Plasmonic organic solar cells with gold nanoparticles

Xu, Xiaoyan

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PLASMONIC ORGANIC SOLAR CELLS
WITH GOLD NANOPARTICLES

XU XIAOYAN

SCHOOL OF ELECTRICAL AND ELECTRONIC
ENGINEERING

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PLASMONIC ORGANIC SOLAR CELLS WITH GOLD NANOPARTICLES

XU XIAOYAN

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Abstract

Bulk heterojunction (BHJ) organic solar cells (OSCs) have many promising characteristics such as lower material cost, simple processing at ambient conditions and the possibility of roll-to-roll printing. The present major limitation of OSCs is relatively low power conversion efficiency (PCE) which is mainly caused by insufficient light absorption of thin active layers. In this thesis, the PCE of both polymer and small molecule (SM) OSCs are enhanced by increasing light trapping using the localized surface plasmon resonance (LSPR) effect of gold (Au) nanoparticles (NPs) embedded in the organic layers.

Two types of sub-wavelength Au NPs were studied. The first is large-sized core shell Au-silica nanorods with a length of about 100 nm. The nanorods have dual LSPR peaks for which the major peak wavelength can be tuned by the aspect ratio (length:diameter). The second type of NPs is Au nanospheres with a diameter of about 10 nm and one LSPR peak at 520 nm when dispersed in chlorobenzene.

Au-silica nanorods with major absorption peak at 720 nm and a silica shell thickness of 17 nm were directly blended into the regioregular poly (3-hexylthiophene):[6,6]-phenyl-C₆₁-butyric acid methyl ester (P3HT:PC₆₀BM) BHJ layer of a conventional OSC device structure. At optimum nanorod concentration, the average PCE of the plasmonic device was enhanced to $3.5 \pm 0.06\%$ with an increase of 13% relative to the reference device due to increased optical absorption from 480 nm to 600 nm.

When these nanorods were embedded within the BHJ layer comprising

poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₀BM), the PCE of $4.4 \pm 0.11\%$ was obtained with a relative enhancement of 25% with respect to the reference device. The significantly greater enhancement than that observed in P3HT:PC₆₀BM device is due to the broader absorption and external quantum efficiency improvement from 500 to 800 nm, especially near the LSPR peak of nanorod. By using diffuse scattering measurements, the plasmonic enhancement in the PCPDTBT:PC₇₀BM device is mainly ascribed to increased light scattering in thick shell large-sized nanorods.

Since solution-processed SM donors have the advantage of monodispersity relative to polymer donors, Au-silica nanorods with shell thickness of 5 nm and aspect ratio of 2.6 were introduced into OSCs based on 7,7'-(4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(6-fluoro-4-(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo[*c*][1,2,5]thiadiazole):PC₇₀BM (p-DTS(FBTTh₂)₂:PC₇₀BM). A high PCE of $8.2 \pm 0.12\%$ with 27% relative enhancement in the p-DTS(FBTTh₂)₂:PC₇₀BM device was achieved. Both current density and fill factor were higher than the P3HT:PC₆₀BM and PCPDTBT:PC₇₀BM devices because the major LSPR peak at 680 nm is well-matched with the absorption peak of p-DTS(FBTTh₂)₂. In addition, its well-balanced and high carrier mobility enhanced the carrier transport and collection as confirmed by electrical characterization. Finite-difference time-domain simulation showed that the localized electric field intensity outside the silica shell decreased with the increase of the silica shell thickness. As a result, both increased localized electric field intensity and increased light

scattering were involved in PCE enhancement for a shell thickness of 5 nm. Furthermore, silica shell was proved that it can avoid the carrier recombination at the surface of Au nanorods by conducting light intensity dependence of short-circuit current density measurements. The optimum nanorod concentration was determined by decrease of carrier mobility and increase of BHJ layer surface roughness at high nanorod concentration.

In order to realize further PCE improvement in the SM device, an alternative device architecture consisting of bare Au nanospheres incorporated into the poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) anode buffer layer and Au-silica nanorods into the p-DTS(FBTTh₂)₂:PC₇₀BM layer simultaneously was adopted. A high PCE of $8.5 \pm 0.22\%$ with a relative increase of 31% over the reference device was achieved. The combination of two types of Au NPs resulted in superior broadband absorption enhancement. Moreover, the fill factor was improved by Au nanospheres which can facilitate hole collection due to reduced series resistance.

