Broadband light absorption enhancement in organic solar cells

Qingyi Yang

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Broadband Light Absorption Enhancement in Organic Solar Cells

YANG Qingyi

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

Principal Supervisor: Prof. ZHU Fu Rong

Hong Kong Baptist University

August 2014
Declaration

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

Signature: ______________________

Date: August 2014
The aim of this thesis was to undertake a comprehensive research to study the broadband light absorption enhancement in organic solar cells (OSCs) with different nano-structures, thereby improving short-circuit current density and efficiency. Absorption enhancement in OSCs having different photonic structures, compared to the control planar cell configuration, was analyzed and studied using the optical admittance analysis and finite-difference time-domain (FDTD) method. After a brief overview of the latest progresses made in OSCs, the basic optical principles of light scattering, surface plasmon polaritons (SPPs), localized surface plasmon resonance (LSPR), diffraction effect and waveguide mode, that had been employed for light trapping in OSCs, are discussed.

Optical admittance analysis reveals that light absorption in inverted OSCs, based on polymer blend layer of P3HT:PCBM, is always greater than the conventional geometry OSCs fabricated using an ITO/PEDOT:PSS anode. The inverted bulk heterojunction OSCs, made with a pair of an ultrathin Al-modified ITO front cathode and a bi-layer MoO3/Ag anode, exhibited a superior power conversion efficiency (PCE) of 4.16%, which is about 13% more efficient than a control normal OSC. It is shown that the reverse configuration allows improving charge collection at cathode/blend interface and also possessing a dawdling degradation behavior as compared to a control regular OSC in the accelerated aging test.

Light absorption enhancement in ZnPc:C60-based OSCs, made with substrates having different structures, for example, surface-modified Ag nanoparticles and 1-D photonic structures, was analyzed. The effect of an ultra-thin plasma-polymerized fluorocarbon film (CFx)-modified Ag nanoparticles
(NPs)/ITO anode on the performance of OSCs was optimized through theoretical simulation and experimental optimization. This work yielded a promising PCE of 3.5 ± 0.1%, notably higher than that with a bare ITO anode (2.7±0.1%). The work was extended to study the performance of OSCs made with CFx-modified Ag NPs/ITO/polyethylene terephthalate (PET) substrate. The resulting flexible OSCs had a relatively high PCE of 3.1±0.1%, comparable to that of structurally identical OSCs fabricated on ITO-coated glass substrate (PCE of 3.5±0.1%). The distribution of the sizes of the Ag NPs, formed by the thermal evaporation, was over the range from 2.0 nm to 10 nm. The results reveal that the localized surface plasmon resonance, contributing to the broadband light absorption enhancement in the organic photoactive layer, was strongly influenced by the size of Ag NPs and the dielectric constant of the surrounding medium.

A new OSC structure incorporating a transparent PMMA/ITO double layer grating electrode was also developed. 1-D PMMA/ITO double layer grating, fabricated using nano-imprinting and low processing temperature ITO sputtering method, has a period of 500 nm. Light absorption in grating OSCs under TM, TE and TM/TE hybrid polarizations was calculated using FDTD simulation in the wavelength range from 400 nm to 800 nm. We profiled the electric field distribution and analyzed the structural requirement for confining the waveguide modes in the organic photoactive layer. The effects of the periodicity and the pitch size on light scattering, simultaneous excitation of horizontally propagating SPPs, LSPR and the waveguide modes for light harvesting in grating OSCs were analyzed. The efficiency enhancement in the grating OSCs (PCE 3.29%) over the planar control device (PCE 2.86%) is primarily due to the increase in the short-circuit current density from 11.93 mA/cm² to 13.57 mA/cm² (13.7% enhancement). The theoretical results agree with the experimental findings in showing that the improved performance in grating OSCs is attributed to the absorption enhancement in the active layer.
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<td>OSC</td>
<td>Organic solar cell</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>NREL</td>
<td>National Renewable Energy Laboratory</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye-sensitized solar cell</td>
</tr>
<tr>
<td>QDSC</td>
<td>Quantum dot solar cell</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>J–V</td>
<td>Current density–voltage</td>
</tr>
<tr>
<td>AM</td>
<td>Air mass</td>
</tr>
<tr>
<td>J_{SC}</td>
<td>Short-circuit current density</td>
</tr>
<tr>
<td>V_{OC}</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident photon-to-electron conversion efficiency</td>
</tr>
<tr>
<td>I_{SC}</td>
<td>Short-circuit current</td>
</tr>
<tr>
<td>FDTD</td>
<td>Finite-difference time-domain</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite element method</td>
</tr>
<tr>
<td>RCWA</td>
<td>Rigorous coupled-wave analysis</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflection</td>
</tr>
<tr>
<td>SPP</td>
<td>Surface plasmon polariton</td>
</tr>
<tr>
<td>LSPR</td>
<td>Localized surface plasmon resonance</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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</table>
VASE Variable angle spectroscopic ellipsometry
TPC Transient photocurrent
XPS X-ray photoelectron spectroscopy
TCO Transparent conductive oxide
AZO Aluminum-doped zinc-oxide
ITO Indium tin oxide
MoO₃ Molybdenum oxide
ZnO Zinc oxide
TiO₂ Titanium dioxide
V₂O₅ Vanadium pentoxide
AlOₓ Oxidized aluminum
FTO Fluorine doped tin oxide
CFₓ Fluorocarbon
PET Polyethylene terephthalate
PATs Poly(alkyl-thiophenes)
CuPc Copper phthalocyanine
ZnPc Zinc phthalocyanine
PPV Poly(p-phenylenevinylene)
PT Polythiophene
PVK Poly(N-vinylcarbazole)
PANI Polyaniline
MEH-PPV Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]
MDMO-PPV Poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene]
P3HT Regioregular poly(3-hexylthiophene)
PCDTBT Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4,7-di-2-thienyl-2',1',3'-benzothiadiazole)]
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>PTB7</td>
<td>Poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl})</td>
</tr>
<tr>
<td>C_{60}</td>
<td>Fullerene</td>
</tr>
<tr>
<td>C_{61}-PCBM</td>
<td>[6,6]-phenyl-C61-butyric acid methyl ester</td>
</tr>
<tr>
<td>C_{71}-PCBM</td>
<td>[6,6]-Phenyl C71 butyric acid methyl ester</td>
</tr>
<tr>
<td>ICBA</td>
<td>Indene-C_{60} bisadduct</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate</td>
</tr>
<tr>
<td>BCP</td>
<td>2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline</td>
</tr>
<tr>
<td>BPhen</td>
<td>4,7-diphenyl-1,10-phenanthroline</td>
</tr>
<tr>
<td>LiF</td>
<td>Lithium fluoride</td>
</tr>
<tr>
<td>CB</td>
<td>Chlorobenzene</td>
</tr>
<tr>
<td>DCB</td>
<td>1,2-Dichlorobenzene</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl alcohol</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
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Chapter 1: Introduction

1.1 Background of Photovoltaic Energy

As the world's energy demands grow continuously along with the evolution of economization and globalization, the issue of energy supply has become a hotly debated topic in the area of sustainable development of society. According to the survey from World Energy Council, energy resources could be classified into fossil resources (coal, oil, both conventional and unconventional gas) and renewable or transitional resources such as peat, nuclear and uranium, hydro power, bio-energy and waste, wind, solar, geothermal and marine energies. Fig. 1.1 \(^1\) shows the global primary energy supply in the years of 1993, 2011 and 2020, with the unit for energy being million tons of oil equivalent (Mtoe). Traditional fossil resources (coal, oil and natural gas) dominate the global energy consumption but there are still obstacles for them. Burning coal or oil produces massive particulates and carbon dioxide which is the largest contributor to the greenhouse effect. Natural gas is considered as a relatively cleaner fossil fuel but it requires huge investment in transportation and delivery. Nuclear resource remains a small share of the total energy supply and the future is bound up with technological advance and public acceptance. In future, with an increasing world population and a developing electrification particularly the information technology industry, shortage of energy sources will become more evident. Despite the large consumption of traditional fossil fuels, it is imperative to investigate and develop the renewable energy resources including wind, solar, geothermal and marine energies and so on.

Solar energy is the most abundant renewable resource, and it can be directly transformed to electrical energy by photovoltaic technology. According to the statistics from International Energy Agency, the total amount of solar energy reaching on the earth’s surface every year is $3.8 \times 10^{24}$ joules $^{[2]}$, while the annual total global energy consumption in 2013 is about $5 \times 10^{20}$ joules. With the aim to utilize this inexhaustible energy resource, photovoltaic technology was getting off the ground in the very early year of 1839 when A. E. Becquerel invented the first photovoltaic device $^{[3]}$. In 1954, D. M. Chapin, C. S. Fuller and G. L. Pearson from Bell Laboratories reported the first p-n junction based silicon solar cell achieving an efficiency of about 6% $^{[4]}$. Up to the present day, significant progresses in photovoltaic technology have been made for applications varying from power generation to aerospace exploration. The global cumulative installed photovoltaic capacities have exceeded 100 gigawatts (GW) with a constant
growth from 2000 to 2012, as shown in Fig. 1.2. Photovoltaic research has been devoted to multiple types of solar cells based on various materials and structures such as III-V multijunction cells, single-junction GaAs cell, crystalline Si cells, thin film cells (copper indium gallium selenide, amorphous Si:H, etc.) and emerging photovoltaic technologies including dye-sensitized solar cells (DSSCs), quantum dot solar cells (QDSCs) and organic solar cells (OSCs). Fig. 1.3 summarizes the best research-cell efficiencies of different solar cells by 2014 from National Renewable Energy Laboratory (NREL). Silicon solar cells are the most prevalent and commercialized photovoltaic technologies which are usually based on crystalline silicon, amorphous silicon (a-Si or a-Si:H), polycrystalline silicon or nanocrystalline silicon. With relatively high efficiency and good performance stability, silicon solar cell shares about 90% of the market. In recent decades, new solar cells such as DSSCs, QDSCs and OSCs have been developed rapidly. Between them, OSCs are experiencing a boost of efficiency in the last few years and show great potential in electricity generation.

1.2 Challenges of Organic Solar Cells

OSC s have attracted much attention due to several advantages such as large scale solution fabrication process at low cost and have leaped forward in a relatively short period of time. From 1950s to 1960s, there are wide studies on photovoltaic effect of organic dye materials such as methylene blue [5], anthracene [6], magnesium phthalocyanines (getting 200 mV voltage sandwiched in glasses) [7] and copper phthalocyanines (rectifying effect with metallic electrodes) [8]. Since that time, the evolution of organic photovoltaic technology has been connected with the organic materials from dyes to conjugated polymers and the device structures such as bi-layer heterojunction, bulk heterojunction and tandem structure.

In 1975, C. W. Tang and Albrecht built a single layer OSC based on the chlorophyll–a (Chl-a) dye material with different metallic electrodes. The optimized device structure was Cr/Chl-a/Hg resulted in a power conversion
efficiency (PCE) of 0.01% \(^9\). Beginning from 1958, polymer materials, which mainly mean polyacetylene \(^{10}\), the poly(alkyl-thiophenes) (PATs) \(^{11}\) and poly(pphenylenevinylene) (PPV), are intensively studied. In 1993, S. Karg and co-workers\(^{12}\) reported a single layer OSC based on PPV polymer with a PCE of 0.1%.

The first bi-layer heterojunction based OSC was introduced by C. W. Tang\(^{13}\) in 1986, using copper phthalocyanine and perylene derivative as donor and acceptor materials \(^{14}\). The two layer OSC resulted in a PCE of ~1% under (air mass) AM2 illumination and a fill factor of 0.65. In 1995, Sariciftci fabricated the first polymer/fullerene based heterojunction cell with a PCE of 0.04\% \(^{15,16}\). Subsequently in 1995, the polymer/polymer heterojunction OSCs based on PPV derivatives were reported by G. Yu\(^{17}\) and J. J. M. Halls\(^{18}\).

To date, with the innovation of organic materials, deeper understanding of device physics and advanced device structure design, the best efficiency of OSCs has reached 12\% \(^{19}\) and that for the organic tandem cells also achieves a PCE of 10.6\% in 2013 \(^{20}\). In future, the performance of OSCs will be further improved by diversified research work from physics, chemistry and engineering area. OSCs will be attractive due to their large area processing flexibility, the distinctive features of organic photoactive materials with tunable optical and electronic properties tailored for photovoltaics. The following is a summary of the advantages of OSCs.

- OSCs are an attractive alternative to silicon based solar cells due to solution fabrication processes and the potential of low manufacturing cost at ~$100/m^2 \(^{21}\).

- Flexible OSCs with light weight can be achieved ascribed to the nature of organic materials, which give the convenience of easy transport, installation and portability compared to the traditional rigid and heavy solar panels.
Semi-transparent OSCs are realizable for application in power generation windows, tension membrane, etc.

There are massive organic materials which can be synthesized and tailored to absorb different wavelength range or for other utilizations.

The commercialization of OSCs is determined by three key factors: efficiency, lifetime and cost. In this thesis, the research was focused on broadband light absorption enhancement in OSCs, thereby improving their short-circuit current density and PCE.

1.3 Objectives

The efficiency of OSCs is limited by many factors related to both optical and electrical aspects. Firstly, light absorption in OSCs is limited due to the low charge carrier mobility of organic materials. Increasing the thickness of the organic layer will attenuate the collection of charge carriers. Consequently, there is a mismatch between optical absorption length and charge transport scale of the organic material and light absorption is restricted resulting in suppressed performance of OSCs.

One solution for this issue is to enhance light trapping in organic materials by new design of device structure. One approach is the optimization of planar OSCs. Using optical admittance analysis, the thickness and materials selection of each layer in planner OSCs can be determined for enhanced light absorption due to interference effect. Another approach is the utilization of photonic structures of the OSCs. Metallic nanoparticles (NPs), nano-grating structures, metallic nanowires and other structures are incorporated in the device to achieve light absorption enhancement, which actually increases the effective thickness of the devices without impairing the electrical properties. Introduction of these photonic
structures brings about new optical phenomena such as scattering effect, surface plasmon resonance, diffraction effect, which will be discussed in detail in the next chapter.

The aim of this research was to achieve broadband light absorption enhancement in OSCs incorporating nanostructure-modified electrodes and photonic structures. The method to enhance light absorption in OSCs is related to two aspects: light distribution and light intensity. For planer structure, these two aspects aimed to improve absorption enhancement via interference effect. For photonic structured OSCs, thermal evaporated Ag NPs and nano-imprinted grating substrate were used, generating surface plasmon resonance effect and diffraction effect to alter light distribution and intensity.

Besides, the optical principles in OSCs require earnest investigation, especially for surface plasmon resonance effect and diffraction effect. In optics research area, there are already intensive study on metallic NPs and nano-grating. But when these objects are applied in organic materials as dispersive mediums with varied refractive index and extinction coefficient, new issues related to practical application will arise. Although the photonic structures designed in inorganic solar cells are widely reported, OSCs with only several hundred nanometer thick active layer, will be more sensitive to the interference of light and other optical phenomena. Therefore, the work was focused on investigating the mechanisms of the broadband light absorption enhancement in OSCs. Numerical simulations based on transfer matrix method and finite-difference time-domain method were used to study light propagation and absorption in photoactive organic layers. With the combination of theoretical simulation and experimental optimization, the physics of the broadband light absorption enhancement in OSCs was interpreted, which can instruct the design rules of other OSCs for better performance. The summarized objectives are shown in Fig. 1.4.
1.4 Organization of This Thesis

This thesis has seven chapters. Chapter 1 introduces the solar energy background, advantages and challenges of OSCs and the objectives for the research work. In chapter 2, the basic knowledge of OSCs is described, including the device structures, the familiar organic materials, the working principles of OSCs and their performance. Then, the approaches towards attaining broadband light absorption enhancement in OSCs are discussed, covering the optical principles of light scattering, surface plasmon polaritons, localized surface plasmon resonance, diffraction effect and waveguide mode.

In chapter 3, experimental procedures in the laboratory and the theory of numerical modelling are discussed. The processes of device fabrication include material formulation, substrate cleaning and modification, spin-coating method, thermal evaporation and magnetic sputtering, current density–voltage (J–V) characteristics and incident photon-to-electron conversion efficiency (IPCE) measurements, etc. Besides, the requisite setups such as ultraviolet photoelectron
spectroscopy, scanning electron microscope, variable angle spectroscopic ellipsometry, transmittance and reflectance measurement, are introduced. For numerical modelling, optical admittance analysis dealing with planar structured device and finite-difference time-domain method dealing with photonic structured device are presented.

Chapter 4 reports the understanding of light absorption enhancement in inverted OSCs. The P3HT:PCBM-based regular and inverted cells were fabricated for comparison studies. Optical admittance analysis demonstrates that the inverted cells always possess a higher light absorbance in the active layer compared to regular cells. Besides, the inverted OSCs also show a better electron collection efficiency, confirmed by transient photocurrent measurement and a much slower degradation process in device performance as compared to the regular OSCs.

In chapter 5, CFx-modified silver nanoparticles were applied to ZnPc:C$_{60}$-based OSCs fabricated on rigid or flexible substrate. Broadband light absorption enhancement in OSCs with Ag nanoparticles is achieved. The analysis of work function shows that the anode with CFx-modified Ag nanoparticles has a similar charge collection efficiency compared to the control device. Significant difference in the localized surface plasmon resonance wavelength of Ag nanoparticles with and without ZnPc:C$_{60}$ dielectric layer over-coated is observed and investigated in details.

Chapter 6 presents the ZnPc:C$_{60}$-based OSCs with front and rear grating electrodes. The substrate grating electrode is composed by the nano-imprinted poly(methyl methacrylate) layer and sputtered ITO in low temperature. Conformal coating of the other layers is achieved by thermal evaporation and the grating OSCs demonstrate an enhanced short-circuit current. Finite-difference time-domain method was used to investigate the surface plasmon polaritons and
waveguide effect due to the grating structures. In addition, modeling of absorption enhancement in two dimensional grating structured devices was carried out. Chapter 7 summarizes the results of experiments and theoretical simulation for realizing broadband light absorption in OSCs with different configurations and future research work with regard to this topic.
Chapter 2: Overview of Light Absorption Enhancement in Organic Solar Cells

2.1 Basics of Organic Solar Cells

2.1.1 Device Structure and Material Choices

This section provides a brief overview of OSC basics, device design to enhance light trapping, optical principles, photovoltaic effect and characterization of solar cells. Organic solar cell shares an analogous architecture and mechanism as compared to the traditional p-n junction based inorganic photovoltaic device. A typical structure of OSC is illustrated in Fig. 2.1. With the irradiation of the incident light from one side of the cell, active layer absorbs photons and generates charge carriers simultaneously. Electron charge carriers can travel freely and be collected by cathode eventually, while hole charge carriers are collected by anode. Usually there are interlayers sandwiched between cathode and active layer, and between anode and active layer used as electron transporting layer, hole blocking layer, hole transporting layer and electron blocking layer separately, realizing improved electrical and optical properties of the OSCs.
Fig. 2.1: Schematic structure of an OSC.

