{BI}	Built-in potential
$ E ^2$	Optical electric field
$I_{AM1.5}$	Irradiance of Air Mass 1.5 solar spectrum
n	Ideality factor
J_o	Reverse saturation current density
R_s	Series resistance
R_{sh}	Shunt resistance
ϕ_B	Barrier potential
RMS	Root mean square
J_{ph}	Photocurrent density
J_{light}	Current density under illumination
J_{dark}	Current density in dark
V_o	Compensation voltage
τ_R	Radiative lifetime
τ_{NR}	Non-radiative lifetime
k_R	Radiative recombination rate
G_{max}	Maximum exciton generation rate

Appendix B

Supplementary Information

Transmission and morphology of titanium suboxide (TiO_x) film

Figure S1 Transmission spectrum of TiO_x film showing a high transmission of 98% in visible region. Inset: Surface morphology of TiO_x film with RMS roughness of 0.51 nm and AFM image height profile showing the film thickness of 10-12 nm.

Atomic composition of titanium suboxide (TiO_x)

Figure S2 Energy dispersive X-ray (EDX) profile of titanium suboxide (TiO_x). The semi-quantitative elemental analysis indicates that atomic compositions of Ti and O are 45.30% and 54.70% respectively resulting in titanium suboxide $\text{TiO}_{1.2}$.

X-ray diffraction (XRD) profile of TiO_x

Figure S3 XRD spectra of TiO_x at room temperature (RT) and at 500°C. No crystalline peak is exhibited at room temperature while the anatase crystalline phase revealed at 500°C.

Determination of optical band gaps of polymers

Figure S4 Absorption spectra of the P3HT, PCDTBT and PTB7 polymers. Optical band gaps (E_g) determined from the absorption onsets at higher wavelength region are 1.9eV, 1.87eV and 1.67eV respectively for P3HT, PCDTBT and PTB7 polymers.

Estimation of lowest unoccupied molecular orbital (LUMO) energy levels of polymers

Figure S5 Cyclic voltammograms of the P3HT, PCDTBT and PTB7 polymers. The oxidation onset potentials (E_{ox}) determined from the intersection of two tangents are 0.66V, 0.95V and 0.90V respectively for P3HT, PCDTBT and PTB7 polymers. E_{HOMO} can be readily calculated using the relation $E_{HOMO} = -[e(E_{ox} - E_{FC}) + 4.8]$ (eV), yielding the calculated E_{HOMO} of 5.13V, 5.42V and 5.37V respectively for P3HT, PCDTBT and PTB7 polymers. The optical band gap E_g from UV-vis absorption together with the E_{HOMO} from CV gives an estimation of E_{LUMO} of the polymers to be 3.23V for P3HT, 3.55V for PCDTBT and 3.70V for PTB7.

Determination of optical band gaps of TiO_x and ZTO

Figure S6 Plots of $(\alpha h\nu)^2$ against energy for titanium suboxide (TiO_x) and zinc-tin oxide (ZTO) films on quartz. The band gaps extracted from these plots are 3.9 eV and 3.6 eV for TiO_x and ZTO respectively.

Model fitting

Figure S7 Real and imaginary part of index (n and k values) for P3HT:PCBM, PCDTBT:PCBM and PTB7:PCBM blends. The parameters were fitted till achieving a good fit between experimental material dispersion and multi-coefficient model (MCM).

Model fitting (continued)

Figure S8 Real and imaginary part of index (n and k values) for glass, ITO and TiO_x. The parameters were fitted till achieving a good fit between experimental material dispersion and multi-coefficient model (MCM).

Model fitting (continued)

Figure S9 Real and imaginary part of index (n and k values) for PEDOT:PSS and Al. The parameters were fitted till achieving a good fit between experimental material dispersion and multi-coefficient model (MCM).

Optical electric field $|E|^2$ distribution across the PCDTBT:PCBM devices with and without TiO_x interlayer

Figure S10 Calculated optical electric field $|E|^2$ distribution profiles at 600 nm incident light in the PCDTBT:PCBM devices with active layer thicknesses of 60 nm, 70 nm and 80 nm. The black and red curves represent $|E|^2$ in reference devices and TiO_x integrated devices respectively.

Optical electric field $|E|^2$ distribution across the PTB7:PCBM devices with and without TiO_x interlayer

Figure S11 Calculated optical electric field $|E|^2$ distribution profiles at 700 nm incident light in the PTB7:PCBM devices with active layer thicknesses of 80 nm, 100 nm and 120 nm. The black and red curves represent $|E|^2$ in reference devices and TiO_x integrated devices respectively.

Absorption, scattering and extinction cross-sections of Au-NWs

Figure S12 Absorption, scattering and extinction cross-sections of Au-NWs (diameter 10 nm and 50 nm) calculated by FDTD optical simulation (Lumerical).

Absorption cross-sections of Au-NWs in different environments

Figure S13 Absorption cross-sections of Au-NWs on glass and in the ITO/PEDOT:PSS environments calculated by FDTD optical simulation (Lumerical). Surface Plasmon resonance of Au-NWs on glass is at ~ 520 nm while that in the ITO/PEDOT:PSS environment is at ~ 630 nm.

AFM topography images

Figure S14 Surface morphology of thin PEDOT:PSS layer on ITO (a) without and (b) with Au-NWs. RMS roughness (a) 2.4 nm, (b) 2.7 nm. (Note: RMS roughness of ITO is 4.8 nm)

Figure S15 Surface morphology of P3HT-PCBM film with thickness 80 nm in (a) control device, (b) device with Au-NWs and with thickness 60 nm in (c) control device and (d) device with Au-NWs. RMS roughness (a) 0.59 nm, (b) 0.61 nm, (c) 0.61 nm and (d) 0.62 nm.