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Common Abbreviations

Abbreviations	Full expressions
BHJ	Bulk heterojunction
OSCs	Organic solar cells
SM	Small molecule
SPR	Surface plasmon resonance
LSPR	Localized surface plasmon resonance
PCE	Power conversion efficiency
NPs	Nanoparticles
P3HT	Poly(3-hexylthiophene)
PC ₆₀ BM	[6,6]-phenyl-C ₆₁ -butyric acid methyl ester
PC ₇₀ BM	[6,6]-phenyl-C ₇₁ -butyric acid methyl ester
PCPDTBT	poly[2,6-(4,4-bis-(2-ethylhexyl)-4 <i>H</i> -cyclopenta [2,1-b:3,4-b']dithiophene)- <i>alt</i> -4,7-(2,1,3-benzoth- iadiazole)]
p-DTS(FBTTh ₂) ₂	7,7'-(4,4-bis(2-ethylhexyl)-4 <i>H</i> -silolo[3,2-b:4,5-b'] dithiophene-2,6-diyl)bis(6-fluoro-4-(5'-hexyl-[2,2'- bithiophen]-5-yl)benzo[<i>c</i>][1,2,5]thiadiazole)
<i>I</i> - <i>V</i>	Current-voltage
<i>J</i> - <i>V</i>	Current density-voltage
<i>J</i> _{sc}	Short-circuit current density
<i>V</i> _{oc}	Open-circuit voltage
<i>FF</i>	Fill factor
FDTD	Finite-difference time-domain
HOMO	Highest occupied molecular orbital
LOMO	Lowest occupied molecular orbital
CB	Chlorobenzene
DCB	1,2-dichlorobenzene
<i>J</i> _{ph}	Photocurrent density

PEDOT:PSS	Poly(3,4-ethylenedioxythiophene):poly(styrene esulfonate)
R_{sh}	Shunt resistance
R_s	Series resistance
IQE	Internal quantum efficiency
EQE	External quantum efficiency
IPCE	Incident photon-to- electron conversion efficiency
η_A	Absorption efficiency of light
η_{ED}	Exciton diffusion efficiency
η_{CT}	Charge transfer efficiency
η_{CC}	Charge collection efficiency
AM1.5G	Air Mass 1.5 Global
MDMO-PPV	Poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene)
MoO ₃	Molybdenum trioxide
CuPc	Copper phthalocyanine
ZnPc	Zinc phthalocyanine
ITO	Indium tin oxide
WO ₃	Tungsten trioxide
LiF	Lithium fluoride
TiO _x	Titanium (sub) oxide
ZnO	Zinc oxide
HTL	Hole transport layer
C_{abs}	Absorption cross section
C_{sca}	Scattering cross section
DDA	Discrete Dipole Approximation
CTAB	Hexadecyltrimethylammonium bromide
TEOS	Tetraethylorthosilicate
TEM	Transmission electron microscope
PL	Photoluminescence
DIO	1,8 octanedithiol

SEM	Scanning electron microscope
AFM	Atomic force microscopy
H_T	Haze factor for transmission
H_R	Haze factor for reflection
DSSC	Dye-sensitized solar cell
SCLC	Space-charge limited current
RMS	Root mean square
$G_{\max}$	Maximum photoinduced carrier generation rate
P_C	Charge collection probability
MIM	Metal-insulator-metal

Chapter 1 Introduction

1.1 Energy Sustainability Issues

With the rapid growth in the modern economy and living standard, global energy demands have been increasing in recent decades. According to the International Energy Outlook 2013 (IEO2013) published by U.S. Energy Information Administration (EIA), world energy consumption per year is predicted to reach 27.2 terawatts (TW) in 2040 with an increase of 56% compared to the 17.3 TW in 2010 [1]. Currently, 78.4% of total energy consumption is provided by traditional fossil fuels such as coal, oil and natural gas [2]. However, fossil fuel as finite resources eventually will have a peak in production rate and then decline. Moreover, due to our excessive use of fossil fuel, the current concentration of carbon dioxide (CO_2) in atmosphere has reached 400 parts per million (ppm) compared with 280 ppm before industrial revolution, which causes global warming [3, 4].