The general construction of an active layer is built on p-n junction concept by utilizing both p-type and n-type organic semiconductor materials. P-type organic material, or the donor material, donates light excited electrons to n-type organic material, thus holes dominate in the donor material. N-type organic material, or the acceptor material, accepts electrons as the majority carriers. Small molecule materials and conjugated polymers are two primary choices for active layer. Small molecules usually possess planar molecular geometries suitable for the formation of self-assembled polycrystalline thin film by using solution process or dry deposition process. Polymer materials refer to a branched molecule with a main chain structure constituted by repeated basic units and can be processed via dissolving in solution.

The key to the semiconductor characteristics of organic materials in active layer is the conjugation of carbon molecules, with carbon molecules being the bricks for organic material systems. The electrons occupying the \( p \) orbital of carbon atoms can form pi bonds (\( \pi \) bonds) and sigma bonds (\( \sigma \) bonds) as depicted in Fig. 2.2. An example of molecular structure of \( \text{C}_2\text{H}_4 \) is also presented. Because the electron clouds in \( \pi \) bonds are relatively far away from atomic nuclei with positive charges, \( \pi \) bonds are weaker than \( \sigma \) bonds in an organic molecule.
consisting of carbon atoms, there are single bond (one σ bond) or double bond (one σ bond and one π bond which is delocalized) between two carbon atoms. The word "conjugation" means alternating the single bond and the double bond, with the migration of electrons in the delocalized π bonds, which endows the conjugated system with semiconductor properties.

Fig. 2.2: π bond, σ bond and the molecular structure of C₂H₄.

From the perspective of energy level, which abstracts the quantized energy of electron, organic molecule possesses conduction band and valence band due to the splitting of energy levels. Band gap is determined by the energy difference between the lowest unoccupied molecular orbital (LUMO) level in the conduction band and the highest occupied molecular orbital (HOMO) level in the valence band. The positions of HOMO level and LUMO level are critical for the electrical properties of the organic molecule and the performance of OSCs, and they are important parameters guiding for the choice of materials.

A variety of organic materials have been investigated and utilized for the active layer. For p-type small molecule materials, the representatives are porphyrin, phthalocyanine and its derivatives, for example the copper phthalocyanine (CuPc) and zinc phthalocyanine (ZnPc) as shown in Fig. 2.3.
Conjugated polymers are widely employed as p-type materials for active layer such as poly(p-phenylenevinylene) (PPV), polythiophenes (PTs), poly(N-vinylcarbazole) (PVK) and polyaniline (PANI). Their derivatives represented by poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) based on PPV, regioregular poly(3-hexylthiophene) (P3HT) based on PT are extensively used in OSCs. In recent years, new conjugated polymers such as poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4,7-di-2-thienyl-2′,1′,3′-benzothiadiazole] (PCDTBT) and poly([4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b: 4,5-b′]dithiophene-2,6-diyl] {3-fluoro-2-[(2-ethylhexyl) carbonyl]thieno[3,4-b]thiophenediyl}} (PTB7) achieve better device performance with a PCE of more than 7% \[22\]. Fig. 2.4 summarizes the molecule structures of the commonly used p-type conjugated polymers.
For n-type small molecule materials, the most influential ones are perylene, fullerene (C$_{60}$), fullerene-C$_{70}$ and their derivatives namely [6,6]-phenyl-C61-butyric acid methyl ester (C$_{61}$-PCBM), [6,6]-Phenyl C71 butyric acid methyl ester (C$_{71}$-PCBM), with improved solubility for device fabrication. Another fullerene based derivatives indene-C$_{60}$ bisadduct (ICBA), mixing with P3HT polymer, could result in a PCE of 6.5% $^{[23]}$. The typical n-type small molecule materials are presented in Fig. 2.5.
In addition to the process flexibility, e.g., functional organic semiconducting layers that can be fabricated via solution-processed method and thermal evaporation, OSCs also enjoy an advantage of various choices of materials for anode, cathode and interlayer. Transparent conductive oxides (TCOs), such as aluminum-doped zinc-oxide (AZO) and indium tin oxide (ITO) with high transparency and low resistivity, are most commonly used for anode. While the cathode materials with low work function, e.g., Ag, Li, Ca and Al are usually used as the cathode in OSCs. For regular OSC structures, the hole transporting layers between anode and active layer have good optical transparency, for example, molybdenum oxide (MoO$_3$) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). Electron transporting layer such as Ca and zinc oxide (ZnO) or hole blocking layer such as 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), 4,7-diphenyl-1,10-phenanthroline (BPhen) and lithium fluoride (LiF) can also be unitized for improving the electrical and optical properties of OSCs.

Accompanied by the development of OSC materials, the design of device
structures has experienced an increasing diversity. Classified according to the difference of active layers, there are single layer OSC, bi-layer OSC and bulk heterojunction OSC as depicted in Fig. 2.6. Single layer OSCs only employ one type of small molecule or polymer for carriers generation and is not practical with a PCE of less than 0.1%\textsuperscript{[24]}. The active layer of bi-layer OSC contains p-type and n-type organic layer working as electron donor and acceptor. To extend the interfacial area between the donor and acceptor, bulk heterojunction OSCs with better device performance can be fabricated by blending the p-type and n-type materials\textsuperscript{[25]}.

The basic device structures, shown in Fig. 2.6, are commonly used in single junction OSCs. Fig. 2.7 presents other structures: tandem, inverted and semitransparent OSCs. To achieve wider range of light absorption spectrum, tandem OSC is used by stacking two cells in series. By covering different wavelength range, the absorption spectra of top cell and bottom cell are usually complementary\textsuperscript{[26]}. Intermediate layer between the two cells plays a role of charge recombination zone and reducing the current mismatch factor of the two cells is crucial for the device performance.
For conventional OSCs, the glass substrate is usually coated with a transparent anode layer for the construction of regular structure. Inverted OSCs can be achieved by fabricating the transparent cathode layer on the substrate, thus illumination is from the cathode side. Inverted OSCs show improved device performance for certain material system. One reason is that the n-type materials such as C60 favor sedimentation in solution fabrication process. This benefits better interfacial contact with cathode layer in inverted structure. In addition, conventional hole transporting layers, e.g., PEDOT:PSS, which introduce instabilities at the interface with ITO, can be removed, resulting in extended device lifetime.

Semitransparent OSCs [27] were proposed with the potential for application in functional window, sensor, tandem OSCs, etc. The transparent top electrode can be built by using metallic nanowires [28], multilayer composed of TCO and thin metallic thin film with several tens of nanometer thick [29]. For instance, the P3HT:PCBM based OSCs [30], with a structure of ITO/titanium dioxide (TiO2)/P3HT:PCBM/ MoO3/Ag/vanadium pentoxide (V2O5) with 10 nm Ag and 40 nm V2O5 layer could achieve a PCE of 1.83% and a transmittance of 90% in the visible light range. For the design of semitransparent OSCs, the trade-off between the transmittance and absorbance of the device is considerable, and
2.1.2 Principles of Photovoltaic Energy Conversion

The energy conversion process for photons to electrons in OSCs consists of four main steps: light absorption and exciton generation, exciton diffusion, charge separation and charge transport. Fig. 2.8 is the energy diagram of a general device structure including anode, donor, acceptor and cathode layers, together with the schematic plot for the interface between donor and acceptor, which represents the formation and transport of exciton and carrier. The following are the details of each step.

![Energy Conversion Diagram](image)

**Fig. 2.8: Schematic diagram of energy conversion processes in OSCs.**

1) Light absorption and exciton generation:

When incident light penetrates into active layer with the photon energy \( E = h\nu \), where \( h \) is Planck constant and \( \nu \) is the frequency of light, not less than the band gap between LUMO and HOMO of the active layer material (usually from 1.5 eV to 3.5 eV), electrons at the HOMO level can be excited into LUMO level and create holes in the prior position. As a result of photo-excitation process, excitons are generated. Due to a low dielectric constant of the organic material,
the excitons are strongly bound by Coulomb force with the energy from 200 meV to 500 meV \[^{31,32}\]. The energy loss mechanism in this step is the attenuation of light ascribed to the reflection at the interface of each layer in OSC and the recombination of excitons \textit{in situ}.

2) Exciton diffusion:

Excitons can drift within one polymer chain and shift to another chain, with a similar case for small molecule materials. The exciton diffusion length is approximately tens of nanometers. Quenching of excitons due to radiative and non-radiative recombination will occur if the excitons fail to arrive at the interface of donor and acceptor within the lifetime. Therefore exciton diffusion process restricts the thickness of active layer and significantly influences the PCE of device. The energy loss mechanism in this stage is the exciton recombination during diffusion.

3) Charge separation:

The energy difference between the LUMO levels of donor and acceptor applies a relatively strong electric field at the interface, which can dissociate the excitons into free electrons and holes. Electrons in donor transfer from LUMO of donor to LUMO of acceptor while holes remain in HOMO of donor. The process of exciton dissociation is accomplished in a time-scale of tens of femtoseconds, much faster than other exciton release mechanisms like photoluminescence \[^{33}\]. The energy loss in this charge separation step is due to recombination of electrons and holes at the interface of donor and acceptor.

4) Charge transport:

In general OSCs, the cathode with a low work function and the anode with a relatively high work function can yield a built-in electric field determined by the potential energy difference. Photo-generated electrons and holes transport to
cathode and anode separately under the electric field. The charge mobility of organic materials are usually in the range from $10^{-1}$ cm$^2$/Vs to $10^{-7}$ cm$^2$/Vs \cite{34}. With the ohmic contact between the cathode and LUMO of acceptor, together with a small potential barrier between the anode and HOMO of donor, free charge carriers are collected by the electrodes eventually. The energy loss mechanism in this step is the recombination of charges during the transport due to the limited charge mobility or at the electrode interface due to the potential barrier.

With the conversion from photons to electrons, OSCs can work as a current source with internal resistance and the feature of diode. Fig. 2.9 displays the equivalent circuitry diagram for a typical OSC connected with a load resistor. Constant current $I_G$, from a current source $G$, represents the total generated electrons and holes by excitons dissociation and does not count in any recombination of the carriers. Diode $D$ and shunt resistor $R_{SH}$ are parallel connected with $G$. Diode $D$ is attributed to the built-in electric field caused by the energy difference between HOMO of donor and LUMO of acceptor, resulting in asymmetric conductance of the device. $R_{SH}$ is determined by the recombination of electrons and holes at the donor/acceptor interface. Series resistor $R_S$ indicates the mobility of charge carriers in organic materials and other layers affected by electron traps and interfacial barriers in the device. For an ideal OSC, $R_{SH}$ should approach infinity and $R_S$ should tend to zero for best power supply properties. Equivalent circuit diagram builds up a bridge between the physical mechanisms in device and the characteristics of device which will be introduced in next segment.
2.1.3 Electrical and Optical Characteristics

One of the critical characteristics for OSCs is the J–V characteristic, which measures the current density from the cell at different biases under the illumination of standard solar spectrum. Generally, the intensity of the solar radiation that falls on an area above the atmosphere of the earth is approximately 1353 W/m\(^2\). The incident angle of solar radiation determines the travel distance through the atmosphere to the ground. This condition can be defined by the AM coefficient followed by a value 1/cos\(\theta\), where \(\theta\) is the zenith angle of the solar radiation in degrees. The AM1.5G solar spectrum is most commonly used for the J–V characteristic measurement. It represents an optical path which is 1.5 times the thickness of the atmosphere, when the sun is at an angle of 48.2\(^{\circ}\) above the horizon and results in a solar flux of 1000 W/m\(^2\). The AM1.5G solar spectrum and the definition of AM coefficient are shown in Fig. 2.10.
Fig. 2.10: AM1.5G solar spectrum and the definition of AM coefficient.

By fixing light intensity and measuring the current with applied voltage, J–V characteristics can be depicted as the solid curve in Fig. 2.11. In the J–V characteristics, point (1) refers to the short-circuit current density (J_{SC}). With applied voltage being zero and the absence of external resistance, J_{SC} is a good indication of photo-current. Point (2) implies the open circuit voltage (V_{OC}), which is the maximum voltage between cathode and anode. The output power of the device in a unit area (in cm^2) is the product of the current density and voltage. At a particular point (3), the output power reaches a maximum P_{max} while the blue shadow rectangle in Fig. 2.11 varies to the largest area. The dashed curve in Fig. 2.11 is the J–V characteristics measured in the dark, which can be used to diagnose the diode property and to extract the R_{SH} value by calculating the slope of J–V characteristics at open circuit condition.
Fig. 2.11: Typical J–V characteristics for OSCs.

One essential parameter to describe the non-linear electrical property of device, namely fill factor (FF), is defined by Eq. 2.1:

$$\text{FF} = \frac{P_{\text{max}}}{J_{\text{SC}} \times V_{\text{OC}}}.$$  \hspace{1cm} (2.1)

PCE (\(\eta\)) is the ratio of \(P_{\text{max}}\) to incident light power \(P_{\text{in}}\) and can be calculated using Eq. 2.2:

$$\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{J_{\text{SC}} \times V_{\text{OC}} \times \text{FF}}{P_{\text{in}}}.$$  \hspace{1cm} (2.2)

For J–V characteristic measurement, PCE will depend on the intensity of incident light, light spectrum and the temperature of device. The standard reporting condition uses AM1.5G spectrum with the incident light power per square centimeter being 100 milliwatts per centimeter squared (mW/cm\(^2\)) at 25℃.

Another characteristic of OSCs revealing both electrical and optical properties of the cells, is the spectral responsivity named external quantum efficiency or IPCE. With irradiation of the subsequently varied monochromatic light, the short-circuit current (\(I_{\text{SC}}\)) of the cell is measured. Via mathematical analysis, the ratio of the collected electrons to a certain amount of incident photons can be calculated, which indicates the spectral response of the cell to the
illumination at a specified wavelength and defines the IPCE as Eq. 2.3:

\[
\text{IPCE} = \frac{n_e}{n_{ph}} = \frac{I_{sc}hc}{P_0\lambda e}.
\]

where \(n_e\) and \(n_{ph}\) are the number of collected electrons and incident photons respectively, \(h\) is the Planck constant, \(c\) is light speed, \(P_0\) is the incident optical power without regard to irradiated area, \(\lambda\) is the wavelength and \(e\) is the electron charge.

![Typical IPCE for two different OSCs.](a)

The typical IPCE measured for practical OSCs are shown in Fig. 2.12 \[^{35}\]. IPCE provides diagnostic information for the exciton dynamic process and light absorption in OSC. The \(J_{sc}\) measured in J–V characteristics can also be calibrated by the convolution of IPCE spectrum and light source spectrum. The measuring methods of the J–V and IPCE characteristics will be discussed in chapter 3.

### 2.2 Approaches Towards Attaining Broadband Light

**Absorption Enhancement in Organic Solar Cells**

Through the development of basic OSCs, much attention has been focused on improving light absorption enhancement in OSCs by optimizing the thickness of
each layer or incorporating metallic nanoparticles, metallic nanowires, nano-grating structures and other nanostructures. The elementary optical principles for attaining light absorption enhancement are light scattering and light wave interference which can be applied to different conditions. For planar OSCs, the optical properties in the cells mainly refer to transmission, reflection and interference of light. For photonic-structured OSCs, the mechanisms of absorption enhancement in OSCs usually involve with surface plasmon resonance and diffraction effect. The physics of these phenomena will be discussed in this section and the research work achieving light absorption enhancement in OSCs will be reviewed in next section.

Before starting, one thing needed for special attention is the essential understanding of light, which refers to light absorption in OSC and also is the prerequisite for optics theories. Based on the wave-particle duality, light can be regarded as light wave described by the wave equation, $E = E_0 \cos(\omega t - kr)$, where $E$ is the electric field. In the view of particle property, the concept of photon is introduced with the energy $E_{\text{photon}} = h\nu$, where $h$ is Planck constant and $\nu$ is the frequency. The optics theories such as transmission, reflection and diffraction applicable for the OSCs are usually based on the wavelike behaviors of light, which is also the supposition for many theoretical modelling methods such as transfer-matrix method, finite-difference time-domain (FDTD) method, finite element method (FEM) and rigorous coupled-wave analysis (RCWA). But for light absorption in the organic active layer of OSCs, light is regarded as photons with the energy transferring to electrons. Hence, although rarely mentioned, there is no consistent numerical analysis method for light from the transmission to absorption in OSCs. One defaulted solution is light intensity. Here the "light intensity" refers to a radiometric quantity "irradiance" measured in watts per meter squared (W/m²), leaving aside the photometric quantity "luminous
intensity measured in candela (cd). For a monochromatic light, the value of intensity \( I \) can be approximated as \( I \approx \frac{cn\epsilon_0}{2}|E|^2 \), based on the wave property of light, where \( c \) is the speed of light in vacuum, \( n \) is the refractive index of medium, \( \epsilon_0 \) is the vacuum permittivity and \( E \) is the complex amplitude of the electric field of waves. From the prospect of particle property of light, intensity can be calculated as \( I = \frac{Nh\nu}{At} \), where \( A \) is the irradiated area and \( N \) is the number of photons irradiating in a time interval \( t \). Therefore, when novel designed device structure results in enhanced or redistributed light intensity, which can be confirmed by theoretical modelling methods on the basis of the wavelike behavior of light, the number of photons will be correspondingly increased or re-allocated leading to the enhanced light absorption in active layer of OSCs. This was also the aim of this thesis to achieve broadband light absorption enhancement in nano-structured OSCs, thereby improving short-circuit current density and efficiency through combination of experimental optimization and theoretical simulation.