Appendix C

Author's Publication Lists

Patent

- [1] **Than Zaw Oo**, Nripan Mathews, Lydia H. Wong, Subodh G. Mhaisalkar, Achmad Zen, Christoph Treutler
"Ultrathin metal nanowires for plasmonic solar cells"
Filed as PCT/2BSC 013 (April 2011)

Journals

- [1] **T.Z.Oo**, N.Mathews, T.L. Tam, G. C. Xing, T. C. Sum, A. Sellinger, L.H. Wong, S.G. Mhaisalkar
"Investigation of Photophysical, Morphological and Photovoltaic Behavior of Poly(p-phenylene vinylene) Based Polymer/Oligomer Blends"
Thin Solid Film, 518 (2010) 5292–5299
- [2] **Than Z. Oo**, Nripan Mathews, Guichuan Xing, Bo Wu, Bengang Xing, Lydia H. Wong, Sum Tze Chien, Subodh G. Mhaisalkar
"Ultrafine Gold Nanowire Networks as Plasmonic Antennae in Organic Photovoltaics"
Journal of Physical Chemistry C (Accepted with minor revision)
- [3] **Than Z. Oo**, Nripan Mathews, Li-Sheng Choo, Heryani Binte Ahmad, Lydia H. Wong, Subodh G. Mhaisalkar
"Decoupling Optical and Electrical Contributions of Titanium Suboxide Interlayer to Photocurrent in Organic Bulk Heterojunctions"
Chemical Physics Letters (Under Revision)

[4] **Than Z. Oo**, Nripan Mathews, Wei Lin Leong, Li-Sheng Choo, Kwan Yue Chau, Tze C. Sum, Alfred C. H. Hujan, Lydia H. Wong, Subodh G. Mhaisalkar

“Role of Titanium oxide in High Efficiency Bulk Heterojunction Organic Solar Cells: Correlating Charge Injection and Surface Segregation”

Journal of Materials Chemistry (Submitted)

[5] **Than Z. Oo**, Devi Chandra R Panicker, Natalia Yantara, Rajiv Ramanujam Prabhakar, Lydia H. Wong, Nripan Mathews, Subodh G. Mhaisalkar

“Zinc Tin Oxide (ZTO) Electron Transporting Buffer Layer in Inverted Organic Solar Cell”

Organic electronics (Accepted)

[6] Mrunal. A. Khaderbad, Verawati Tjoa, **Than Z. Oo**, Jun Wei, Madhu Sheri, Ravikanth Mangalampalli, V. Ramgopal Rao, Nripan Mathews, Subodh G. Mhaisalkar

“Facile fabrication of graphene devices through metalloporphyrin induced photocatalytic reduction”

RSC Advances (Under review)

[7] Bo Wu, Xinfeng Liu, **Than Zaw Oo**, Guichuan Xing, Nripan Mathews and Tze Chien Sum

“Resonant Aluminum Nanodisk Array for Enhanced Tunable Broadband Light Trapping in Ultra-thin Bulk Heterojunction Organic Photovoltaic Devices”

Plasmonics (Under review)

Conference presentations

[1] **Than Zaw Oo**, Teck Lip Tam, Lydia Helena Wong, Nripan Mathews, Subodh Mhaisalkar, Alan Sellinger

“Structural, optical and morphological properties of poly (p-phenylene vinylene) based polymer/oligomer blends for organic photovoltaics applications”

International conference on Materials for advanced technologies ICMAT, Singapore, (2009)

Oral presentation (A00921-01677)

[2] **Than Zaw Oo**, Nripan Mathews, Teck Lip Tam, Gui Chuan Xing, Tze Chien Sum, Lydia Helena Wong and Subodh Mhaisalkar

“Energy and charge transfer processes within PPV- based polymer/oligomer blends for organic photovoltaics cells”

2nd AUN/SEED-Net regional conference on materials engineering: materials for changing world, Chonburi Thailand, (2009)

Oral presentation

[3] **Than Zaw Oo**, Firdaus Bin Suhaimi, Choo Li-Sheng, Nripan Mathews, Lydia H Wong, Subodh G Mhaisalkar

“The Role of Titanium Suboxide Layer in Single and Stacked Organic Photovoltaic Cells”

2nd International Conference on Science and Engineering (ICSE), Yangon Myanmar, (2010)

Proceeding Vol. 3, Page 188 (Awarded The Best Presenter)

Posters

[1] **Than Zaw Oo**, Nripan Mathews, Huajun Feng, Bengang Xing, Lydia H. Wong, Subodh G. Mhaisalkar

“Surface plasmon enhanced organic photovoltaic devices with gold nanowires”

4th MRS-S conference on advanced materials, IMRE Singapore, (2010)

Poster (P130)

[2] **Than Zaw Oo**, Nripan Mathews, Guichuan Xing, Bo Wu, Bengang Xing, Lydia H. Wong, Tze Chien Sum, Subodh G Mhaisalkar

“Ultrafine Gold Nanowire Networks for Surface Plasmon Enhanced Organic Photovoltaics”

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[3] Bo WU, Liu Xing Feng, Liew Hwi Fen, **Than Zaw Oo**, Li Xianglin, Xing Guichuan, Fan Hongjin, Lew Wen Siang, Nripan Mathews, Sum Tze Chien

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