The above mentioned sustainability issue and CO_2 emission thereby promote the growth of renewable energy source as the promising solution. The renewable energy resource is defined as any energy source which can replenish itself in human timescale for sustainable extraction. It mainly includes solar energy, hydroelectric power, wind energy, biomass energy, and geothermal energy [5]. Most of them are intermittent energy sources except geothermal energy. However, some of these renewable resources have adverse impact on the environment. For example, hydroelectric energy changes both the water quality and water flow in the downstream, which has negative effects on the

fauna and flora [6]. Some of these renewable sources can reduce food supply such as biofuels from food crops like corn. Compared to these renewable sources, solar energy has almost negligible environmental impact without any pollutant release and ecological damage. Moreover, the sun light is available in all parts of the world and can provide a continuous energy supply per year of 86000 TW to the earth which is far more than the world energy consumption per year of 17.3 TW in 2010 [7]. To put this in perspective, if a desert with land area of $650 \text{ km} \times 650 \text{ km}$ is all covered with solar panels with a power conversion efficiency (PCE) of 25%, it can supply the 17 TW of electricity that the world used in 2010. Therefore, solar energy is proved to be one of the most important renewable sources because of its environment compatibility, abundance and availability. Solar energy can be actually utilized only after conversion to more practical energy forms like electricity via photovoltaic technology and solar thermal technology.

1.2 Solar Cells

Electricity generated directly from solar energy is preferred because it is convenient to be applied to all kinds of electrical and electronic products. The direct conversion of light to electricity by photovoltaics or solar cells was attributed to the discovery of the photovoltaic effect by Becquerel in early 19th century [8]. The photovoltaic effect is the generation of the electrons and holes (or photocurrent) when a semiconductor junction is exposed to sun light. In 1954, Chapin et al. from Bell Laboratories first applied the photovoltaic effect in semiconductor p-n junction and unveiled the first crystalline silicon solar cell

with remarkable PCE of 6% [9]. In the past 60 years, many solar cell technologies had been developed and these can be classified into three generations.

First generation solar cells are mainly based upon crystalline silicon wafers and consist of p-n junction diodes. Due to the Shockley-Queisser limit, the maximum efficiency of these solar cells with a single junction is limited to 33% [10]. At present, the crystalline silicon solar cells dominate 90% of the solar cells market and the highest PCE of such devices reaches 27.6% as shown in Fig. 1-1 [11, 12]. Although this generation of solar cells has high efficiency, its production cost is also high due to the use of thick silicon wafer which need the minimum thickness at least 125 μm to absorb incident sunlight. In addition, the energy consumption of the high-temperature production process is also high.

In order to reduce the material usage, the second generation solar cells called “thin-film” solar cells were developed and these cells could reduce the production cost without use of silicon wafers compared to the first generation solar cells. Thin-film solar cells mainly include crystalline silicon thin-film solar cells, amorphous silicon thin-film solar cells, organic solar cells (OSCs), dye-sensitized solar cell (DSSC), cadmium telluride (CdTe) thin-film solar cells and copper indium gallium selenide (CIGS) solar cells [13]. Although the cost of thin-film solar cells is lower than crystalline silicon solar cells, they also have lower PCE of about 10-20% compared with first generation solar cells [14]. Therefore, more of these cells are needed for supplying same amount of power.

Figure 1-1 Best research-cell efficiencies 1976-2014 [12]. The arrows indicate OSCs (various types).

The third generation of solar cells can be subdivided into IIIa and IIIb. Generation IIIa strives for very high efficiency by using novel approaches such as multijunction, hot carrier, multiple carrier ejection and intermediate band, which can potentially overcome the Shockley-Queisser limit [13]. Recently, the concentrator triple-junction compound solar cell has already achieved the efficiency up to 44.4%, which created a new world record efficiency by Sharp corporation [15]. However, these cells require the use of high cost compound semiconductors. Generation IIIb solar cells are supposed to have only moderate efficiency but very low cost. These cells in the long term may include the perovskite solar cells, OSCs and so on, which have recently emerged as a promising alternative. Perovskite solar cells have seen a rapid development with the efficiency enhancement from 3.8% to 19.3% in the past five years [16]. However, the best perovskite solar cells contain lead, which is very toxic and cannot be commercialized in the photovoltaic market. OSCs have the unique

advantages because organic materials are readily synthesized available, cheap and can be tailored in mechanical, optical and electrical properties. Furthermore, they can be simply fabricated by roll-to-roll printing technology to realize large-scale manufacture. Thus, OSCs have great potential to far lower production cost than previous solar cells. However, according to the latest report, the highest PCE of OSCs has only reached ~11% [17]. Thus at the present stage of development, it is more appropriate to classify OSCs as generation II solar cells.

Figure 1-2 Efficiency-cost analysis for the three generations of solar cell technology [18].