### 2.2.1 Light Scattering

Light scattering usually means the deviation of the propagation direction of light due to the irregularities in the medium. The elastic scattering such as Rayleigh scattering and Mie scattering refers to very tiny energy transfer and the scattered light remains the same wavelength. Another type of light scattering is the inelastic scattering which involves in the rotational energy level, vibrational level of molecules and atoms, the lattice vibration or other forms of particle movement, causing the frequency shift of the scattered light. Representative elastic scattering includes Brillouin scattering, Raman scattering, Compton scattering, etc.
The primary comprehension of light scattering starts from Rayleigh scattering which occurs when the size of the scatterer is optically much smaller than the wavelength of light and described as the root mean squared radius of the particle \( \sqrt{\langle s \rangle^2} < \lambda/20 \), where \( \lambda \) is the wavelength of light. As shown in Fig. 2.13(a), for incident light polarized in z direction and propagating along x direction, the electric field at the position of the particles is:

\[
E_z = E_0 \cos\left(\frac{2\pi ct}{\lambda}\right),
\]  

(2.4)

where \( E_0 \) is the amplitude, \( c \) is the speed of light, \( t \) is time and \( \lambda \) is the wavelength. In the particle, the dipole will be excited with the applied electric field and the dipole moment is:

\[
p = \alpha_p E_0 \cos\left(\frac{2\pi ct}{\lambda}\right),
\]  

(2.5)

where \( \alpha_p \) is the polarizability. The scattered light is regarded as the radiation from the dipole moment. In the position with a distance \( r \) from the particle and a zenith angle \( \theta_z \), the observed radiation \( E_s \) will be proportional to \( (\sin\theta_z)(1/r)(1/c^2)(d^2p/d^2t) \). Thus, the scattered light intensity \( I_s \) can be expressed as:

\[
I_s = (E_s)^2 = \left(\sin\theta_z\right)^2 \left(\frac{1}{r} \frac{d^2p}{c^2 dt^2}\right)^2 = I_0 \frac{16\pi^4 \alpha_p^2}{r^2 \lambda^4} \sin^2\theta_z,
\]  

(2.6)

where \( I_0 \) is the intensity of the incident light.

For the unpolarized incident light, as illustrated in Fig. 2.13(b), \( \theta, \theta_y \) and \( \theta_z \) are the angle between the observation direction and the x, y and z axis respectively, which follow the rule of \( \cos^2\theta + \cos^2\theta_y + \cos^2\theta_z = 1 \). The scattered light intensity is the summation of the equal parts of the scattered intensity \( \frac{1}{2} I_{sy} \) and \( \frac{1}{2} I_{sz} \) along y and z axis separately and can be calculated as:
\[ I_s = \frac{1}{2} I_{sy} + \frac{1}{2} I_{sz} = I_0 \frac{8\pi^4 \alpha_p^2}{r^2 \lambda^4} (\sin^2 \theta_y + \sin^2 \theta_z) = I_0 \frac{8\pi^4 \alpha_p^2}{r^2 \lambda^4} (1 + \cos^2 \theta). \]  

(2.7)

The Rayleigh scattering intensity is directly proportional to \(1/\lambda^4\) which can interpret the blue color of the sky. Fig. 2.13(c) is the shape of scattered light intensity depending on \(\theta\) for a small particle.

![Fig. 2.13: (a) The incident polarized light and (b) incident unpolarized light scattered by a small particle; (c) shape of scattered light intensity.](image)

With the increase in the size of the scatter, the characterization of light scattering should be renovated based on Rayleigh scattering. In 1908, German physicist Gustav Mie calculated light scattering by a spherical particle with the diameter comparable to the wavelength of light. Mie solution was developed and used to describe the scattering of the radiation by a dielectric sphere, which was in the form of an analytical infinite series with slow convergence. Mie scattering can derive the optical cross section, determining how much light is scattered and the form factor, depicting the spatial distribution of scattered light. The dependence of the scattered light intensity on wavelength is not as strong as Rayleigh scattering, which accounts for the white color of the colloidal suspension and the clouds.
Fig. 2.14(a) presents light scattering by a large particle and there are many polarized dipoles in the particle. Radiation from the dipoles is coherent. Therefore, interference of scattered wavelets from the dipoles can arise in certain spatial position and the variation of scattering with direction will be expected. Fig. 2.14(b) gives an example of the scattering diagrams for a small particle and a large particle. The enlargement of the particle size will lead to destructive interference resulting in reduced scattered light intensity, especially in the forward direction. For practical light scattering, the size and shape of the particle, which determine the phase relation of the scattered wavelets, will strongly significantly affect the scattering diagram.

![Diagram of light scattering](image)

Fig. 2.14: (a) Light scattering by a large particle; (b) scattering diagrams for a small particle and a large particle.

In a broad sense, light scattering shares a primary principle with most of the optical phenomena such as transmission and diffraction that can be introduced to OSCs. Based on the classical electromagnetic theory, light propagating in the dielectric medium excites dipoles in the atoms or molecules which can re-radiate. For absolutely homogeneous medium, no scattered light is observed due to the destructive interference of wavelets. With the density fluctuation of the medium or the existence of other particles, scattered electromagnetic field appears. The distinct interference of light results in different optical phenomena, for instance, light scattering, reflection, transmission, diffraction, etc.
2.2.2 Coupling of Surface Plasmon Polaritons and Localized Surface Plasmon Resonance

Surface plasmon polaritons (SPPs) refers to the coupling of the plasma oscillations of surface electrons in the metal ("surface plasmon") and the electromagnetic waves in the dielectric or air ("polariton"). With the excitation of SPPs, there are longitudinal density fluctuations of the surface electrons and electromagnetic waves can travel along the metal-dielectric or metal-air interface. As shown in Fig. 2.15, we assume that the field of SPP propagates along x axis while z axis is perpendicular to the metal-dielectric interface. The frequency $\omega$ of the SPP is bound to the wave vector $k_x$ along x direction by the dispersion relation $\omega(k_x)$.

![Fig. 2.15: Electromagnetic field of SPPs in the x direction.](image)

To acquire the dispersion relation $\omega(k_x)$, electric field of SPPs is firstly described by:

$$E = E_0^\pm \exp\left[+i(k_xx \pm k_zz - \omega t)\right],$$

where $E_0^\pm$ is the amplitude with + for $z \geq 0$ and - for $z \leq 0$, $k_z$ is the component of wave vector along z direction. In the dielectric medium 2 with dielectric constant $\varepsilon_2$ and the metal layer 1 with complex dielectric constant $\varepsilon_1 = \varepsilon'_1 + i\varepsilon''_1$, the wave vectors comply with the rule of:
\[ \varepsilon_i \left( \frac{\omega_i}{c} \right)^2 = k_i^2 + k_{z_i}^2, \quad i = 1, 2, \quad (2.9) \]

where \( c \) is the speed of light. According to the continuity of electric field at the metal-dielectric interface we get Eq. 2.10:

\[ \frac{k_{z1}}{\varepsilon_1} + \frac{k_{z2}}{\varepsilon_2} = 0, \quad (2.10) \]

The simultaneous system of Eq. 2.9 and Eq. 2.10 can be solved and we obtain that \( k_{z1} \) and \( k_{z2} \) are imaginary and \( k_x = k'_x + ik''_x \) is a complex with:

\[ k'_x = \frac{\omega}{c} \left( \frac{\varepsilon'_1 \varepsilon_2}{\varepsilon'_1 + \varepsilon_2} \right)^{\frac{1}{2}}, \quad (2.11) \]

\[ k''_x = \frac{\omega}{c} \left( \frac{\varepsilon'_1 \varepsilon_2}{\varepsilon'_1 + \varepsilon_2} \right)^{\frac{3}{2}} \frac{\varepsilon''_x}{2(\varepsilon'_1)^2}. \quad (2.12) \]

The imaginary part \( k''_x \) implies the internal damping of SPPs with energy being converted into heat. The propagation length of SPPs is defined as \( L_i = (2k''_x)^{-1} \).

Eq. 2.11 identifies the dispersion relation of SPPs which depends on the real part \( k'_x \). In the following, \( k'_x \) will be written as \( k_x \) in general.

Fig. 2.16(a) shows the curve of the dispersion relation \( \omega(k_x) \) for non-radiative SPPs. The excitation of SPP with certain \( \omega^{SPP} \) and \( k_x^{SPP} \) requires that the incident electromagnetic field possesses the equal frequency and wave vector with \( \omega^{light} = \omega^{SPP} \) and \( k_x^{light} = k_x^{SPP} \). For incident light at the planar metal-air interface with the angle of incidence \( \theta_0 \) as depicted in Fig. 2.16(b), the dispersion relation \( \omega(k_x) \) is \( \omega = \frac{c}{\sin \theta_0} \cdot k_x \), which lies in the shadow region in Fig. 2.16(a). Therefore, the dispersion relation lines of SPP and light cannot intersect each other, and SPP will not be excited.
Fig. 2.1: (a) Dispersion relation for SPP and light at the planar metal-air interface; (b) schematic diagram for irradiated planar metal-air interface.

To achieve the excitation of SPPs, two couplers could be utilized, namely grating coupler and attenuated total reflection (ATR) coupler. When light falls on the surface of grating at an angle $\theta_0$, a displacement of the wave vector $\Delta k_x$ will be generated due to the perturbation in the grating surface, which is expressed as:

$$k_x^{\text{light}} = \frac{\omega}{c} \sin \theta_0 \pm \frac{2\pi n}{a}, \quad (2.13)$$

where $n$ is the integer and $a$ is the grating period as depicted in Fig. 2.17(b).

The shift of $k_x^{\text{light}}$ could meet the requirements for the excitation of SPPs when $\omega^{\text{light}} = \omega^{\text{SPP}}$ and $k_x^{\text{light}} = k_x^{\text{SPP}}$, which is represented in Fig. 2.17(a) with the transition from point 1 to point 2. For the ATR coupler in Fig. 2.17(c), wave vector of the evanescent wave is $k_x^{\text{light}} = \frac{\omega}{c} \sqrt{\varepsilon_0} \sin \theta_0$ while for another configuration in Fig. 2.17(d), light at the metal-air interface has a wave vector of $k_x^{\text{light}} = \frac{\omega}{c} \sqrt{\varepsilon_1} \sin \theta_{\text{incidence}}$. Both of the two ATR couplers can excite SPPs at the metal-air interface.
Another mode of SPP is the localized surface plasmon resonance (LSPR) at the surface of metallic nano-sphere with a diameter much smaller than the wavelength of light. As illustrated in Fig. 2.18, density fluctuation of the electron cloud in the metal sphere is induced under the incident electromagnetic field. Distinct from the propagating electric field of SPPs in the grating coupler or ATR coupler, the field at the surface of the sphere is localized and LSPR exhibits a different dispersion relation. We use the quasi-static approximation \[^{36,37}\] and solve Maxwell’s equations to obtain the electric field $E_{\text{out}}(x, y, z)$ around the metal sphere as:

$$E_{\text{out}}(x, y, z) = E_0 \hat{z} - \left[ \frac{\varepsilon_m - \varepsilon}{\varepsilon_m + 2\varepsilon} \right] a^3 E_0 \left[ \frac{2}{r^3} (x \hat{x} + y \hat{y} + z \hat{z}) \right], \quad (2.14)$$

where $E_0$ is the amplitude, $\varepsilon_m$ and $\varepsilon$ are the dielectric constant of the sphere and the surrounding medium respectively, $a$ is the radius of the sphere.

Fig. 2.17: (a) Dispersion relation for the excitation of SPPs; (b) grating coupler; (c) and (d) two configurations for ATR coupler.
According to the denominator in Eq. 2.14, when $\varepsilon_m + 2\varepsilon = 0$ the electric field reaches the maximal value and LSPR will be excited. The dispersion relation of LSPR is described as Eq. 2.15\textsuperscript{[38]}:

$$\frac{\text{Re}(\omega_{LSP})}{\varepsilon} + \frac{L+1}{L} = 0,$$

where $L$ is the angular momentum of LSPR. For a small metal sphere satisfying quasi-static approximation, $L=1$, and LSPR is based on dipole mode. With the increase of the radius of the sphere, resonance with multi-pole mode will occur.

For both general SPPs and LSPR, one important feature of the surface plasmon is field enhancement effect resulted in large electromagnetic field enhancement that occurs in the vicinity of the metal surface, which can be applied to color-based biosensor, light emitting diode, solar cell, etc.

### 2.2.3 Diffraction Effect and Waveguide Mode

The general diffraction of light refers to the diverging of the original direction of propagation when light encounters an obstacle or a slit with the size comparable to the wavelength of light. The theoretical explanation of diffraction is based on the Huygens Fresnel principle, which regards each irradiated spatial point as a
source of the spherical wavelets and deduces that the form of the secondary wave is decided by the interference of these wavelets. From the prospect of observation, diffraction of light can be classified into Fresnel diffraction and Fraunhofer diffraction. The former one is the near-field diffraction observing the diffraction of spherical wave at a limited distance while the latter one is the far-field diffraction observing the diffraction of plane wave from infinite distance.

The elementary numerical analysis of diffraction is the single-slit diffraction as plotted in Fig. 2.19(a). Using Fraunhofer diffraction equation, the intensity of the diffracted light at a given angle $\theta$ is derived as:

$$I(\theta) = I_0 \left( \frac{\sin(d \frac{\theta}{\lambda})}{d \frac{\theta}{\lambda}} \right)^2,$$

(2.16)

where $I_0$ is the intensity of the incident light, $d$ is width of the single-slit. The diffraction grating such as the transmission grating or reflection grating, can diffract or split the incident light with periodic optical components as shown in Fig. 2.19(b). When light illuminate the grating with an incident angle $\theta_i$, the diffraction angle $\theta_m$ which denotes the maximum diffracted light intensity can be determined with the grating equation:

$$d(\sin \theta_m + \sin \theta_i) = m\lambda,$$

(2.17)

where $d$ is grating period, $m$ is an integer identifying the order of diffraction with the value of $0, \pm 1, \pm 2, \cdots$. The zeroth order with $m=0$ indicates the direction corresponding to the direct transmission or direct specular reflection by transmission grating or reflection grating respectively. The positive or negative $m$ specify other intensity maxima on both sides of the zeroth order.
Fig. 2.19: Diffraction of light by (a) single-slit and (b) reflection grating or transmission grating.

The configuration of transmission grating or reflection grating can be incorporated into OSCs by achieving nano-structured electrodes or active layer. Diffraction effect in solar cells will incline the direction of light propagation and extend the optical path length, resulting in light absorption enhancement of the device. Due to the diffraction effect, light can be coupled into waveguide mode when we regard the device as an optical waveguide with relatively high refractive index compared to the surrounding medium.

The conduction of light in the waveguide is based on total internal reflection. According to Maxwell’s equations and the boundary conditions, there are limited propagation mode and frequencies for light. The lowest allowed frequency for propagation in the waveguide is defined as cutoff frequency. The value of cutoff frequency depends on the parameters of the optical waveguide and is derived from the Helmholtz equation. For the simplest rectangular shaped waveguide, the cutoff frequency $\omega_c$ is described as:

$$\omega_c = c \sqrt{\left(\frac{m\pi}{a}\right)^2 + \left(\frac{n\pi}{b}\right)^2} ,$$

(2.18)

where $n$ and $m$ are the mode numbers, $a$ and $b$ are the width and height of the rectangular. For the waveguide mode in OSCs, the practical investigation is usually conducted with numerical modelling.
2.3 Optical and Optimal Design of Organic Solar Cells

2.3.1 Optimization of Single Junction and Tandem Organic Solar Cells

Based on the optical principles, designing of the device for light absorption enhancement has been widely investigated and reported. For planar device and tandem organic solar cells, light intensity distribution can be adjusted for the optimized light absorption by tuning the layer thickness of the device or adding optical spacer layer, which is based on interference of light such as micro-cavity effect. The optimized thickness of each layer is determined by theoretically modelling or experimental test. Fig. 2.20(a) presents the distinct electric field distribution in the CuPc:C$_{60}$ based devices with different layer thickness and configurations [39]. Except for the optical design of device, the trade-off between light absorption and carrier transport also requires deliberation, especially for tandem OSCs. The best efficiency of device is usually decided by practical device fabrication. Fig. 2.20(b) is a three dimensional picture for the generated current density of the front sub-cell (wine color) and back sub-cell (green color) depending on the layer thickness in a polymer tandem solar cell [40]. The matching of generated current from the sub-cells is critical for the performance of the tandem OSC.
2.3.2 Organic Solar Cells Incorporating Metal Nanoparticles

Metal nanoparticles (NPs) have been incorporated into OSCs for improved device performance. The usually Ag or Au NPs are blended in front interlayer, active layer or the back layer by solution process or physical vapor deposition methods. Enhanced \( I_{SC} \) of the devices with different metal NPs are widely reported, which is generally attributed to the scattering effect or enhanced local electric field around the NPs with LSPR phenomenon.

Fig. 2.20: (a) Electric field distribution in CuPc:C\textsubscript{60} based device at a wavelength of 626 nm; (b) generated current density of sub-cells as a function of the active layer thickness.

Fig. 2.21: (a) P3HT:PCBM based OSC with Au NPs; (b) introduction of Ag NPs.
Fig. 2.21 exhibits an example of plasmonic-enhanced OSCs based on P3HT:PCBM system \[^{[41]}\]. Au NPs with diameters of 30–40 nm were blended into the PEDOT:PSS buffer layer by solution process. Using Au NPs with a weight ratio of 20%, the highest PCE of 4.19% was achieved compared to a 3.48% PCE of the control device. In another work \[^{[42]}\] as shown in Fig. 2.21(b), introduction of Ag NPs at both organic/ITO and organic/cathode interfaces resulted in an increased in the efficiency. It is also revealed that the contribution from LSPR was more obvious when the active layer contacted with the Ag NPs directly. Generally for the OSCs with metallic NPs, there are relatively few discussions on the electrical contribution from the NPs. Besides, broadband enhancement in IPCE is frequently reported, which cannot be sufficiently explained by the narrow resonance peak of the LSPR spectrum. In this thesis, these issues will be studied and discussed in chapter 5.

### 2.3.3 Grating-structured Organic Solar Cells

One dimensional or two dimensional grating structures for OSCs can be realized by photolithography method, nano-imprint lithography method, laser interference holography method, etc. In Fig. 2.22(a), the one dimensional Ag grating strip with the 220 nm period is used as the substrate \[^{[43]}\]. Thermal evaporated CuPC:C_{60} active layer and other layers form the diffraction grating structure. Fig. 2.22(b) presents the polymer OSC with grating structure fabricated by laser interference lithography method \[^{[44]}\]. When the grating substrate possesses the optimal size parameters with 2 μm period and 300 nm height, the solution processed P3HT:PCBM active layer can be conformally coated on the subjacent grating.
For grating OSCs, the polarized TM and TE illuminations have different optical influences on the cells. The former may induce the SPP at the surface of metallic grating. The enhanced light absorption in device incorporated with grating are usually ascribed to the SPP effect or the coupled waveguide mode by the diffraction effect. The related work on the utilization of grating structures and the distinction of the optical mechanisms will be discussed in chapter 6.
Chapter 3: Experimental Optimization and Theoretical Simulation

In this chapter, the experimental basis for the general OSC fabrication processes will be described. Experimental facilities for material preparation, fabrication and characterization of OSCs are presented. For theoretical modelling, the methods of optical admittance analysis and FDTD are discussed.