For the commercialization of the solar cells, the production cost and efficiency are two important factors which need careful trade-off. Fig. 1-2 displays the efficiency versus cost per unit area for the above mentioned three generations of solar cells, which was proposed by Martin Green [18]. The cost per watt (cost/W) appears as lines where the gradient increases with decreasing cost/W. First generation solar cells have high efficiency but very high cost. Second generation solar cells have modest efficiency and lower cost. Both of

them have cost/W between US\$ 1.00/W and US\$ 3.50/W. Generation IIIa solar cells have cost/W between US\$ 0.20/W and US\$ 0.50/W due to very high efficiency. On the other hand, the cost per unit area (cost/m²) for generation IIIa is lower than that for generation I and efficiency is higher while the cost/m² for generation IIIa is slightly higher than that for generation II because of complex processing. Generation IIIb solar cells can have both the lowest cost/m² (US\$ 0-100/m²) and cost/W (US\$ 0.10-0.50/W) owing to moderate efficiency and lowest cost. Therefore, OSCs as one of potential generation IIIb solar cells have attracted much attention because of commercialization possibility.

OSCs are divided into two categories according to the organic materials used. Polymer-based OSCs are called polymer OSCs while small molecule (SM)-based OSCs are called SM OSCs. During the past few decades, the efficiencies of OSCs have been rising steadily with improved organic materials and device architectures. The first OSCs consisted of the single organic layer sandwiched between two electrodes. The formed Schottky junction at the organic/electrode interface could not efficiently dissociate excitons and led to very low efficiency around 0.7% [19]. This motivated the bilayer architecture by successive deposition of donor layer and acceptor layer. In 1986, C. W. Tang reported the first bilayer SM OSCs with the efficiency of ~1%, which were fabricated by vapor evaporation technique [20]. The breakthrough came with the observation of the ultrafast charge transfer at the interface of the donor (phthalocyanine derivative) and acceptor (perylene derivative), which greatly enhanced the exciton dissociation efficiency [21]. In 1995, bulk heterojunction (BHJ) architecture was introduced to achieve higher efficiency since the

mixture of the donor and acceptor components largely increased the donor/acceptor interface and provided more sites for exciton dissociation [22]. The most commonly used BHJ OSCs based on poly(3-hexylthiophene):[6,6]-phenyl-C₆₁-butyric acid methyl ester (P3HT:PC₆₀BM) have reached the PCE of 4-5% by extensive study of the effect of processing conditions on the morphology of BHJ [23]. In order to further increase the device's PCE, new donor materials with broadband light absorption and good charge transport properties were synthesized. For example, OSCs based on low bandgap polymers were investigated and have achieved the PCE of 5.5% by harvesting of long wavelength photons [24]. Recently, a PCE higher than 9% in SM OSCs has been reported due to the wide absorption range and balanced and high charge carrier mobilities of the solution-processed SM donor [25]. However, single junction OSCs with new donors and device architecture still cannot exceed the efficiency of 11% and there had been no further efficiency enhancement in the last two years as shown in Fig. 1-1. To realize commercialization in the competitive solar cells market, the efficiency of 15% in OSCs is necessary. Therefore, there is urgent need to investigate other techniques to boost efficiency.

1.3 Objectives

As mentioned above, OSCs have been intensely investigated and have achieved rapid development in the past few decades. However, the efficiency still needs to increase for future commercialization. The low efficiency in OSCs is mainly caused by insufficient light absorption in the very thin active layer

(~100 nm). This is despite the fact that organic semiconductors have high absorption coefficients. The use of thin active layer is necessitated by the short exciton diffusion length (~10 nm) and low carrier mobilities ($\sim 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) of organic semiconductor materials. In addition, the spectral mismatch between the absorption spectrum of organic semiconductors and the incident irradiance solar spectrum will result in longer wavelength photons not being absorbed. As a result, an approach to enhance light absorption without increasing the thickness of the active layer is necessary. The most effective way is to synthesize new organic materials with broadband absorption and good charge transport properties. Thus far, many organic materials have been well developed but the synthesis approach has yielded few new donor materials in recent years.

Metallic nanoparticles (NPs) as one of the most promising light trapping technologies have been widely introduced into polymer OSCs for enhanced light harvesting induced by the plasmonic effect of metallic NPs. Currently, most of the studies focus on the spherical NPs with a diameter less than 50 nm. However, the localized surface plasmon resonance (LSPR) spectrum of these NPs is not only narrow but also in a short wavelength range. In addition, the limitation of small size and spherical shape in these NPs greatly weakens the light scattering of NPs inside of OSC devices.

In order to overcome the above mentioned issues, the objectives in this thesis consist of the following four aspects with the aim of achieving higher OSCs efficiency. First, the large-sized gold (Au) nanorods with silica shell are introduced to the OSC devices for harvesting more sun light. Second, the light trapping induced by these nanorods is studied respectively in the conventional

polymer OSCs, low bandgap polymer OSCs and solution-processed SM OSCs. The mechanisms of enhanced light absorption as another important aspect are investigated by experiments and theoretical simulation. Finally, a new device structure with the incorporation of two types of Au NPs are proposed to take full advantage of the broadband optical absorption and better hole transport.

1.4 Major Contributions

This thesis focuses on the fabrication and characterization of plasmonic OSCs embedded by Au NPs. The significantly enhanced performance of both polymer and SM OSCs are demonstrated by incorporation of Au NPs into the organic layers. The detailed mechanisms behind the increased optical absorption in these cells are attributed to both enhanced localized electric field and light scattering induced by Au NPs which is theoretically and experimentally confirmed. Optical characterizations including incident photon-to-electron conversion efficiency (IPCE) and current-voltage (*I-V*) characteristics show that optimum concentration of Au-silica nanorods in the OSCs is at 1 weight percentage (wt%) of donor/acceptor blend weight. The factors that determine the optimum concentration of nanorod in plasmonic device are studied by charge carrier mobility characterization and morphology measurements of the active layers.

The contributions are summarized as follows:

- 1) Silica coated Au nanorods with the length of ~100 nm and a silica shell thickness of 17 nm were incorporated into the polymer BHJ OSC. They have the major absorption peak at 720 nm and were directly blended into the BHJ

layer comprising P3HT:PC₆₀BM and poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)]:[6,6]-phenyl-C₇₁-butyric acid methyl ester (PCPDTBT:PC₇₀BM). The P3HT:PC₆₀BM device and PCPDTBT:PC₇₀BM device with optimized concentration of Au-silica nanorods showed an improvement of efficiency from 3.1% to 3.5% and from 3.4% to 4.4% respectively. The superior performance in the plasmonic PCPDTBT:PC₇₀BM device than that observed in P3HT: PC₆₀BM device is due to the better matching of absorption spectra between PCPDTBT and Au-silica nanorods from 500 to 800 nm. For the thick shell large-sized nanorods, the plasmonic enhancements in these devices are mainly ascribed to the increased light scattering confirmed by diffuse scattering measurements.

2) Plasmonic solution-processed SM OSCs have been realized for the first time. Au-silica nanorods with the major absorption peak at 680 nm and 5 nm silica shell were introduced into the OSCs based on 7,7'-(4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(6-fluoro-4-(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo[*c*][1,2,5]thiadiazole):PC₇₀BM (p-DTS(FBTTh₂)₂:PC₇₀BM). A high PCE of 8.29% with 27% relative enhancement in the p-DTS(FBTTh₂)₂:PC₇₀BM device was achieved due to its well-balanced and high carrier mobility and well-matched absorption spectra between p-DTS(FBTTh₂)₂ and Au-silica nanorods.

3) The optimized conditions and mechanisms of the Au-silica nanorods have been explored in detail. The effect of shell thickness and concentration of Au-silica nanorods on the device performance were studied by finite-difference time-domain (FDTD) simulation, carrier mobility and surface roughness

characterization of the active layers respectively. As a result, the optimum shell thickness is 5 nm and optimum Au-silica nanorod concentration is given as 1 wt% of donor/acceptor blend weight.

4) In order to realize further PCE improvement in the device, a new device architecture was developed by incorporating different shapes of Au NPs into both anode buffer layer and the active layer of the device. The combination of Au nanosphere and core-shell Au-silica nanorods realized a broad extinction spectrum as well as facilitated the hole collection due to reduced series resistance (R_s). The maximum PCE of 8.72% was achieved by incorporating Au nanospheres and nanorods into organic layers.

1.5 Organization

This thesis contains the following eight chapters.

Chapter 1 outlines the motivation of this thesis and reviews the three generations of solar cells. Their historical development and the existing problems of OSCs as a promising technology are presented, followed by the objectives and major contributions of this study.

Chapter 2 introduces the fundamentals of OSCs including organic semiconducting materials, fabrication techniques, device working principles, device architectures and solar cell characterization. In addition, the approaches for efficiency enhancement for OSCs are discussed.