3.1 Materials Formulation and Device Fabrication

Generally, the processing environments for the device fabrication are the glove box (MBRAUNMB 20/200) and the multi-chamber vacuum system. With leak-proof construction and filled with high purity nitrogen gas, glove box furnishes a protective atmosphere for the storage and processing of the organic materials or other types of materials. The gas composition in glove box can be maintained with H$_2$O < 1 parts per million (ppm) and O$_2$< 1 ppm, by using the gas circulatory system and gas purifier system which can remove water, oxygen and other solvents. In the laboratory, glove box is connected to the vacuum systems as a sequence of sample preparation chamber, evaporation chamber and sputtering chamber. This design can keep the cell from the contamination of the ambient moisture and oxygen, which may cause the degradation of the device performance. The samples can be transferred between vacuum chambers and glove box by the transmission rod.

3.1.1 Material and Substrate Preparation

For easily oxidized materials especially for organic materials, the storage is in the
glove box. Other materials such as oxide materials are stored in a dry box with a relative humidity < 20%. Solutions requiring low temperature, for example the dispersed silver nanoparticles in aqueous buffer, were kept in refrigerator with tight sealing.

Organic materials for the active layer of OSCs were formulated and prepared in advance of the device fabrication. For thermal evaporation, materials were loaded into quartz crucible, boron nitride crucible or boron nitride boat for different evaporating conditions. With regard to the wet processing such as spin-coating method, organic materials were dissolved inorganic solvents such as chlorobenzene (CB), 1,2-Dichlorobenzene (DCB) and toluene. A given mass of materials was weighed by an electronic analytical balance (SHIMADZU AUW 220). Subsequently the material was transferred to a clean vial, mixed in a specified volume of organic solvent and a magnetic stir bar. The formulation was prepared by complete dissolving the materials in the solvent using the digital stirring hotplate (Thermo Scientific Super Nuova) for 1-2 hr. The stirring frequency with 350 rpm and the setting temperature ranging from 60°C to 80°C helped to promote the solubility of organic materials in the solvents.

Another preparation work prior to the device fabrication is the substrate cleaning. The most usual substrate of device is the ITO coated glass, while other options are AZO or fluorine doped tin oxide (FTO) coated glass. The glass sheets were vertically placed in glassware filled with different solvents and was ultrasonically cleaned by the ultrasonic cleaner (Branson 2510-MTH). The steps for the usage of solvents are shown as follows.

- Firstly the substrates were soaked and ultrasonically cleaned in detergent for 30 min to remove large grained impurities and lipid impurities.
- Deionized water was then used to eliminate the residual of detergent and water-soluble stain for 30 min.
• Subsequently the substrates were cleaned by acetone for 20 min to remove the residual organic impurities on the surface of substrates.

• Ultimately the substrates were steeped in isopropyl alcohol (IPA) for 20 min, which can clean the remains of acetone and dissolve a wide range of non-polar compounds.

The cleaned substrates were blown dry with a high purity nitrogen beam and kept in an oven (Memmert UNE 200) at a temperature of 100 °C for further processing.

3.1.2 Surface Treatment

The wet-cleaned substrates were underwent surface plasma treatment in sample preparation chamber as shown in Fig. 3.1(a). The substrate was fixed on one side of the metal plate. The vacuum chamber was purged with stable gas flow at a given flow rate, maintaining a gas pressure of ~64 Pa. As the mechanism for plasma treatment presented in Fig. 3.1(b), the gas molecules will be ionized with the alternating voltage applied between the metal plates. The plasma is constituted of ions, radicals and metastable energetic particles on the surface of substrates can then be removed prior to the device fabrication.

Fig. 3.1: (a) Sample preparation chamber; (b) schematic diagram of surface plasma treatment process.
The benefits of surface plasma treatment include removing the organic contaminants and other small molecule adhesion to the substrate surface, wiping the adsorbed moisture, adding new functional molecular groups and improving the surface electronic properties of the substrate. Oxygen plasma treatment is most commonly used due to an obvious enhancement in the work function of the substrate. Besides, argon and fluorocarbon gas are also exploited for different applications. Another surface treatment method is cleaning the substrate by ozone in ultraviolet ozone cleaner.

3.1.3 Films Prepared with Solution Process

On the treated substrate, active layer and the interlayer can be fabricated by spin-coating method. Fig. 3.2(a) illustrates the steps for spin-coating process. The substrate was loaded on the stage of the spin-coater and was fixed by vacuum suction. A given volume of solution is dripped and deposited on the substrate by the pipettor. Subsequently, the stage with the substrate is spun at a certain spin speed usually ranging from 500 rpm to 3000 rpm. Excess solution was then ejected from the substrate and the fluid spreads out and coats the substrate surface. The fluid was stabilized when the viscous shear drag balances the centrifugal force due to rotational acceleration. During or after the spin coating step, solvent in the fluid was evaporated and a uniform thin film was formed. The thickness and property of the spin-coated thin film depends on various influencing factors such as the spin speed, the concentration of materials in the solution, the surface energy or polarity of the substrate surface and the air turbulence above the substrate.
3.1.4 Films Prepared by Thermal Evaporation and Sputtering

The interlayer, small molecule based active layer and electrode contact of OSCs were deposited using thermal evaporation in the evaporation chamber. Magnetron sputtering was also used for TCO deposition, as shown in Fig. 3.3(a) and Fig. 3.3(b) respectively.
Fig. 3.3: (a) Evaporation chamber and (b) sputtering chamber.

Configuration of the two facilities is schematically plotted in Fig. 3.4. Both of the two chambers are connected to the multi-chamber vacuum system, backed with mechanical pump and turbomolecular pump. Vacuum pressure in the chamber is measured by the resistance vacuum pressure gauge with a range of 100–0.1 Pa and the ionization high vacuum pressure gauge with a range of 0.1–1.0×10^{-6} Pa. The deposition rate of films is measured using a quartz crystal resonator, based on the piezoelectric effect of the crystal.

In the experiment, substrates were transferred from glove box to the vacuum chamber without exposure to air. For thermal evaporation method, functional materials such as ZnPc, C_{60} and MoO_{3} were evaporated using quartz crucibles, while the electrode materials such as Ag and Al were evaporated using a boron nitride boat. The source materials were evaporated from the heated crucible or boat and deposited on the substrate at a given deposition rate.
Fig. 3.4: Drawings showing the (a) evaporation chamber and (b) sputtering chamber.

For magnetron sputtering, argon gas was introduced into the chamber. Direct voltage or alternating voltage is applied between the negative metal plate adjacent with the target material and the positive metal plate fixed with the substrate, which ionizes the argon atoms. With the argon-ion ballistically impacting the target, material is sputtered from the target and deposited on the substrate for thin film formation.

3.2 Material and Device Characterization

3.2.1 Solar Simulator and Current Density–Voltage Characteristics

J–V characteristics of OSCs are the most imperative measurement for the fabricated device. Fig. 3.5(a) shows the photo picture of the calibrated solar simulator (SAN-EI ELECTRIC XEC-301S), integrated with the glove box, and the system for J–V characteristic measurement is illustrated in Fig. 3.5(b). The output of the solar simulator is firstly adjusted to the given light intensity by a
calibrated Si reference cell. Then with light exposure and a continuously varied voltage applied to the device, the output current is measured. For an OSC having a given area, J–V characteristics were calculated and plotted. The dark J–V characteristic measurement can also be carried out without irradiation.

The main errors of the measurements are from the spectrum mismatch between simulator and AM1.5G, and the deviation between spectral response of testing and reference cells. In the procedure of calibrating light intensity by Si reference cell, because the spectrum of simulator differs from the AM1.5G, the Si reference cell has a broadband absorption in the near infrared region, and the calibration of light intensity will result in a discrepancy of the spectrum in the visible light region. With absorption region of OSCs located in visible range, the incorrect light intensity will lead to a misestimated PCE. In this work, the intensity of solar simulator is adjusted by a monosilicon detector (with a KG-5 visible filter), calibrated by NREL to minimize spectral mismatch \[45\].

Fig. 3.5: (a) SAN-EI ELECTRIC XEC-301S solar simulator; (b) J–V characterization measurement system.
To assess the measurement error stemmed from the spectral mismatches, the mismatch factor is introduced and described as:

\[ M = \frac{\int E_R(\lambda)S_R(\lambda)\,d\lambda}{\int E_S(\lambda)S_R(\lambda)\,d\lambda} \times \frac{\int E_S(\lambda)S_T(\lambda)\,d\lambda}{\int E_R(\lambda)S_T(\lambda)\,d\lambda}, \]  

(3.1)

where \( E_R(\lambda) \) is spectral irradiance of AM1.5G, \( E_S(\lambda) \) is the spectral irradiance of simulator, \( S_R(\lambda) \) is spectral response of reference cell and \( S_T(\lambda) \) is the spectral response of test solar cell. In ideal case, the reference cell shares the same spectrum with the test cell, which determines \( M = 1 \). With application of KG5 filter, the mismatch factor will obtain a typically value of \( 1 \pm 0.05 \).

### 3.2.2 Spectral Responsivity

Equipment set-up and IPCE measurement system are shown in Fig. 3.6. The output light from the xenon lamp is guided to a monochromator for illumination of single wavelength. The wavelength coverage can be varied from 300 nm to 900 nm. The produced monochromatic light is firstly chopped by the optical chopper with a given frequency. The optical chopper is connected with the lock-in amplifier, which can distinguish the signal from background noise and raise the signal-to-noise ratio. The \( I_{SC} \) of a Si reference cell \( I_{Si}(\lambda) \) depending on wavelength can be measured under the radiation of monochromatic light. Then the \( I_{SC} \) of the test cell \( I_t(\lambda) \) is measured in the same position. With a given IPCE spectrum of the Si cell \( IPCE_{Si} \), the IPCE of test cell is calculated as:

\[ IPCE = \frac{I_t(\lambda)}{I_{Si}(\lambda)} \times IPCE_{Si}. \]  

(3.2)
Fig. 3.6: (a) Equipment set-up and (b) schematic diagram for IPCE measurement system.

The spectral response of the test cell referring to generated current under unitary radiation power can be calculated as:

\[ S(\lambda) = IPCE \times \frac{e\lambda}{hc}, \]  
(3.3)

where \( e \) is elementary charge, \( h \) is the Planck constant and \( c \) is the speed of light. For the test device irradiated by the solar spectrum, the \( J_{sc} \) can be calibrated as:

\[ J_{sc} = \int_{\lambda_1}^{\lambda_2} S(\lambda) P(\lambda) d\lambda, \]  
(3.4)

where \( P(\lambda) \) is the given spectral intensity distribution of light.

3.2.3 Ultraviolet Photoelectron Spectroscopy

Besides the J–V and IPCE characteristics of OSCs, the material or surface characterization methods are essential for studying the electrical properties and optical properties in details. Ultraviolet photoelectron spectroscopy (UPS) was used to investigate the energy levels of valence electrons and the fine structures of the functional materials, for example, ITO, electrode/organic. UPS measurement is based on photoelectric effect and Fig. 3.7(a) schematically depicts the system of
equipment. Ultraviolet light supplied by the photon source irradiates the sample surface and photoelectrons with certain kinetic energy are emitted. In the vacuum environment, the photoelectrons are collected by the hemispherical electron energy analyzer or the cylindrical mirror electron energy analyzer.

![Diagram](image)

**Fig. 3.7:** (a) System for UPS measurement; (b) typical UPS spectrum of ITO surface.

A typical UPS spectrum measured for ITO surface is shown in Fig. 3.7(b). The ultraviolet source is the HeI line with photon energy of 21.22 eV. Work function of ITO can be determined by:

\[
\Phi_{ITO} = 21.12 \text{ eV} - \Phi, \quad (3.5)
\]

where \( \Phi \) is the energy difference between the inelastic cutoff and Fermi energy.

### 3.2.4 Scanning Electron Microscope

Scanning Electron Microscope (SEM) was used to study the surface topography and composition of the films. Fig. 3.8 exhibits the SEM equipment together with the energy dispersive X-ray (EDX) spectroscopy. Samples were placed in the vacuum chamber. High energy electrons, accelerated by a voltage as high as 20000 volts, scan through the sample surface. Signals from the sample including
back-scattered electrons, secondary electrons, characteristic X-rays can be collected and analyzed for surface imaging and other information. The magnification of SEM can be varied from dozens to hundreds of thousands times. EDX analysis can confirm the composition of the sample and picture the element distribution maps.

Fig. 3.8: Photo pictures taken for SEM and EDX used in this work.

Besides SEM and EDX, other surface analysis techniques include atomic force microscopy (AFM), transmission electron microscopy (TEM) and surface profilometer. AFM can analyze the solid state surface including insulation material without vacuum environment and give the three-dimensional images of the surface for size measurement of the nano-structured sample. The thickness of layers in the OSC samples were measured by the Dektak 150 surface profilometer. The profilometer uses a contacting stylus tip capable of causing no significant surface damage and can measure the surface roughness, topography and step heights.
3.2.5 Variable Angle Spectroscopic Ellipsometry

To study optical properties of the device, variable angle spectroscopic ellipsometry (VASE) is momentous for measuring the film thickness, optical constant, and other information. Fig. 3.9 shows the basic theory for the VASE method and the setup for measurement. The incident polarized light is reflected by the sample with a shift in amplitude and phase denoted by Psi ($\Psi$) and Delta ($\Delta$) respectively. The complex Fresnel reflection coefficients for the component of electric field in p-plane (plane of incidence) $r_p$ and s-plane (perpendicular to plane of incidence) $r_s$ is described as:

$$r_p = \frac{N_0 \cos \theta_i - N_0 \cos \theta_r}{N_0 \cos \theta_i + N_0 \cos \theta_r}, \quad (3.6)$$

$$r_s = \frac{N_0 \cos \theta_i - N_0 \cos \theta_r}{N_0 \cos \theta_i + N_0 \cos \theta_r}, \quad (3.7)$$

where $N = n + ik$ is the complex refractive index of the sample with $n$ as the refractive index and $k$ as the extinction coefficient, $N_0$ is usually the refractive index of air with a value of 1, $\theta_i$ and $\theta_r$ are the incidence angle and reflection angle respectively. The relationship of the deviation of polarization state and the reflection coefficients is expressed as:

$$\tan(\Psi) e^{i\Delta} = \frac{r_p}{r_s}. \quad (3.8)$$

With the measured $\Psi$ and $\Delta$ by VASE, $n$ and $k$ of the sample can be derived by inversion analysis method.

![Diagram of reflection of polarized light by the sample](a)

![Setup of VASE](b)

Fig. 3.9: (a) Reflection of polarized light by the sample; (b) setup of VASE.
In the experiment, monochromatic light will scan the sample with the wavelength varied in visible light band at a fixed incident angle usually between 15° to 90°. A silicon wafer is firstly detected for the reference and the test sample is measured. The measured exponential curve in Eq. 3.8 is used for regression analysis and \((n, k)\) is estimated by fitting a suitable model. The computed \((n, k)\) can characterize the optical properties of the film and be applied to numerical modelling.

### 3.2.6 Transmittance and Reflectance Measurement

Transmittance and reflectance measurements indicate the direct optical characterization of the sample. Fig. 3.10 is schematic diagram of the setup for measuring transmittance and reflectance. The incident light is conducted by an optical fiber from the xenon lamp. Transmitted or reflected light by the sample is collected by another optical fiber and analyzed for plotting transmittance spectrum or reflectance spectrum. With the transmittance \(T(\%)\) and reflectance \(R(\%)\), absorbance of the whole sample will be calculated by 100% - \(T(\%)\) - \(R(\%)\). But the absorbance of each layer in the sample cannot be separated by experimental methods. Therefore, to investigate the details of optical characterization for the device, theoretical modelling is essential and required.

![Setup for transmittance and reflectance measurement](image)

Fig. 3.10: Setup for transmittance and reflectance measurement.
3.3 Theoretical Modelling

The optical properties of OSCs such as absorbance and light intensity distribution in certain layer were analyzed using theoretical simulation. The results were then used to guide the design and optimization of OSCs. There are diverse modelling methods including optical admittance analysis, FDTD method, RCWA and FEM. The first two methods were utilized in this thesis. Besides, RCWA is an effective method to analyze the scattering effect from the periodic dielectric structure such as the diffraction grating. FEM, for example the Ansoft software, provides an approximate result by solving the Maxwell's equations with given boundary conditions. Variational methods are utilized to minimize an error function and generate a stable solution.

3.3.1 Optical Admittance Analysis

Optical admittance analysis is a basic and efficient numerical modelling method for planar structured OSCs. The optical admittance generates from the calculation of transfer matrix dealing with the reflection and transmission in the multilayer system. Fig. 3.11 illustrates an ideal thin film with two smooth surfaces, the simplest system of three media for transfer matrix method. The sequent layers possess refractive indices of \( n_0 \), \( n_1 \) and \( n_s \) respectively while the thickness of the thin film is \( h \) and the other two media are considered having the infinite thickness. The electric field and magnetic field are assumed to be parallel to the principal plane. The incidence angle and refraction angle at boundary I are donated as \( \theta_{iI} \) and \( \theta_{iII} \), while the incidence angle and refraction angle at boundary II are donated as \( \theta_{iII} \) and \( \theta_{iIII} \).
The electric field at boundary I and boundary II can be expressed as:

\[ E_I = E_{III} + E'_{III}, \quad (3.9) \]

\[ E_{II} = E_{III} + E_{dII} = E_{III} e^{+ikh} + E'_{dII} e^{-ikh}, \quad (3.10) \]

where \( E'_{III} \) is the total reflected electric field from boundary II arriving boundary I. The phase shift relationships with \( E_{III} = E_{III} e^{ikh} \) and \( E_{dII} = E_{dII} e^{-ikh} \) are used in Eq. 3.10. The magnetic field can be determined by

\[ \vec{H} = \frac{\varepsilon_0 n \cdot (\vec{k} \times \vec{E})}{\mu_0}. \]

By relating Eq. 3.9 and Eq. 3.10, we get:

\[ H_I = (E_{III} - E'_{dII}) Y_1, \quad (3.11) \]

\[ H_{II} = (E_{III} e^{-ikh} + E'_{dII} e^{+ikh}) Y_1, \quad (3.12) \]

where \( Y_1 = \frac{\varepsilon_0 n_{III} \cos \theta_{III}}{\mu_0} \) is defined as the optical admittance of the middle layer.