Chapter 3 presents recent overview of plasmonic OSC devices embedded with metallic NPs. Au nanospheres and nanorods have LSPR effect upon the light excitation which is interpreted theoretically and can be applied in the

OSCs for light trapping. The properties of Au especially in optical properties demonstrate that the Au is a good candidate plasmonic material for the applications compared to other metals.

Chapter 4 describes the experimental methods concerning the OSC device fabrication and characterization. The experimental results of the P3HT:PC₆₀BM OSC devices enhanced by Au-silica nanorods are discussed by optical absorption, photoluminescence (PL) spectrum measurements and current density-voltage (J - V) characteristics.

Chapter 5 presents the enhanced performance of low bandgap PCPDTBT:PC₇₀BM OSC devices by incorporation of Au-silica nanorods. The scattering effect of Au-silica nanorods as major mechanism of improved light absorption in the device is demonstrated by diffuse scattering measurement.

In chapter 6, the plasmonic effect of Au-silica nanorods is introduced to SM OSCs for the first time. The mechanisms are investigated in detail by both electromagnetic field simulation and diffuse scattering measurement. The optimization of the silica shell thickness is also determined by this simulation. Silica shell prevents the carrier recombination at the surface of metal, which is confirmed by light intensity dependence of short-circuit current density (J_{sc}). The influence of nanorods concentration on the device performance is analyzed by charge mobility and the surface roughness of the active layer.

Chapter 7 presents a novel device structure by incorporation of Au nanospheres and Au-silica nanorods into the buffer and BHJ layers of SM OSCs respectively. The superior broadband absorption and enhanced hole collection induced by the combination of two types of NPs are demonstrated by the

optical and electrical characterization.

In chapter 8, the conclusion and the outlook of the studies are described.

Chapter 2 Review of Organic Solar Cells

2.1 Introduction

OSCs have been under development for the past three decades [19-21]. However, in the last few years, it has experienced a substantial increase in efficiencies, with the highest reported efficiency around 11% comparable to the best DSSC and stabilized amorphous Si:H cells [14].

OSCs derive their name from the use of semiconducting SM, oligomers or polymers that exhibit the photovoltaic effect [26-28]. Compared with inorganic semiconductors such as silicon, they have low cost and relatively strong absorption coefficient as high as 10^5 cm^{-1} allowing very thin OSCs with thickness of several hundred nanometers (nm) [29]. Moreover, due to the diversity of organic molecules, OSCs could be easily modified to change their optical, electronic and mechanical properties [30-33]. Therefore, OSCs have triggered commercial interest due to its low price materials, ease of solution processing and mechanical flexibility [34-37].

2.2 Organic Semiconducting Materials

Organic semiconducting materials are categorized into SM and polymers according to molecular weight (MW) and structural complexity. SM materials normally consist of a few hundred atoms and have MW less than 1000. Polymers are long-chain molecules with undefined number of repeating units and therefore have high MW up to 10^6 . Both of them are usually used as the active materials including hole-conducting donors and electron-conducting

acceptors in organic optoelectronic devices. This is because SM and polymers with conjugated pi (π) electron system allow charge carrier transport and absorption of visible light within the solar spectrum due to the sp^2 -hybridized carbon atoms.

Figure 2-1 Bonding in conjugated molecules. The purple lines represent the σ bonds. Two of σ bonds of each carbon atom are not shown for clarity.

In these conjugated molecules, the four valence electrons of the carbon atom along a chain undergo what is called sp^2 hybridization. Three of the resulting sp^2 electrons form σ -bonds with other atoms, which become the molecular structure. The remaining p_z -electron occupies a dumbbell shaped orbital perpendicular to the sp^2 orbitals. Overlap of adjacent p_z orbitals forms π - π^* molecular orbitals (π -bonds), which leads to a repeated single and double bond structure. Because of the Peierls effect, these π -bonds are in fact of a delocalized nature, leading to high electronic polarizability. Since the π -bonds are much weaker than the σ -bonds, the lowest energy electronic transitions in conjugated molecules are the π - π^* transitions (Fig. 2-1) with energy band gaps ranging from 1.5 to 3 eV, which leads to light absorption of conjugated

molecules in the visible range.

Figure 2-2 Energetics of organic semiconductors.

The delocalized π -bonds result in an electronic structure that resembles the energy bands in crystalline semiconductors (Fig. 2-2). There is a ‘valence band’ and a ‘conduction band’ separated by an energy gap. Φ is called the electron affinity (typically ~ 3 eV). IP is called the ionization potential (typically ~ 5 eV). The top of the ‘valence band’ and the bottom of the ‘conduction band’ are defined as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. The HOMO and LUMO levels determined the open-circuit voltage (V_{OC}) in OSCs.