The system of Eq. 3.9, 3.10, 3.11 and 3.12 can be solved leading to:
\[ E_t = E_\mu \cos k_0 h + H_\mu (i \sin k_0 h)/Y_t, \]  
\[ H_t = E_\mu Y_0 \sin k_0 h + H_\mu \cos k_0 h. \]

Eq. 3.13 and Eq. 3.14 can be written in matrix form as:
\[
\begin{bmatrix}
E_t \\
H_t
\end{bmatrix} = 
\begin{bmatrix}
\cos k_0 h & (i \sin k_0 h)/Y_t \\
Y_0 \sin k_0 h & \cos k_0 h
\end{bmatrix} 
\begin{bmatrix}
E_\mu \\
H_\mu
\end{bmatrix},
\]

which can be represented as:
\[
\begin{bmatrix}
E_t \\
H_t
\end{bmatrix} = \mu_t \begin{bmatrix}
E_\mu \\
H_\mu
\end{bmatrix} \quad \text{or} \quad \begin{bmatrix}
m_{11} & m_{12} \\
m_{21} & m_{22}
\end{bmatrix} 
\begin{bmatrix}
E_\mu \\
H_\mu
\end{bmatrix}.
\]

On the other hand, the electric fields at boundary I and boundary II can be determined by:
\[ E_t = E_{t\alpha} + E_{t\beta}, \]
\[ E_\mu = E_{\mu\beta}, \]

In the same way, the magnetic field can be calculated as:
\[ H_t = (E_{\mu\beta} - E_{\alpha\beta})Y_0, \]
\[ H_\mu = E_{\mu\beta}Y_s, \]

where \( Y_t = \sqrt{\frac{\varepsilon_0 n_t \cos \theta_{\alpha\beta}}{\mu_0}} \) and \( Y_0 = \sqrt{\frac{\varepsilon_0 n_0 \cos \theta_{\mu\beta}}{\mu_0}} \) are the optical admittances of the two media above and below the thin film. The Eqs. 3.17, 3.18, 3.19 and 3.20 can also be written in matrix form as:
\[
\begin{bmatrix}
E_t \\
H_t
\end{bmatrix} = 
\begin{bmatrix}
(E_{\alpha\beta} + E_{\beta\beta}) & (E_{\mu\beta} - E_{\alpha\beta})Y_0 \\
(E_{\mu\beta} - E_{\alpha\beta})Y_0 & (E_{\mu\beta} - E_{\alpha\beta})Y_s
\end{bmatrix},
\]

\[
\begin{bmatrix}
E_\mu \\
H_\mu
\end{bmatrix} = 
\begin{bmatrix}
E_{\mu\beta} \\
E_{\mu\beta}Y_s
\end{bmatrix}.
\]

Eq. 3.21 and Eq. 3.22 are substituted into Eq. 3.16 as:
\[
\begin{bmatrix}
(E_{\alpha\beta} + E_{\beta\beta}) \\
(E_{\mu\beta} - E_{\alpha\beta})Y_0
\end{bmatrix} = \mu_t \begin{bmatrix}
E_{\mu\beta} \\
E_{\mu\beta}Y_s
\end{bmatrix}.
\]

We expand Eq. 3.23 and obtain the simultaneous equations as:
\[ I + r = m_{11}t + m_{12}Y_{t}, \quad (3.24) \]
\[ (I - r)Y_{0} = m_{21}t + m_{22}Y_{t}, \quad (3.25) \]

where \( r = \frac{E_{d}}{E_{i}} \) is defined as the reflectance and \( t = \frac{E_{III}}{E_{i}} \) is defined as the transmittance at boundary I and boundary II, which can be derived by solving Eq. 3.24 and Eq. 3.25 as:

\[ r = \frac{Y_{0}m_{11} + Y_{0}Y_{m_{12}} - m_{21} - Y_{s}m_{22}}{Y_{0}m_{11} + Y_{0}Y_{m_{12}} + m_{21} + Y_{s}m_{22}}, \quad (3.26) \]
\[ t = \frac{2Y_{0}}{Y_{0}m_{11} + Y_{0}Y_{m_{12}} + m_{21} + Y_{s}m_{22}}. \quad (3.27) \]

For a multilayer thin film system, the transfer matrix is the product of the matrix corresponding to each layer shown as:

\[ \mu = \mu_{I}\mu_{II}\mu_{III}...\mu_{p} = \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix}. \quad (3.28) \]

The relationship of the electromagnetic field in the initial layer and final layer can be expressed as:

\[ \begin{bmatrix} E_{t} \\ H_{t} \end{bmatrix} = \mu_{I}\mu_{II}\mu_{III}...\mu_{p} \begin{bmatrix} E_{p+1} \\ H_{p+1} \end{bmatrix}. \quad (3.29) \]

With the given thickness and optical constants of each layer \((n, k)\), the correlative optical admittance can be calculated, which can be applied to analyze the reflection, transmission and absorption by each thin film of the device. In practical numerical modelling, the Semiconducting Thin Film Optics Simulation software (SETFOS) is utilized to study and optimize the OSCs.

### 3.3.2 Finite-difference Time-domain Numerical Simulation

For photonic structured OSCs, FDTD method was applied to calculate the electromagnetic field in each position of the device by rigorously solving the
Maxwell's equations. The device was meshed by using the grid-based differential time-domain model. The time-dependent Maxwell's equations can be discretized using central-difference approximations to the space and time partial derivatives. Fig. 3.12 is the Yee cell used for calculation with distributed electric and magnetic field components. Each field component is surrounded by other four field components. The time interval between the electric field and magnetic field is a half of the time-step $\Delta t$ and all the electromagnetic field components are summarized in TABLE 3.1.

![Fig. 3.12: Yee cell for FDTD method.](image)

**TABLE 3.1: The spatial coordinates and time base for field components.**

<table>
<thead>
<tr>
<th>Field component</th>
<th>Spatial coordinates</th>
<th>Time base</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_x$</td>
<td>$i + 1/2$</td>
<td>$j$</td>
</tr>
<tr>
<td>$E_y$</td>
<td>$i$</td>
<td>$j + 1/2$</td>
</tr>
<tr>
<td>$E_z$</td>
<td>$i$</td>
<td>$j$</td>
</tr>
<tr>
<td>$H_x$</td>
<td>$i$</td>
<td>$j + 1/2$</td>
</tr>
<tr>
<td>$H_y$</td>
<td>$i + 1/2$</td>
<td>$j$</td>
</tr>
<tr>
<td>$H_z$</td>
<td>$i + 1/2$</td>
<td>$j + 1/2$</td>
</tr>
</tbody>
</table>
Assuming that the electric field \( E_x^n, E_y^n \) and \( E_z^n \) at the time \( n \Delta t \) and the magnetic field \( H_x^{n+1/2}, H_y^{n+1/2} \) and \( H_z^{n+1/2} \) at the time \( (n + 1/2) \Delta t \) are known, the electric field \( E_x^{n+1} \) can be calculated as:

\[
E_x^{n+1}(i + \frac{1}{2}, j, k) = CA(m) \cdot E_x^n(i + \frac{1}{2}, j, k) + CB(m) \cdot \\
\left[ \frac{H_x^{n+1/2}(i+\frac{1}{2}, j, k) - H_x^{n} (i+\frac{1}{2}, j, k)}{\Delta y} - \frac{H_y^{n+1/2}(i, j, k+\frac{1}{2}) - H_y^{n} (i, j, k+\frac{1}{2})}{\Delta x} \right],
\]

(3.30)

where \( CA(m) = \frac{\varepsilon(m)}{\Delta t} + \frac{\sigma(m)}{2} \) and \( CB(m) = \frac{1}{\varepsilon(m) + \frac{\sigma(m)}{2}} \) with \( m = (i + \frac{1}{2}, j, k) \), \( \varepsilon \) and \( \sigma \) are the dielectric constant and conductivity respectively, which are initially given variables. With the analogous numerical method, the \( E_y^{n+1} \) and \( E_z^{n+1} \) for electric field and \( H_x^{n+3/2}, H_y^{n+3/2} \) and \( H_z^{n+3/2} \) for magnetic field can be calculated. This process will be repeated continuously until the desired transient or steady-state electromagnetic field behavior is fully developed. Fig. 3.13 shows the leapfrog algorithm for the calculation of electromagnetic field.

![Leapfrog algorithm](image)

**Fig. 3.13**: Leapfrog algorithm for the electromagnetic field.

With the deduced electric and magnetic field in every point of the device, every aspect of the optical properties can be analyzed. The Poynting vector
\( \vec{S} = \vec{E} \times \vec{H} \) can characterize the energy flux density and light intensity distribution can be mapped. The absorption in a unit volume at each light frequency \( \omega \) is decided as:

\[
A(\vec{r}, \lambda) = -\frac{1}{2} \omega |\vec{E}(\vec{r}, \lambda)|^2 \text{Im}[\varepsilon(\vec{r}, \lambda)] .
\]  

(3.31)

Other optical parameters such as transmittance and reflectance at the interface can also be determined.

In practical numerical modelling process, Lumerical FDTD Solutions is the software used to deal with all kinds of design issues for photonic structures. The structure of device is firstly illustrated or imported, with setting the \((n, k)\) optical constants measured from VASE. For periodic structure as shown in Fig. 3.14 \cite{46}, one elementary unit is studied in the simulation region and the lateral boundary condition is set as periodic boundary. As regards the simulation results, the accuracy will be influenced by the mesh level of the device, fitting error of the \((n, k)\) constants and other factors.

Fig. 3.14: Simulation for periodic structured device.
Chapter 4: Light Absorption Enhancement in Inverted Organic Solar Cells

4.1 P3HT:PCBM-Based Regular and Inverted Cells

The commonly solution processed OSCs employ the regular device structure with the active layer sandwiched by the front transparent anode layer and the back reflective cathode layer. P3HT:PCBM is the typical used blend layer for planar OSCs and PEDOT:PSS layer serves as the hole transporting layer, improving the extraction of holes and furnishing a smooth surface for the spin-coating of P3HT:PCBM blend layer. The optimized regular structure of P3HT:PCBM based OSC is ITO/PEDOT: PSS (40 nm)/P3HT:PCBM (200 nm)/Al (100 nm), obtained through experimental optimization and theoretical optimization.

To improve the performance of device, the inverted OSC is proposed and designed. One reason is that the substitution of the interlayer and altering of device structure may enhance light absorption in active layer, benefit the charge carriers collection at the interface of layers or promote the transport of carriers. The inverted OSC also has a potential of longer device lifetime. In the regular OSC, the acidic PEDOT:PSS layer will corrode the underlying ITO layer \cite{47} and the metal cathode layer usually experiences the oxidation \cite{48} over a long period of time. Another degradation mechanism is the unbalanced charge carrier mobility in the active layer stemmed from the oxygen-induced charge carrier traps \cite{49}. Two distinct degradation approaches \cite{50} were identified, including the incremental charge carrier recombination due to the moisture corrosion and the oxidation at organic/cathode interface. This indicates that the inverted OSCs may be more favorable for efficient device operation.
For inverted OSCs, the ITO substrate was coated by the transparent cathode layer with relatively low work function, such as solution-processed TiO$_2$\cite{51}, ZnO \cite{52} and Cs$_2$CO$_3$\cite{53}, metals of Al \cite{54} and Ca \cite{55}, and the surface dipole-inducing materials \cite{56}. In this work \cite{57}, the ITO substrate was modified by an ultrathin Al film and the rear anode was the MoO$_3$/Ag suitable for dry deposition. The inverted device had a structure of ITO/Al (\~{}1.2 nm)/P3HT:PCBM (200 nm)/MoO$_3$ (5 nm)/Ag (100 nm). The 1.2 nm Al film is thick enough for electrons collection also with good transmittance. The thickness of MoO$_3$ layer was optimized to be \~{}5.0 nm for hole transport. For device characterization, transient photocurrent (TPC) measurement was used to study the interfacial exciton dissociation at the Al/PCBM interface. X-ray photoelectron spectroscopy (XPS) was also used to analyze the surface electronic properties of Al-modified ITO cathode.

Fig. 4.1: Structures of P3HT:PCBM-based regular and inverted OSCs.

The P3HT:PCBM-based regular and inverted cells were fabricated and the device structures are illustrated in Fig. 4.1. The active area of both types of OSCs is 3.0 mm \times{} 3.0 mm, made with ITO/glass having a sheet resistance of \~{}15\Omega/square. The blend polymer of P3HT (Rieke Metals) and PCBM (Nano-C) was dissolved in 1,2-dichlorobenzene solvent with a weight ratio of 1:0.8 in the glove box for spin-coating process. For regular device, the ITO surface was treated with oxygen plasma, followed with a PEDOT:PSS buffer layer formed by
spin-coating in atmospheric environment. For inverted device, Al ultrathin film with a thickness of 1.2 nm was firstly deposited on ITO surface by thermal evaporation method at a low pressure of $1.0 \times 10^{-4}$ Pa and the deposition rate of 0.1 Å/s. The ultrathin Al film modified ITO/glass substrate was then transferred to the adjacent glove box without oxygen plasma treatment, which simplifies the process of device fabrication.

The J–V characteristics of the regular and inverted cells were measured under the AM1.5G illumination with a light intensity of 100 mW/cm$^2$. TABLE 4.1 summarizes the device parameters of the J–V characteristics. The $J_{SC}$ of the inverted cells increased from 9.98 mA/cm$^2$ to 10.30 mA/cm$^2$ and the FF enhanced from 0.63 to 0.68 compared to regular cell, resulting in the 13% increase in PCE from 3.67% to 4.16%. The J–V characteristics of the regular and inverted cells are shown in Fig. 4.2, showing an evident enhancement in the $J_{SC}$, which implies that the charge carrier transport and light absorption are more preferable in the inverted cells.

**TABLE 4.1:** Device performance of the regular and inverted OSCs, the values in parentheses were calibrated by IPCE spectrum.

<table>
<thead>
<tr>
<th>Cell configuration</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$R_S$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Regular OSC</td>
<td>0.59</td>
<td>9.98</td>
<td>0.63</td>
<td>3.67</td>
<td>8.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(9.43)</td>
<td></td>
<td>(3.47)</td>
<td></td>
</tr>
<tr>
<td>(b) Inverted OSC</td>
<td>0.60</td>
<td>10.30</td>
<td>0.68</td>
<td>4.16</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(9.72)</td>
<td></td>
<td>(3.93)</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 4.2: J–V characteristics measured for the regular cell of ITO/PEDOT:PSS (40 nm)/P3HT:PCBM (200 nm)/Al (100 nm) and the inverted cell of ITO/Al (~1.2 nm)/P3HT:PCBM (200 nm)/MoO₃ (5 nm)/Ag (100 nm).

IPCE of the regular cells and inverted cells were measured and are plotted in Fig. 4.3. In the wavelength range from 460 nm to 620 nm, referring to maximum absorption profile of P3HT:PCBM layer, there is an evident enhancement in IPCE for the inverted cell compared to the regular cell. The J_{SC} is also calibrated by the IPCE and given in TABLE 4.1. The broadband enhancement in IPCE of the inverted cells indicates improved electrical and optical properties of the device. In the next section, TPC measurement and XPS measurement are used to investigate the interfacial properties of the devices. Light absorption is studied by optical admittance analysis. Besides, the aging process for OSCs under light soaking was also performed.
4.2 Electrical and Optical Properties of Devices

The utilization of ultrathin metal modified TCO substrate has been reported \[58,59\]. Improved charge carrier collection and better matching of energy level can be realized by the insertion of an ultrathin metal interlayer. In this work, the interfacial exciton dissociation at the Al-modified ITO/PCBM interface is examined by TPC measurement. The structures for regular and inverted configurations are ITO/PEDOT:PSS(40 nm)/PCBM(400 nm)/Al(30 nm) and ITO/Al(10 nm)/PCBM(400 nm)/MoO\(_3\) (5 nm)/Ag (100 nm) respectively. The two samples were illuminated by a Nd:YAG laser both from the cathode sides of Al(10 nm)/PCBM(400 nm) and Al(30 nm)/PCBM(400 nm). The wavelength of the laser light is 355 nm and the pulse duration is less than 5 ns. The 1M input terminal of an oscilloscope was connected to the samples for the transient photovoltage measurement, which was converted to transient photocurrent by the internal resistor of the functional generator at a forward bias of 0.4 V.
Fig. 4.4 presents the results of TPC measurement. For the regular configuration with a structure of ITO/PEDOT:PSS (40 nm)/PCBM (400 nm)/Al (30 nm), there is a polarity change from negative to positive in the transient photocurrent. The negative transient photocurrent indicates a rapid interfacial exciton dissociation at the interface of Al (30 nm)/PCBM (400 nm), which weaken the electron collection. For the inverted configuration with a structure of ITO/Al (10 nm)/PCBM (400 nm)/MoO\textsubscript{3} (5 nm)/Ag (100 nm), the transient photocurrent is always positive. The interface of Al (10 nm)/PCBM (400 nm) is preferable for electron collection. The different behaviors of the transient photocurrent for the two samples confirm that the interfacial exciton dissociation at the Al/PCBM interfaces of the regular and inverted OSCs is not equivalent. The ultrathin Al-modified ITO and PCBM form a more abrupt interface than the regular configuration. Therefore, the inverted OSCs are favorable for efficient electron collection compared to that in regular OSCs.

![Graph showing transient photocurrent for regular and inverted configurations](image)

Fig. 4.4: Transient photocurrent measured for regular and inverted configurations with structures of ITO/PEDOT:PSS (40 nm)/PCBM (400 nm)/Al (30 nm) and ITO/Al (10 nm)/PCBM (400 nm)/MoO\textsubscript{3} (5 nm)/Ag (100 nm) respectively.
To further study the electronic properties of ultrathin Al-modified ITO surface, 5 nm Al and 10 nm Al films are deposited on ITO substrate and the corresponding XPS spectra were measured and plotted in Fig. 4.5. For Al (5 nm)/ITO sample, the Al$_{2p}$ XPS peak corresponding to the binding energy of 75.8 eV demonstrates the existence of oxidized aluminum (AlO$_x$). When the thickness of Al film was increased to 10 nm, another Al$_{2p}$ XPS peak at 73 eV is observed, confirming the metallic Al. Therefore, the first few nanometer thick Al on ITO surface was oxidized forming AlO$_x$ instead of metallic Al. For the inverted P3HT:PCBM based cell with 1.2 nm Al film deposited, the work function of ITO reduces with the modification of AlO$_x$, which benefits the electron extraction efficiency. The corresponding increase in $V_{OC}$ of the inverted cells is indicated in TABLE 4.1. The ultrathin Al-modified ITO substrate is suitable for being the cathode from the perspective electrical property.