Figure 2-3 Molecular structure of most commonly used (a) SM materials and (b) Polymers in OSCs [29].

Fig. 2-3 (a) shows the structural formulae of the most commonly used SM materials. The phthalocyanines such as copper phthalocyanine (CuPc) and zinc phthalocyanine (ZnPc) are the representative examples of hole-conducting donors [38]. The 3,4,9,10-perylenetetracarboxylic-3,4:9,10-bis-methylimide (MePTC), 3,4,9,10-perylenetetracarboxylic bisbenzimidazole (PTCBI) and buckminster fullerene C_{60} are typically used as electron-conducting acceptors [39]. Both of these SM are not easy to be dissolved in the solvents and thus can only be co-evaporated for efficient SM OSCs. However, the evaporation of these materials is a batch process and needs vacuum processing. Recently, a solution-processed SM OSC with the efficiency of 4.4% was reported by T. -Q. Nguyen's group who used the new SM based on diketopyrrolopyrrole (DPP) and oligothiophene (OT) building blocks [40].

Compared to most of the SM, the polymers as depicted in Fig. 2-3 (b) are solution-processable due to their side-chain solubilizing groups. The representative examples of polymer donor are poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) [41], P3HT [42], poly(9,9'-dioctylfluorene-co-bis-*N,N'*(4-butylphenyl)-bis-*N,N'*-phenyl-1,4-phenylenediamine (PFB) and poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole) (PCDTBT). The fullerene derivatives such as $PC_{60}BM$ and $PC_{70}BM$, are the most studied acceptors used in conjunction with these polymers [43].

Typically, these SM and polymers have energy band gaps around 2 eV (620 nm), which limit the sun light absorption because the absorption spectra of these materials have small overlap with the standard Air Mass 1.5 Global

(AM1.5G) terrestrial solar spectrum. Nevertheless, by adjusting the band gaps via chemical modification, the organic materials with low bandgap can have more light absorption in the longer wavelength region of the solar spectrum. For example, 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) [44, 45] with band gap of 1.6 eV and PCPDTBT [24, 46] with band gap of 1.5 eV have wide absorption spectrum up to 700 nm and 800 nm, respectively. However, these polymeric materials suffer from low carrier mobility such as the PCPDTBT:PC₇₀BM with hole mobility of $3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and PTB7:PC₇₀BM system with $5.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively, [47]. In addition, there is carrier mobility imbalance between hole mobility and electron mobility in these polymer systems [48].

Recently, solution-processed SM donors have been widely studied as a viable alternative to the conjugated polymers for OSCs due to broad and strong light absorption and the well-balanced and high charge carrier mobilities ($\sim 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [40]. Moreover, this type of SM donor offers simple synthesis, purification and monodispersity compared to polymeric materials. In 2012, a solution-processed SM donor, 5,5'-bis{(4-(7-hexylthiophen-2-yl)-thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine}-3,3'-di-2-ethylhexylsilylene-2,2'-bithiophene (DTS(PTTh₂)₂), was reported by A. J. Heeger's group which demonstrated the efficiency of 6.7% for this solution-processed SM OSCs [49]. Recently, the p-DTS(FBTTh₂)₂:PC₇₀BM solar cell with a high efficiency up to 9% was also reported by them [25]. Here, the difference between the 5-fluorobenzo[c]-[1,2,5]thiadiazole (FBT) and [1,2,5]-thiadiazolo[3,4-c]pyridine (PT) is that the

fluorine atom in FBT provides an electron-withdrawing functionality [50].

2.3 Fabrication Techniques

Evaporation and solution processing are the two main techniques for organic thin film deposition. For evaporation processing, materials are required to be thermally stable while for solution processing, materials should be soluble in the solvent used. Generally, polymers have better solubility but less thermal stability than SM as mentioned above. Hence, semiconducting polymers are mainly solution-processed, whereas SM are normally deposited by thermal evaporation.

(a) Evaporation

SM and metals are normally deposited by vacuum thermal evaporation (VTE) [38] technique at high temperature as shown in Fig. 2-4 (a). Other evaporation techniques such as organic vapor phase deposition (OVPD) [51] and electron beam evaporation illustrated in Fig. 2-4 (b) are also available. Basically, the heat is applied by either ohmic current or electron beam bombardment. The material sublimates and travels by line of sight to all exposed surfaces. In order to achieve high device performance, it is necessary to reduce and eliminate the oxygen (O_2) and water inside the chamber because the metals and organic semiconducting materials are sensitive to water and O_2 . For VTE, a vacuum of $10^{-7} \sim 10^{-6}$ mbar or evaporation chamber set inside the glove box with nitrogen (N_2) can be applied prior to thermal evaporation of thin films. As a result, using the evaporation technique for fabrication of OSCs will involve more complex operation conditions and wasteful of materials.