![Fig. 4.5: Al$_{2p}$ XPS peaks measured for two samples of Al (5 nm)/ITO and Al (10 nm)/ITO in vacuum.](image)

For the study of optical properties of OSCs, light absorption in specific layer cannot be measured by experimental method. Numerical modelling method is applied to investigate the optical details in the device, for example, using optical
admittance analysis and FDTD method. To model the OSC with planar structure, the device can be regarded as a multilayer system and optical admittance analysis based on transfer matrix method is a simple and efficient approach for accurate results. The refractive indices and extinction coefficients of the layers in the regular and inverted OSCs, including ITO, PEDOT:PSS, P3HT:PCBM blend layer, MoO3, Al and Ag layer, were measured by VASE. With determined thickness of each layer, light absorbance $A(\lambda)$ in P3HT:PCBM blend layer was calculated. The J–V characteristics were measured under AM1.5G illumination, integrated absorbance of the active layer $\bar{A}$ is computed by Eq.4.1 [60,61]:

$$\bar{A} = \frac{\int A(\lambda)F(\lambda)d\lambda}{\int F(\lambda)d\lambda} ,$$

where $F(\lambda)$ is the flux of solar light. For the regular and inverted OSCs based on P3HT:PCBM system, the thicknesses of PEDOT:PSS, MoO3, Al and Ag are already optimized for best electrical properties and have no occasion to be altered. Therefore, the optimization of the device structures is mainly focused on the thickness of P3HT:PCBM active layer.

![Graph showing calculated integrated absorbance of P3HT:PCBM active layer as a function of its thickness varying from 0 to 300 nm for both regular and inverted cells.](image)

Fig. 4.6: Calculated integrated absorbance of P3HT:PCBM active layer as a function of its thickness varying from 0 to 300 nm for both regular and inverted cells.
Fig. 4.6 shows the calculated integrated absorbance of the active layer depending on the P3HT:PCBM thickness from 0 to 300 nm, for both regular and inverted cells. There are two absorption peaks in the integrated absorbance curves at the thickness of 75 nm and 220 nm for regular cell, and 70 nm and 200 nm for inverted cells. The inverted OSCs always absorb more light than the regular OSCs for any thickness of active layer. 200 nm is the optimal thickness for P3HT:PCBM layer in inverted cells. Light absorption enhancement is achieved compared to the regular cell with a 225 nm thick active layer, which contribute to the enhanced $J_{SC}$ of the inverted cell. With thinner active layer in inverted cells with enhanced light absorption, the exciton recombination losses are reduced and the drift velocity of charge carriers is accelerated with higher built-in field. Therefore, the inverted cell with a 200 nm thick P3HT:PCBM active layer possess the best device performance. With the optical admittance analysis, it is demonstrated that the inverted device structure allows enhancing light absorbance and thus the PCE of the cells.

The fabricated regular and inverted cells are kept in the glove box for 3 days for stabilization and then encapsulated. The encapsulated cells were then removed from the glove box for aging in air. To accelerate the aging process, the regular and inverted OSCs were in continuous light soaking by AM1.5G illumination with light intensity of 100 mW/cm$^2$ in the open-circuit condition at 60±5°C. The $V_{OC}$, FF, $J_{SC}$ and PCE of both regular and inverted cells were measured and normalized as presented in Fig. 4.7. The cell parameters were averaged from a set of regular and inverted cells for accurate and reliable results. Taking the PCE as an example, the inverted cell experienced a fast decay in PCE initially and shows a 40% loss for the first 70 hours. After the initial 70 hours, the performance of inverted cell is stabilized. For regular cell, the PCE undergoes a faster degradation with a 60% loss in the first 70 hours and a continuous decay afterwards. The results demonstrate that inverted OSCs are more stable than the regular OSC,
which agrees with the degradation mechanisms discussed previously and the TPC measurement indicating that interfacial contact in the inverted cell is better for the durability of device compared to regular cell.

Fig. 4.7: $J_{SC}$, FF, $V_{OC}$ and PCE as a function of aging time measured under continuous light soaking AM1.5G illumination with light intensity of 100 mW/cm$^2$.

4.3 Limitation of Light Absorption in Planar Organic Solar Cells

For the P3HT:PCBM based planar OSCs, light absorption enhancement is realized by converting regular configuration to inverted configuration. As to other types of OSCs with multilayer structures, the optical properties can be optimized by altering the thickness of each layer in devices. In a joint research work with the
Centre for Organic Photonics & Electronics in The University of Queensland, the ITO-free OSC is fabricated with large active area of 25 cm$^2$ utilizing a transparent molybdenum oxide/silver/zinc sulfide anode. The OSC is based on PCDTBT:C61-PCBM active layer with a weight ratio of 1:1 exhibits a PCE of 2.7%, relatively high for device with large area. Fig. 4.8(a) shows the device structures of glass/Al (100 nm)/PCDTBT:PCBM/MoO$_3$/Ag/ZnS. Considering the inverted OSCs with two different active layer thicknesses of 80 nm and 110 nm, integrated absorbance of the PCDTBT:PCBM blend layer is calculated. For the upper semitransparent anode, MoO$_3$, Ag and ZnS are used as optical spacer layer, conductor layer and index matching layer respectively. Thickness of individual layers in anode stack MoO$_3$/Ag/ZnS will be optimized to maximize the absorbance of active layer in inverted cells.

![Diagram](image)

Fig. 4.8: (a) Inverted semitransparent cells with a structure of glass/Al (100 nm)/PCDTBT:PCBM/MoO$_3$/Ag/ZnS; (b) calculated integrated absorbance of the 80 nm and 100 nm PCDTBT:PCBM layer as a function of the thickness of MoO$_3$ layer.

The thicknesses of Ag layer and ZnS layer are initially assumed to be 15 nm and 25 nm separately for appropriate electrical and optical properties of the anode. The integrated absorbance of active layer with the thickness of MoO$_3$ layer

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ranging from 3 to 35 nm is simulated, using the 80 nm and 100 nm PCDTBT:PCBM layer and as shown in Fig. 4.8(b).

Fig. 4.9: Optimization of the thicknesses of ZnS index matching layer (a), and Ag upper semitransparent electrode (b) in the cells with a 110 nm thick PCDTBT:PCBM layer, and influence of ZnS (c) and Ag contact (d) thickness on the integrated absorbance of structurally identical OSCs with an 80 nm thick PCDTBT:PCBM layer.

Based on the results, the optimized thicknesses of MoO$_3$ optical spacer layer are 10 nm and 5 nm for 80 nm and 100 nm PCDTBT:PCBM layer respectively. The thicknesses of Ag layer and ZnS index matching layer are then modified for light absorption enhancement in the devices. For the 110 nm PCDTBT:PCBM layer, its integrated absorbance in the cell with MoO$_3$ (5 nm)/Ag (15 nm)/ZnS (5–80 nm) anode is simulated and presented in Fig 4.9(a) while Fig. 4.9(b) is for the cell with MoO$_3$ (5 nm)/Ag (3–18 nm)/ZnS (30 nm). For the 80 nm PCDTBT:PCBM layer, its integrated absorbance in the device with the anode of
MoO$_3$ (10 nm)/Ag (15 nm)/ZnS (5–80 nm) and MoO$_3$ (10 nm)/Ag (3–18 nm)/ZnS (25 nm) are calculated and shown in Fig. 4.9(c) and Fig. 4.9(d). To summarize the numerical modelling results, the optimized device structures for the inverted semitransparent cells are glass/Al (100 nm)/PCDTBT:PCBM/MoO$_3$ (10 nm)/Ag (15 nm)/ZnS (25 nm) for the 80 nm PCDTBT:PCBM layer and glass/Al (100 nm)/PCDTBT:PCBM/MoO$_3$ (5 nm)/Ag (11 nm)/ZnS (30 nm) for the 110 nm PCDTBT:PCBM layer.

With the introduced light absorption enhancement in the inverted P3HT:PCBM based OSCs and the PCDTBT:PCBM based OSCs, it is shown that for the OSCs with planar structures, the broadband light absorption enhancement can be achieved by modifying the device configuration and optimizing the thickness of each layer in the cell, which will regulate light interference and light field distribution for improved absorbance in the active layer. However, light absorption is still limited to some extent, and moreover, altering the thickness of interlayer may sacrifice the electrical properties of the device. Therefore, to further enhance light absorption in the active layer or improve the absorbance without changing the layer thickness in device, photonic structured OSCs were designed and studied, the results of absorption enhancement in nano-structured OSCs will be discussed in detail in chapter 5 and chapter 6.
Chapter 5: Organic Solar Cells with CFx-modified Silver Nanoparticles

5.1 ZnPc:C₆₀-Based Cells with CFx-modified Silver nanoparticles

In this chapter, performance enhancement in ZnPc:C₆₀-based OSCs with CFx-modified Ag NPs/ITO anode was analyzed. Ag NPs were incorporated in the OSCs fabricated on rigid or flexible substrates to enhance light absorption [⁶²]. CFx plasma treatment was used to modify Ag NPs as the CFx modified Ag anode has already been employed to enhance the charge carrier collection efficiency in organic light-emitting diode devices [⁶³]. The ZnPc:C₆₀-based OSCs on rigid ITO/glass substrate are firstly fabricated. The structure of control cell is glass/ITO/ZnPc:C₆₀ (35 nm)/C₆₀ (25 nm)/BPhen (7 nm)/Ag(100 nm) and the thickness of each layer has been optimized for the best device performance. Device incorporated with CFx-modified Ag NPs are designed with a structure of glass/ITO/Ag (1.5 nm)/ZnPc:C₆₀ (35 nm)/C₆₀ (25 nm)/BPhen (7 nm)/Ag (100 nm). Cross-sectional views of OSCs with CFx-modified anode and the control cells are presented in Fig. 5.1.
Fig. 5.1: (a) Control cell with a structure of glass/ITO/ZnPc:C_{60} (35 nm)/C_{60} (25 nm)/BPhen (7 nm)/Ag (100 nm), and (b) Ag NPs incorporated cell with a structure of glass/ITO/Ag (1.5 nm)/ZnPc:C_{60} (35 nm)/C_{60} (25 nm)/BPhen (7 nm)/Ag (100 nm).

To fabricate the control cell and Ag NPs incorporated cell, the patterned ITO/glass substrates were initially cleaned by detergent, deionized water, acetone and IPA in ultrasonic cleaner. For control cell, The ITO surface is treated with oxygen plasma to enhance the work function of ITO and for further surface cleaning. For Ag NPs incorporated cells, Ag with a mass thickness of 1.5 nm was deposited on the ITO surface by thermal evaporation at a rate of 1 Å/s. ITO surface was not treated with oxygen plasma. The "mass thickness" refers to the thickness value monitored by quartz crystal resonator while Ag with 1.5 nm mass thickness can only form discrete Ag NPs instead of Ag thin film. For both control cell and Ag NPs incorporated cells, ZnPc and C_{60} were co-evaporated at a weight ratio of 1:1 on bare ITO surface or CFx-modified Ag NPs/ITO surface to form a 35 nm thick active layer. The 25 nm thickness C_{60} electron transporting layer, 7 nm thick BPhen exciton blocking layer and 100 nm Ag cathode layer were subsequently deposited, resulting in OSCs with an active area of 3.0 mm × 3.0 mm. The pressure for all the evaporation processed was maintained at 1.0×10^{-4} Pa.
The J–V characteristics of the control cell and Ag NPs incorporated cells were measured under the AM1.5G irradiation with the KG-5 filter, calibrated light intensity of 100 mW/cm². The parameters of J–V characteristics are summarized in TABLE 5.1 and J–V characteristics are plotted in Fig. 5.2. The \( J_{sc} \) of Ag NPs incorporated cells is enhanced from 11.13 mA/cm\(^2\) to 13.10 mA/cm\(^2\), leading to an obvious increase in PCE from 2.7% to 3.5% as compared to the control cells.

**TABLE 5.1: Device performance of the control cell and Ag NPs incorporated cell**

<table>
<thead>
<tr>
<th></th>
<th>( \text{Voc (V)} )</th>
<th>( \text{Jsc (mA/cm}^2)</th>
<th>( \text{FF} )</th>
<th>( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control cell</td>
<td>0.52±0.05</td>
<td>11.13±0.50</td>
<td>47±5</td>
<td>2.7±0.1</td>
</tr>
<tr>
<td>Ag NPs incorporated cell</td>
<td>0.52±0.05</td>
<td>13.10±0.50</td>
<td>51±5</td>
<td>3.5±0.1</td>
</tr>
</tbody>
</table>

![Fig. 5.2: J–V characteristics measured for the control cell and the Ag NPs incorporated cells.](image)

IPCE of the two cells were measured and plotted in Fig. 5.3. In the wavelength range from 300 nm to 480 nm and 560 nm to 800 nm, broadband
enhancement in IPCE is observed for the Ag NPs incorporated cell. This implies a broadband light absorption enhancement in the ZnPc:C_{60} blend layer or improved charge collection efficiency at the CFx-modified Ag NPs/ITO surface. In the following sections, the surface electronic properties of the anode surface and the impact on the overall performance of the OSCs are also investigated.

Fig. 5.3: IPCE of the control cell and the Ag NPs incorporated cell.

For further design of device and to utilize the merits of organic material of portability and lightweight, flexible OSCs fabricated on plastic substrates, such as polyethylene and polyethylene terephthalate (PET), are widely investigated and reported. The utilization of electrode and interlayer is critical for the performance of flexible OSCs. Conductive polymer such as PEDOT:PSS or metallic lines namely metal nanowires \cite{64,65}, nanotubes \cite{66,67} or grids \cite{68} have been exploited. However, transparent conducting oxides, such as ITO, are still an option due to their high transparence and low sheet resistance. For ITO based flexible OSCs, as the melting point of plastic materials is between 100–200°C, conventional high processing temperature ITO fabrication is not compatible with plastic substrate. Therefore a low processing temperature ITO deposition method was applied.
In the previous work, ITO films were grown by sputtering process at a temperature below 60°C \[69\]. This low-temperature (L.T.) ITO film, with a thickness of 130 nm and sheet resistance of 30 ± 5 Ω/sq, possesses a transmittance of over 85% in the wavelength range of 400 nm to 800 nm. Good adhesion between the ITO-based anode and the substrate can be achieved with the incorporation of an intermediate acrylic layer \[70\]. In this work, the L.T. ITO-coated PET substrates were used for fabrication of the flexible OSCs. In the experiment, structure of the designed flexible OSCs is PET/LT. ITO (130 nm)/Ag (1.5 nm)/ZnPc:C\textsubscript{60} (35 nm)/C\textsubscript{60} (25 nm)/BPhen (7 nm)/Ag (100 nm). The control cell is not incorporated by Ag NPs with a structure of PET/LT. ITO (130 nm)/ZnPc:C\textsubscript{60} (35 nm)/C\textsubscript{60} (25 nm)/BPhen (7 nm)/Ag (100 nm).

LT. ITO was firstly deposited on PET by RF magnetron sputtering in a hydrogen-argon gas mixture, with a process pressure from about 1.0–3.0 × 10\(^{-3}\) Pa and a substrate temperature < 60°C. The introduction of hydrogen was to increase the carrier concentration and allow a broader process window for preparation of the ITO film with a high conductivity. For a 130 nm thick ITO film, the average visible transparency is above 85% and the sheet resistance is 30±5 Ω/sq. Fig. 5.4 presents the transmittance of PET and LT.ITO/PET substrate. Photolithography method was employed to pattern the ITO film.
The prepared PET/LT. ITO substrates were subsequently cleaned in detergent, deionized water, acetone and IPA in ultrasonic cleaner, and then dried by nitrogen gas blown and stored in a 60°C oven. For flexible control cell, the dried substrates were subjected to oxygen plasma treatment using a 13.56 MHz RF generator for 10min. The base pressure in the treatment chamber was ~5.0×10⁻⁴ Pa while the process pressure was ~9.5×10⁻¹ Pa at 100 W. For flexible Ag NPs incorporated OSCs, Ag NPs were deposited on PET/LT. ITO surface by thermal evaporation with a mass thickness of 1.5 nm in the vacuum chamber with a base pressure of 1.0×10⁻⁴ Pa, followed by CFx plasma treatment to form a composite CFx-Ag NPs anode. For both types of OSCs, a 35 nm thick ZnPc:C₆₀ active layer in a volume ratio of 1:1 was deposited via co-evaporation on the substrates. Next, a 25 nm thick C₆₀ electron transporting layer was deposited on the ZnPc:C₆₀ blend layer followed with a 7.0 nm thick BPhen exciton blocking layer. OSCs were then completed with a 100 nm thick Ag layer formed on BPhen by thermal evaporation, having an active area of 3.0 mm × 3.0 mm.
The J–V characteristics of both types of OSCs were measured under AM1.5G illumination at 100 mW/cm². The Jsc, Voc, FF and PCE (η) of the cells are summarized in TABLE 5.2. The flexible OSCs made with CFx-modified Ag NPs/ITO had a PCE of 3.1±0.1%, which compares well to the ZnPc:C₆₀ based OSC fabricated on rigid ITO/glass substrate. Comparing the two flexible cells, the device performances show great enhancement in FF (from 46±2% to 51±1%), Jsc (10.9±0.1 mA/cm² to 11.5±0.1 mA/cm²) and PCE (from 2.6±0.2% to 3.1±0.1%) when CFx modified Ag NPs is utilized to ITO surface, which is clear in the J–V characteristics plotted in Fig. 5.5.

**TABLE 5.2:** A summary of the photovoltaic characteristics measured for the flexible cells with LT-ITO/PET and CFx-modified Ag NPs/LT-ITO/PET substrates.

<table>
<thead>
<tr>
<th>Device</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LT.ITO/PET</td>
<td>0.53 ± 0.01</td>
<td>10.9 ± 0.1</td>
<td>46 ± 2</td>
<td>2.6 ± 0.2</td>
</tr>
<tr>
<td>CFx/Ag/LT.ITO/PET</td>
<td>0.53 ± 0.01</td>
<td>11.5 ± 0.1</td>
<td>51 ± 1</td>
<td>3.1 ± 0.1</td>
</tr>
</tbody>
</table>
Fig. 5.5: J–V characteristics measured for flexible control OSCs and flexible OSCs made with CFx-modified Ag NPs/ITO. Insert: photo picture taken for a flexible OSCs made with CFx-modified Ag NPs/ITO.

IPCE of the two cells are presented in Fig. 5.5. Enhancement in IPCE over wavelength range from 350 nm to 500 nm and 610 nm to 770 nm is clearly shown for the flexible OSCs with CFx-modified Ag NPs/ITO. In the following section, we will discuss the mechanisms of CFx-modified Ag NPs contributing to light absorption enhancement in flexible OSCs, thereby increasing $J_{SC}$ and efficiency.
For both rigid OSCs and flexible OSCs, the incorporation of Ag NPs results in the improvement of device performance. In order to better understand the effect of CFx-modified Ag NPs on OSC performance, surface electronic properties and optical properties of the Ag NPs/ITO were investigated. The surface electronic properties of modified ITO anode were studied by UPS measurement.

The UPS spectra of bare ITO, Ag NPs/ITO, and CFx-modified Ag NPs/ITO are exhibited in Fig. 5.7. Work function can be deduced by the difference between the photon energy \( (h \nu = 21.2 \text{ eV}) \) and the secondary electron cutoff in UPS spectra. The spectra indicate that work function of Ag NPs-modified ITO decreased from 4.4 eV to 4.1 eV. However, the combinatory layer of CFx-modified Ag NPs and ITO possesses an enhanced work function of 5.4 eV. Fig. 5.8 shows the energy level diagram of OSCs. The difference in energy level between the work function of anode layer and the HOMO of ZnPc (5.17 eV) can
be reduced with the presence of CFx-modified Ag NPs at the interface between ITO and organic layer.

Fig. 5.7: UPS spectra measured for bare ITO, Ag NPs/ITO, and CFx-modified Ag NPs/ITO.

Fig. 5.8: Energy level diagram of ZnPc:C_{60}-based OSC.
For the device performance, there is a crucial influence from the interfacial energy level alignment at the interface of electrode and active layer. The charge collection efficiency is dependent on the energy offset between the work function of ITO anode and the HOMO of ZnPc. With the CFx modification, the reduced energy barrier at the interface of ITO/CFx-Ag NPs/ZnPc is preferable for charge carrier extraction and collection. Besides, the enhanced built-in field in the OSCs also help contributing the charge carrier transport and suppress the carrier recombination. Therefore, the results indicate that the CFx-modified Ag NPs and the ITO compose a suitable anode for the OSCs. However, the work function of bare ITO with oxygen plasma treatments is also 5.4 eV, which implies a similar charge carrier collection efficiency compared to CFx-modified Ag NPs/ITO anode. To understand the broadband enhancement in IPCE of the OSCs made with CFx-modified Ag NPs/ITO, electrical contribution cannot account fully for this improvement. Light absorption enhancement in OSCs due to LSPR effect of the Ag NPs will be investigated in the following section.

5.3 Study of Localized Surface Plasmon Resonance Effect

For optical contribution to the broadband light absorption enhancement, new findings about the role of CFx-modified Ag NPs were studied by experimental optimization and theoretical simulation. The interaction between the incident light and Ag NPs with a size much smaller than wavelength of light results in the LSPR effect. With LSPR effect of Ag NPs, the strongly enhanced local electromagnetic field and the LSPR scattering phenomenon enhanced light absorption in ZnPc:C_{60} active layer. In the present OSCs, the CFx layer is too thin to affect the optical properties of the substrate, which can be neglected optically. From optical point of view, existence of the C_{60} (25 nm)/BPhen (7 nm)/Ag (100 nm) multilayer also function as the optical spacer. In this work, the absorption enhancement in the
ZnPc:C\textsubscript{60} layer due to LSPR effect of Ag NPs was analyzed. The effect of LSPR on absorption enhancement in ITO/Ag NPs/ZnPc:C\textsubscript{60} system was analyzed.

One issue is that the extinction spectrum of LSPR for small Ag NPs has a relatively narrow half peak width, indicating a narrowband of the LSPR effect. LSPR of Ag NPs usually occurs at a wavelength of around 400 nm [71], which cannot contribute the absorption enhancement in the OSCs made with CF\textsubscript{x}-modified Ag NPs/ITO. One reasonable explanation is that the Ag NPs are not of uniform size and the diverse sizes may result in different LSPR effect. To investigate this question, a batch of Ag NPs with mass thickness varying from 0 nm to 3.5 nm were deposited on ITO surface, for optical studies. The distribution of sizes or the amount of Ag NPs on ITO substrate was achieved by adjusting the mass thickness of Ag NPs. Supposing that our assumption is valid, the LSPR effect can be tuned with varying the mass thickness of Ag NPs. Fig. 5.9(a) shows the samples with a structure of ITO/Ag (0–3.5 nm), with increased mass thickness of Ag NPs arrayed from left to right. However, although samples were dimmed with the mass thickness of Ag NPs increasing, the color almost remains invariant, implying a slight change in the LSPR wavelength. Fig. 5.10(a) plots the transmittance spectra measured for bare ITO and samples of ITO/Ag (0–3.5 nm). The dip in transmittance curve indicates the LSPR wavelength. It is shown that for ITO/Ag (0–3.5 nm) layer, the LSPR wavelength shifts slightly with the increase in the Ag mass thickness.

Because the effective length of the enhanced local field of the LSPR can be tens of nanometers, a 10 nm thick and a 35 nm thick ZnPc:C\textsubscript{60} layers were coated on ITO/Ag substrate to study the influence of dielectric (ZnPc:C\textsubscript{60}) on LSPR effect. Two batches of samples were fabricated with structures of ITO/Ag (0–3.5 nm)/ZnPc:C\textsubscript{60} (10 nm) and ITO/Ag (0–3.5 nm)/ZnPc:C\textsubscript{60} (35 nm). Fig. 5.9(b) and Fig. 5.9(c) show the samples and Fig. 5.10(b) and Fig. 5.10(c) are the measured
transmittance spectra. It is interesting to note that when the Ag NPs covered with a 10 nm thick ZnPc:C\textsubscript{60} dielectric layer, there is a significant variation in LSPR wavelength, and is Ag mass thickness dependent. This is rarely considered in other reported work. For the 35 nm ZnPc:C\textsubscript{60} over-coated ITO/Ag samples, the increase in the ZnPc:C\textsubscript{60} layer thickness causes a further red shift of LSPR wavelength. In Fig. 5.10(c), the LSPR wavelength cannot be determined due to the overlap of the LSPR of Ag NPs and absorption of ZnPc:C\textsubscript{60} in the curves. It is hard to ascertain the allocation of light absorption in the Ag NPs and ZnPc:C\textsubscript{60} layer only by the transmittance spectra. But the Ag/ZnPc:C\textsubscript{60} composite exhibits obvious broadband light absorption enhancement compared to ITO/ZnPc:C\textsubscript{60} (35 nm) layer. The variation in LSPR wavelength with and without ZnPc:C\textsubscript{60} (10 nm) is shown in Fig. 5.10(d). The influence of ZnPc:C\textsubscript{60} layer on LSPR is obvious, which demonstrates a combined impact on LSPR by the sizes of Ag NPs and refractive index of the dielectric layer. To clarify this broadband light absorption enhancement in the Ag NPs/ZnPc:C\textsubscript{60} composite, further analysis on the Ag NPs are required. Firstly, we introduce the effective medium theory for the roughly accounting for the phenomenon and then the SEM measurement for the Ag NPs on ITO substrate is conducted.

Fig. 5.9: Evaporated Ag NPs with increase in mass thickness from left to right: (a) ITO/Ag (0.5–3.5 nm); (b) ITO/Ag (0.5–3.5 nm)/ZnPc:C\textsubscript{60} (10 nm); (c) ITO/Ag (0.5–3.5 nm)/ZnPc:C\textsubscript{60} (35 nm).
Fig. 5.10: Transmittance spectra measured for (a) ITO/Ag (0–3.5 nm); (b) ITO/Ag (0.5–3.5 nm)/ZnPc:C_{60} (10 nm) and (c) ITO/Ag (0–3.5 nm)/ZnPc:C_{60} (35 nm). (d) LSPR wavelength calculated for ITO/Ag (0.5–3.5 nm) and ITO/Ag (0.5–3.5 nm)/ZnPc:C_{60} (10 nm).

The effective medium theory or effective medium approximation refers to the effective medium with an effective dielectric constant, the inhomogeneous medium composed by different materials with distinct dielectric constant. Although the optical analysis on the devices can be conducted accurately by the numerical modelling such as FDTD method nowadays, effective medium theory is still useful for intuitively presenting the relationship of one optical phenomenon and the related parameters. There are several approximations in the effective medium theory for different structures of the medium. In this work, Maxwell-Garnett theory is used to analyze the optical properties of Ag metallic
NPs mixed evenly in ZnPc:C_{60} layer and examine the change in LSPR wavelength as a function of the thickness of the over-coated dielectric. According to Maxwell-Garnett theory, the effective dielectric constant of the Ag/ZnPc:C_{60} composite $\varepsilon(\lambda)$ can be expressed as:

$$\frac{\varepsilon(\lambda) - \varepsilon_{\text{act}}(\lambda)}{L_{Ag}\varepsilon(\lambda) + (1 - L_{Ag})\varepsilon_{\text{act}}(\lambda)} = q \frac{\varepsilon_{Ag}(\lambda) - \varepsilon_{\text{act}}(\lambda)}{L_{Ag}\varepsilon_{Ag}(\lambda) + (1 - L_{Ag})\varepsilon_{\text{act}}(\lambda)},$$  \hspace{1cm} (5.1)

where $\varepsilon_{\text{act}}(\lambda)$ and $\varepsilon_{Ag}(\lambda)$ are the dielectric constant of ZnPc:C_{60} active layer and Ag NPs respectively, $L_{Ag}$ is the depolarization factor of Ag NPs and $q$ is the filling factor of Ag NPs in ZnPc:C_{60} layer. The depolarization factor of metallic particle depends on the shape of NPs, unrelated to the volume of NPs. For spherical metallic nanoparticle, the value of depolarization factor is $\frac{1}{3}$, which is applicable to the Ag NPs in this work.

Drude model is used to modify the $\varepsilon_{Ag}(\lambda)$, which can be described in plural form as $\varepsilon_{Ag}(\omega) = \varepsilon_{Ag1}(\omega) + i\varepsilon_{Ag2}(\omega)$. $\varepsilon_{Ag1}(\omega)$ and $\varepsilon_{Ag2}(\omega)$ are adjusted as:

$$\varepsilon_{Ag1}(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + \tau^2},$$  \hspace{1cm} (5.2)

and

$$\varepsilon_{Ag2}(\omega) = \frac{\omega_p^2}{\omega(\omega^2 + \tau^2)},$$  \hspace{1cm} (5.3)

where $\varepsilon_{\infty}$ is the high frequency dielectric constant of Ag NPs, $\omega_p$ is the free electron plasma frequency and $\tau$ is the collision time. LSPR is excited when the real part of $\varepsilon(\lambda)$ is zero. Solving Eq. 5.1 we obtain $^{[72]}$:

$$\lambda_{LSPR} = \lambda_p \left[ \frac{\varepsilon_{\text{act}}(\lambda)}{(1-q)L_{Ag}} - \varepsilon_{\text{act}}(\lambda) + \varepsilon_{\infty} \right]^{\frac{1}{2}},$$  \hspace{1cm} (5.4)

where $\lambda_p$ is silver's bulk plasma wavelength. According to Eq. 5.4, the increase of filling factor $q$, which is relevant with Ag mass thickness, will enlarge $\lambda_{LSPR}$. The value of $\varepsilon_{\text{act}}(\lambda)$ will impact the dependence of $\lambda_{LSPR}$ on $q$, videlicet the Ag mass thickness, corresponding to different slope factors of the two curves in Fig. 5.10(d). Considering the $\varepsilon_{\text{act}}(\lambda)$ of the ZnPc:C_{60} layer is relatively large.
compared to the air, this accounts for the difference of the LSPR effect of the ITO/Ag (0–3.5 nm) and ZnPc:C₆₀ over-coated ITO/Ag (0–3.5 nm) samples.

In order to further study the size and distribution of Ag NPs with respect to mass thickness, SEM measurement was applied to exam the ITO/Ag (0.5–3.5 nm) samples as shown in Fig. 5.11. The SEM images are analyzed by image processing program [73] for the distribution of sizes with the results plotted in Fig. 5.12. The frequency of Ag NPs with the radius located in certain unit interval is counted. The count area is 1.0 μm × 1.0 μm and the length of an interval is 0.5 nm. The counts for the Ag NPs with a radius less than 2.0 nm are not accurate, due to the systematic error in the image processing program. It is observed that with the mass thickness of Ag NPs increasing, the average size of the Ag NPs enlarges following a Gaussian distribution while the number of Ag NPs with dominant sizes reduces. Fig. 5.13 summarize the distribution of the radius of Ag NPs and for clear exhibition, the length of an interval is set as 1.0 nm.

Fig. 5.11: SEM measurement for ITO/Ag with a mass thickness of (a) 0.5 nm; (b) 1.0 nm; (c) 1.5 nm; (d) 2.0 nm; (e) 2.5 nm; (f) 3.0 nm and (g) 3.5 nm.
Fig. 5.12: Size distribution of Ag NPs as a function of mass thickness varying from 0.5 nm to 3.5 nm.

Fig. 5.13: Distribution of the radius of Ag NPs with respect to different Ag mass thickness of 0.5 nm –3.5 nm on ITO, calculated over an area of 1.0 μm × 1.0 μm.
Based on both transmittance and SEM measurement results, for ITO/Ag (0.5–3.5 nm), radius of the dominant Ag NPs increases as the mass thickness increases, but the LSPR wavelength weakly depends on the Ag NPs sizes. However, with the over-coated ZnPc:C₆₀ layer, there is significant red shift in LSPR wavelength for the Ag NPs with larger radius due to the relatively higher $\varepsilon_{\text{act}}(\lambda)$. Therefore as a result of the varied radius of Ag NPs, the broadband light absorption enhancement, instead of the narrowband absorption enhancement, is achieved for ITO/Ag/ZnPc:C₆₀ layer compared to ITO/ZnPc layer, which may be effective for OSC device.

Although the broadband light absorption enhancement in the composite of Ag NPs/ZnPc:C₆₀ is confirmed, the allocation of light absorption in Ag NPs and ZnPc:C₆₀ layer is not determined. Besides, the optical behavior of Ag NPs/ZnPc:C₆₀ in the whole OSC is not ensured, with the C₆₀ (25 nm)/BPhen (7 nm)/Ag (100 nm) multilayer incorporated. To further investigate these issues, simulation based on FDTD method using LUMERICAL software was carried for the complete cell. Fig. 5.14 is the SEM image of bare ITO substrate and Ag NPs modified ITO substrate. For the randomly located Ag NPs, we take them as semi-ellipsoids with circular base faces and then select one Ag NP as an example. The diameter of the Ag NP’s circular base face is $D_{xy} = 9$ nm and the height of the semi-ellipsoid is $H_z = 7$ nm. For the periodic unit with one Ag NP occupied, the size is 12 nm×12 nm.
Fig. 5.14: SEM images of ITO and Ag nanoparticles modified ITO (semi-ellipsoid: \(D_x=D_y=9\) nm, \(H_z=7\) nm, period=12 nm).

Fig. 5.15 depicts the simulated total reflection spectra of the control device and Ag NPs incorporated device. The significant reduction in reflectance in the wavelength region from 400 nm to 900 nm indicates that the Ag NPs are efficient in coupling light into the device. This is because the quadrupole resonance scattering is excited for the Ag NPs under illumination of broadband incident light \([74]\). The inset of Fig. 5.15 shows the normalized field distribution of \(E_z\) at normal incidence of \(y\)-polarized 550 nm light, which displays that the electric field distribution of the quadrupole resonance suffers obvious distortion due to the up-down asymmetric property of Ag NPs. Specially, in the wavelength region of 550 nm to 750 nm which covers the main absorption region of the ZnPc:C\(_{60}\) active layer, the reflectance is decreased from 30% to \(~0\)%, revealing a complete adsorption by the device.
Simulated absorptions of the ZnPc:C$_{60}$ active layers in two OSCs with and without Ag NPs are presented in Fig. 5.16. By monitoring the absorbed power in ZnPc:C$_{60}$ active layer for the two devices, it is found that the incorporation of Ag NPs indeed improves the absorption of light in the active layer over a broadband wavelength range. Beyond that, part of the forward scattered light is inevitably lost due to the absorption of Ag NPs, as shown by the blue curve in Fig. 5.16. At the wavelength around 520 nm and 800 nm, the absorption due to Ag NPs is relatively strong. However, in the main absorption region of ZnPc:C$_{60}$ (from 550 nm to 750 nm), the absorption loss due to Ag NPs decreases very sharply and the absorbance is only about 10%, the power absorbed by ZnPc:C$_{60}$ layer is dominant with an efficiency around 80%. The increased energy absorption in ZnPc:C$_{60}$ film is produced by the local electric field enhancement in the vicinity of the Ag NPs or the forward-scattering due to LSPR effect. As a result, the majority of the forward scattered energy can be absorbed by ZnPc:C$_{60}$, leading to an increase in the $J_{SC}$. 

Fig. 5.15: Simulated total reflectance of two devices.
Fig. 5.16: Simulated absorptions of active layers in two devices and the absorption of Ag nanoparticles.

To further study the role of Ag NPs in OSCs, the integrated absorbance in the active layer as a function of the thickness of ZnPc:C\textsubscript{60} layer was simulated and is plotted in Fig. 5.17. The integrated absorbance was also calculated by the Eq. 4.1 in the visible light region from 370 nm to 870 nm. It is shown that light absorption enhancement due to Ag NPs is attenuated as the active layer increased, and the introduction of Ag NPs cannot contribute to absorption enhancement in the active layer, as compared that in the control cell, when the thickness of ZnPc:C\textsubscript{60} layer exceeds 70 nm. This implies that the main mechanism of the broadband light absorption enhancement is due to the enhanced local field in the vicinity of the Ag NPs. For ZnPc:C\textsubscript{60} layer with a thickness exceeding 70 nm, the contribution from the enhanced local field is not evident anymore. With a thicker active layer, the LSPR scattering effect of the Ag NPs can have exhibited the contribution, which is not obvious here. This indicates a secondary role of the forward-scattering from the LSPR effect.
Fig. 5.17: Integrated absorbance in the ZnPc:C₆₀ layer as a function of the thickness.

5.4 Conclusion

In conclusion, CFx-modified Ag NPs was incorporated into ZnPc:C₆₀ based OSCs, made on both rigid and flexible substrates. The CFx-Ag NPs/ITO anode has advantages of improved charge carrier collection efficiency at the interface of anode/organic layer and enhanced light absorption in the active layer. The broadband light absorption enhancement in the ZnPc:C₆₀ blend layer can be achieved with the application of Ag NPs, resulting in improved device performance. The main contribution is ascribed to the local field enhancement effect from the LSPR of Ag NPs. It shows that there is a significant difference in LSPR wavelength of Ag NPs with and without ZnPc:C₆₀ dielectric layer over-coated, which can be interpreted by effective medium theory.
Chapter 6: Transparent Grating Electrode for Performance Enhancement of Organic Solar Cells

6.1 Organic Solar Cells with Front and Rear Grating Electrodes

In addition to the approach incorporating Ag NPs in OSCs to boost light absorption, periodic metallic gratings are also good candidates for the broadband light absorption enhancement in OSCs without increasing the thickness of active layer, which can introduce the diffraction effect or SPP effect. These metallic gratings, commonly using Ag material, can be fabricated on the cathode side to reflect the incident light backwards \[75\]. Otherwise, they can substitute the conventional anode layer as transparent conductive electrode resulted in broadband optical absorption enhancement \[76,77\]. In some other report, metallic grating can be applied as a grating-type textured substrate \[78,79,80\]. The grating layer and the metal cathode in the OSCs form a metal-dielectric-metal sandwich structure, allowing for an efficient light trapping in the cells. For the extensively used metallic grating, the improved performance of the solar cells usually contribute to the enhanced optical field by the surface plasmonic effect or the enhanced optical pass length due to the diffraction effect \[81\].

In this work, a poly(methyl methacrylate) (PMMA)/ITO double layer grating structure was used for application in ZnPc:C\textsubscript{60}-based OSCs. PMMA/ITO grating is used as the transparent substrate, while the reflective rear grating, formed by conformal coating of Ag on grating stack, is a wavelike Ag cathode layer. This dual-grating structure enables light diffraction occurred at both the front and back sides of the cell, which will be presented in the following discussion. The grating
OSC\(\text{s}\) had a structure of glass/grating structured PMMA (120 nm)/ITO (150 nm)/ZnPc:C\(_{60}\) (40 nm)/C\(_{60}\) (28 nm)/BPhen (8 nm)/Ag (120 nm). To demonstrate the device performance, the control cells with a planar structure based on the same layers were fabricated. The cross-sectional views of grating and planar control OSC\(\text{s}\) are illustrated in Fig. 6.1.

![Cross-sectional views of OSCs](image)

**Fig. 6.1:** Schematic cross-sectional views of (a) grating OSC\(\text{s}\); (b) planar control cell.

To fabricate the grating OSC\(\text{s}\), we started with a flat cleaned glass substrate and spin-coat the PMMA layer on it. The one dimensional grating structured PMMA was formed by nano-imprint method, with the procedures of the method shown in Fig. 6.2. A Si mold was used for imprinting, which has a period of 500 nm with a line width of 250 nm, spacing of 250 nm and depth of 250 nm. The glass/PMMA substrate was initially heated to 160°C and embossed by the Si mold with a pressure of 60 bar for 5 min. Then the substrate was cooled to 70°C for detaching the Si mold. The one dimensional PMMA grating was then prepared with a period of 500 nm.
LT. ITO is then deposited on the PMMA grating substrate using RF magnetron sputtering at a pressure of $1.0 - 3.0 \times 10^{-3}$ Pa at a process temperature of $< 60^\circ C$, avoiding the possible damage to the underlying PMMA grating due to the sputtering process. The coated LT. ITO layer also forms a grating in sinusoidal shape with a period of 500 nm. On the PMMA/ITO grating substrate, a 40 nm thick ZnPc:C$_{60}$ active layer in a volume ratio of 1:1 was then deposited by co-evaporation, followed with a 28 nm thick C$_{60}$ electron transporting layer, an 8 nm thick BPhen exciton blocking layer and a 120 nm Ag cathode layer, forming a grating OSC. AFM measurement was performed for the LT.ITO/PMMA grating structure and the Ag cathode layer of grating OSCs. The surface images measured for the cathode side of OSCs are presented in Fig. 6.3. It is revealed that the thermally evaporated layers could conform the one dimensional grating pattern with a period of 500 nm and the peak to valley amplitude in the conformally deposited layer is 110 nm. Besides the prepared grating OSCs, a planar control OSC was also fabricated on the flat LT. ITO layer, sputtered on the planar PMMA layer without nano-imprint process.
Fig. 6.3: AFM images measured from (a) LT.ITO/PMMA grating structure; and (b) Ag cathode layer of a grating OSC, showing the sinusoidal shape of the periodic grating (peak to valley amplitude ~110nm) structure and periodicity of 500 nm.

The J–V characteristics of the grating OSCs and the planar control cells were measured under calibrated AM1.5G illumination of 100 mW/cm². The device parameters are summarized in TABLE 6.1. The J–V characteristics are plotted in Fig. 6.4. It shows that there is an obvious enhancement in performance of the grating OSCs with a PCE of 3.29% over the planar control cell with a PCE of 2.86%, which is mainly due to the increase in the J_{sc} from 11.93 mA/cm² to 13.57 mA/cm² (13.7% enhancement). The similar V_{oc} and FF for both types of cells indicate that the PMMA/ITO double layer grating transparent electrode can be a suitable approach for application in high performance OSCs.

TABLE 6.1: Summary of photovoltaic characteristics measured for grating OSCs and the planar control cell.

<table>
<thead>
<tr>
<th>Device</th>
<th>Voc (V)</th>
<th>J_{sc} (mA/cm²)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar</td>
<td>0.54</td>
<td>11.93</td>
<td>44.19</td>
<td>2.86</td>
</tr>
<tr>
<td>Grating</td>
<td>0.54</td>
<td>13.57</td>
<td>45.17</td>
<td>3.29</td>
</tr>
</tbody>
</table>
Fig. 6.4: J–V characteristics measured for grating OSCs and a planar control cell under AM1.5G (100 mW/cm²).

In order to further investigate effect of grating electrode on the improvement of device performance, IPCE of the grating OSCs and the planar control cell at different polarizations were measured. The transverse electric (TE) mode of polarization refers to that the oscillation direction of electric field is parallel to the orientation of grating electrode, which will not generate the SPPs in the cells. The transverse magnetic (TM) mode of polarization, denotes the oscillation of electric field that is orthogonal to the direction of the grating electrodes, resulting in the possibility of SPPs excitation. In the IPCE measurement, a polarizer was placed in front of the cells and such that IPCE with TE and TM polarized light can be measured. The IPCE of the grating and planar control cells are presented in Fig. 6.5. Broadband enhancement in IPCE is observed for both TE and TM polarized incident light in the grating OSCs as compared to the planar control cell, due to the introduction of the dual-grating structure.
Fig. 6.5: IPCE measured for grating OSCs and the planar control cell under (a) TE polarization; and (b) TM polarization.

In order to better understand the effect of absorption enhancement in OSCs due to the use of grating electrode, an enhancement factor is introduced, which is obtained by taking the ratio of IPCE measured for the grating OSCs to that of a planar control OSC. The enhancement factor due to the grating at different wavelengths is shown in Fig. 6.6. The curves reveal the significant enhancement in IPCE at a broadband wavelength region for both TE and TM polarized incident light and there are several peaks in the enhancement factor curves. This indicates a broadband light absorption enhancement in the active layer in grating OSCs, considering that increase in the organic/electrode contact area in the grating OSCs will not result in the particular wavelength, as shown in the enhancement factor curve. Here we assume that the electrical properties of the two types of cells are similar due to the same stack of layers. Thus, absorption enhancement over the wavelength range from 400 nm to 800 nm is primary due to light trapping in the grating OSCs.
6.2 Study of Waveguide Mode

With the utilization of grating structures, diffraction effect is introduced and SPPs can be excited. Both effects contribute to light absorption enhancement because the former effect increases the optical path length and the latter one produces enhanced local field at the vicinity of grating Ag cathode surface. To determine the contribution in light absorption from the two mechanisms, the details in the optical properties of the OSCs were studied by numerical modelling. The optical absorption in the active layers in both the grating and the planar control OSCs was calculated using FDTD method. The complex refractive indices of the organic materials were obtained from the VASE measurement. Base on the size parameters obtained from the AFM measurement on the cathode surface of the grating OSCs, we assigned a sinusoidal profile for the metal cathode, organic stack and ITO anode on the PMMA grating. Fig. 6.7 is the simulated absorbance in the ZnPc:C₆₀ active layer in the grating and control cells under TE and TM polarized light. Broadband light absorption enhancement in the active layer of grating OSCs is clearly observed.
Fig. 6.7: Simulated absorbance in the active layer of the grating OSCs and the planar control cell under (a) TE polarization; and (b) TM polarization.

Corresponding to the peaks in the enhancement factor curves, shown in Fig. 6.6 (450 nm, 548 nm, 762 nm for TM polarization and 796 nm for TE polarization), the electric field distribution at these wavelengths were calculated and are presented in Fig. 6.8. For the planar control cell, as shown in Fig. 6.8(a), the maximum electric field is not always located in ZnPc:C_{60} layer. Besides, the maximum electric field in the planar control cell is relatively lower than that of the grating OSCs, considering that the scale bar has the field intensity value from 0.1 to 2.5. For the grating OSCs under TE and TM polarized illumination in Fig. 6.8(b) and Fig. 6.8(c), the strong localized field in the active layer is observed, indicating that the incident light is coupled into waveguide modes in the ITO/organic/metal system. This aside, if SPPs are excited by the TM polarized light, the maximum electric field will be generated at the edge of the Ag cathode, which is not observed in Fig. 6.8(c), implying that the maximum electric field is located in ZnPc:C_{60} layer. Therefore, it can be concluded that the main mechanism contributing to light absorption enhancement is the diffraction effect from the grating structure. Incident light is diffracted by the front PMMA grating and the rear Ag cathode, which couples light into waveguide modes with enhanced localized electric field and prolonged optical path length, resulting
broadband light absorption enhancement in the active layer in the grating OSCs.

(a) Planar

(b) TE

(c) TM

Fig. 6.8: Simulated electric field distribution in (a) planar control cell; and grating structured cell with incident light of (b) TE polarization; and (c) TM polarization.
To further understand the effect of diffraction and waveguide modes on absorption enhancement, we consider that incident light will be firstly diffracted forward to the active layer by PMMA grating and then diffracted backward by the reflective Ag grating. For a given wavelength, the diffraction should satisfy the following equation:

\[ m\lambda = n_{\text{eff}} p (\sin \theta_i + \sin \theta_d) \]  

(6.1)

where \( m \) is the diffraction order, \( n_{\text{eff}} \) is the effective refractive index of the stack of organic layers, \( p \) is the grating period, \( \theta_i \) and \( \theta_d \) are the incidence and diffraction angles respectively. For instance, assuming \( n_{\text{eff}} = 2 \) and \( p = 500 \text{ nm} \), according to Eq. 6.1, for the wavelength from 300 nm to 500 nm and from 500 nm to 700 nm under normal incidence, \( m \) takes values of 0, ±1, and ±2 and values of 0 and ±1, respectively. In fact, because the zeroth order reflection is reduced by periodic gratings, the diffraction at high orders occurs and the diffracted light at high orders can be bent by 90°. For example, when \( \lambda = 325 \text{ nm} \), the first and second order reflections can be bent by 18.9° and 40.5°, respectively. If \( \lambda = 500 \text{ nm} \), the first and second order reflections can be bent by 30° and 90°, respectively. Therefore, the optical path length in the active layer can be enhanced across a broad wavelength range with the application of the grating structure and the diffracted light can be coupled into waveguide modes.

6.3 Modeling of Absorption Enhancement in 2D-grating Structured Devices

Based on the one dimensional grating OSCs, light absorption enhancement in two dimensional grating OSCs was investigated by numerical modelling method. In a joint research work with the Centre for Organic Photonics & Electronics in The
University of Queensland, the OSCs based on PCDTBT:C_{70}-PCBM active layer were fabricated. The 120 nm thick PCDTBT:PCBM blend layer was spin-coated on planar ITO/PEDOT:PSS substrate and then it was patterned by nano-imprinting method using Si molds with the structures of two dimensional pillar arrays. The pillars have three series of diameters and pitches of 100 nm, 500 nm, and 2 μm, respectively. On the nano-structured PCDTBT:PCBM active layer, three batches of cathode, namely Al (80 nm), samarium (Sm) (1 nm)/Al (80 nm) and Ag (2 nm)/Al (80 nm) are deposited by thermal evaporation to form the two dimensional grating structures. For comparison, the planar control cell based on the same organic layers without 2D nano-structures was fabricated. The integrated absorbance in the PCDTBT:PCBM active layer of the OSCs with different period and cathode layers is simulated and summarized in TABLE 6.2, which is using the flux of solar light in the visible light region from 370 nm to 870 nm.

TABLE 6.2: Calculated integrated absorbance in active layer for OSCs with different periodicities and cathode contacts. The values in the parentheses are the increased percentage of the absorbance in grating structured cells compared to planar cell.

<table>
<thead>
<tr>
<th></th>
<th>Al cathode Integrated absorption</th>
<th>Sm/Al cathode Integrated absorption</th>
<th>Ag/Al cathode Integrated absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar</td>
<td>54.81%</td>
<td>53.18%</td>
<td>53.34%</td>
</tr>
<tr>
<td>Structured-100 nm</td>
<td>65.19% (~18.9%)</td>
<td>62.70% (~17.9%)</td>
<td>63.71% (~19.4%)</td>
</tr>
<tr>
<td>Structured-500 nm</td>
<td>56.43% (~2.9%)</td>
<td>55.21% (~3.8%)</td>
<td>55.55% (~4.1%)</td>
</tr>
<tr>
<td>Structured-2μm</td>
<td>58.50% (~6.7%)</td>
<td>57.65% (~8.4%)</td>
<td>57.78% (~8.3%)</td>
</tr>
</tbody>
</table>

It is shown that compared to a planar control cell, there is an obvious absorption enhancement in the nano-structured OSCs. This is realized via light trapping effect contributed by the two dimensional periodicity grating structures.
As to the structures used in the simulation model, the nano-structure with a period of 100 nm results in the largest light absorption enhancement. With the increase in the periodicity, the beneficial coherent interference of diffracted light will be reduced. Besides, in any structure (planar, 100 nm pillar, 500 nm pillar and 2000 nm pillar), the device with only Al cathode will possess the highest light absorption in PCDTBT:PCBM layer. The study on the two dimensional grating OSCs also demonstrates light absorption enhancement produced by the grating structures, which may be applied to other OSCs based on different materials with the modification in the size parameters.

6.4 Conclusion

In conclusion, a new device structure incorporating a PMMA/ITO double layer grating electrode was developed for application in OSCs. Broadband light absorption enhancement in ZnPc:C₆₀–based OSCs has been demonstrated using a PMMA/ITO double layer grating front electrode. On the transparent grating substrate, the standard OSCs can be directly applied with thermal evaporation process. It is demonstrated that the enhancement in performance of the grating OSCs (PCE 3.29%) over the planar control cell (PCE 2.86%) is mainly due to the increase in the Jₜₜ from 11.93 to 13.57 mA/cm² (13.7% enhancement) for grating OSCs. The investigation based on FDTD method reveals that the diffraction effect of the grating is the main contribution in the broadband light absorption enhancement in the ZnPc:C₆₀ active layer. Incident light can be coupled into different waveguide modes, resulting in enhanced optical path length and strong localized electric field. Light absorption enhancement in the solution processed OSCs, having 2D grating structures, was also investigated.
Chapter 7: Summary and Future Work

7.1 Summary

Broadband light absorption enhancement in OSCs with different nano-structures was investigated systematically using theoretical simulation and experimental optimization. The mechanisms of enhancement in $J_{SC}$ of different types of OSCs, including inverted OSCs, the OSCs made with CFx-modified Ag NPs/ITO and grating OSCs, were explored. Optical properties of these types of cells were studied using optical admittance analysis and FDTD method. Light absorption enhancement in OSCs, based on different light trapping features, including interference of light, LSPR, light scattering, SPPs and diffraction of light has been examined and analyzed.

Firstly, the inverted bulk heterojunction OSCs based on P3HT:PCBM active layer was fabricated. With a pair of an ultrathin Al-modified ITO front cathode and a bi-layer MoO$_3$/Ag anode, the inverted cell exhibited a superior PCE of 4.16%, which was about 13% more efficient than a control normal OSC using the ITO/PEDOT:PSS anode. Optical admittance analysis revealed that light absorption in inverted OSC was always greater than the conventional cell. It was demonstrated that the reverse configuration allowed improving charge collection at cathode/blend interface and also possessing a dawdling degradation behavior as compared to a control regular OSC in the accelerated aging test.

To further enhance light absorption in active layer, thermally evaporated Ag NPs were applied to the ZnPc:C$_{60}$ based OSCs. For the OSCs fabricated on rigid ITO/glass substrate, the $J_{SC}$ of OSCs made with CFx-modified Ag NPs/ITO was enhanced from 11.13 mA/cm$^2$ to 13.10 mA/cm$^2$, leading to an obvious increase in
PCE from 2.7% to 3.5% as compared to control cell. And as to flexible OSCs prepared on PET substrate, the flexible OSCs made with CFx-modified Ag NPs/ITO had a PCE of 3.1±0.1%, higher than the 2.6% PCE of the flexible control cell. CFx modification on the Ag NPs can improve the work function of the anode and achieved a similar charge carrier collection efficiency with the oxygen plasma treated bare ITO surface. The broadband light absorption enhancement in the ZnPc:C₆₀ blend layer was ascribed to the local field enhancement effect from the LSPR of Ag NPs. It was revealed that there was a significant difference in LSPR wavelength of Ag NPs with and without ZnPc:C₆₀ dielectric layer over-coated, which was interpreted by effective medium theory and the detailed analysis based on SEM measurement and FDTD simulation.

Lastly, the broadband light absorption enhancement in the ZnPc:C₆₀ active layer was achieved by the design of a dual-grating structured OSC using nano-imprint technique. The grating OSCs had an enhanced PCE of 3.29% compared to the planar control cell (PCE 2.86%), which was mainly due to increase in the J_sc from 11.93 mA/cm² to 13.57 mA/cm² for grating OSCs. Simulation based on FDTD method revealed that the incident light was firstly diffracted forward to the ZnPc:C₆₀ active layer by PMMA grating and then diffracted backward by the reflective Ag grating. The diffracted light can be coupled into different waveguide modes, resulting in enhanced optical path length and strong localized electric field, which was the main contribution in the broadband light absorption enhancement in the ZnPc:C₆₀ active layer.

7.2 Future Work

There is a plethora of opportunities and potential for the studied approaches for broadband light absorption enhancement to be applied for the OSCs based on
other materials. For example, for the OSCs made with CFx-modified Ag NPs/ITO, the size and coverage of the Ag nanoparticles can be further optimized for better device performance. Also, solution-processed OSCs can be fabricated with the incorporation of Ag NPs, especially for the PCDTBT:PCBM system with a relatively high PCE. Solution-processed Ag NPs can also be attempted for easier fabrication process of the device. For grating OSCs, the one dimensional or two dimensional Si molds can be applied to solution-processed system. Period of the grating structures should be optimized with FDTD method and the details in the optical contribution from the grating structures should be further investigated. In addition, we can go a step further from grating architecture to randomly textured substrate for easier large scale fabrication of OSCs.
Appendices

Publications


List of References


[46] https://www.lumerical.com/
Curriculum Vitae

Academic qualifications of the thesis author, Mr. YANG Qingyi:

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