Figure 2-4 Schematic diagrams of (a) vacuum thermal evaporation and (b) electron beam evaporation.

(b) Solution processing

Polymer OSCs are usually solution processed because many of the polymers are soluble in organic solvents such as chlorobenzene (CB) and 1,2-dichlorobenzene (DCB) or in aqueous solvent such as Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) in ethanol/water. The mixture of polymer donor and fullerene derivative acceptor can also be dissolved in those solvents. To avoid the contamination with water and O_2 , solution processing is normally carried out inside the glove box filled with N_2 . The most commonly used solution processing techniques include spin-coating [52], screen printing [34], doctor blade [53] and inkjet printing [54] as shown in Fig. 2-5. These solution processing technologies offer the potential large-scaled fabrication with low energy consumption. Spin coating uses the rotated substrate to spread the fluid to form a uniform thin film. A thin film is also formed by doctor blade which applies a blade to remove the liquid from the outside surface of the gravure cylinder. Screen printing can form a desired image by pressing the ink through the mesh openings onto a substrate below by

a squeegee or blade. Inkjet printing involves jetting of ink droplets onto the substrate and creates any pattern with the control of the computer pattern generator [55].

Figure 2-5 Schematic diagrams of spin coating, screen printing, doctor blade and inkjet printing.

2.4 OSC Device Operating Principles

The operating principle of OSCs is quite different from inorganic semiconductor solar cells. In inorganic semiconductors, free charge carriers are directly generated upon photoexcitation due to large dielectric constants. In contrast, coulombically bounded electron-hole pairs (excitons) are spontaneously formed after photoexcitation in the organic semiconductors. The exciton binding energy can be 0.5 eV or higher due to the low dielectric constant (~ 3), which thereby requires a strong electric field to assist the exciton dissociation into free hole and electron for photovoltaic conversion [28]. Fig. 2-6 illustrates the photovoltaic energy conversion process in a heterojunction OSC with the corresponding loss mechanisms.

Figure 2-6 Device operating principle of a heterojunction OSC.

(a) Light absorption

The first photovoltaic conversion step is light absorption. When an incident photon with energy more than the band gap of the organic material is absorbed, it can excite an electron into the LUMO of the donor while a hole still stays in the HOMO of the donor. Thereafter, a tightly bounded exciton is formed. During this process, the light can be also lost due to reflection at the device surface, or when passing through the transparent electrode. Moreover, a fraction of light is lost due to spectral mismatch between the band gap of the organic semiconductors and incident irradiance spectrum.

(b) Exciton diffusion

Once the excitons are generated, they start to diffuse to the interface between the donor and acceptor. This exciton diffusion is in competition with the exciton recombination during the diffusion process. This is because the

generated excitons beyond the exciton diffusion length will decay fast. The diffusion length of an exciton mainly depends on the mobility and the minority carrier lifetime of the organic semiconductors and has typical length from 5 nm to 20 nm [56, 57].

(c) Charge transfer

When the exciton reaches the donor/acceptor interface, electrons at the LUMO of donor will transfer into the LUMO of the acceptor while the hole stays, yielding a bound electron-hole pair [21]. The energy level difference between LUMO of donors and LUMO of acceptors supplies the quasi-electric field for the charge transfer [58].

(d) Electron-hole pair dissociation

The bound geminate electron-hole pair is dissociated into free charge carriers by a strong electric field. This electric field can be derived from the external electric field via work function difference between two electrodes or internal potentials at the interfaces of donor and acceptor.

(e) Charge transport

Once the free hole and electron are generated, the free hole will transport along the donor to the anode with a high work function, while the free electron will transport to the cathode with a low work function through the acceptor by the driving force. The driving force originates from the electric field created by the work function difference between anode and cathode or chemical potential gradient in holes and electrons. During the charge transport process, charge carriers may be trapped and have high recombination if carrier mobility of the organic materials is low.

(f) Charge collection

After the charge carriers transport through their respective phases to the interfaces of electrodes and active layer, free holes will be transferred to Fermi level of anode from HOMO level of donor whilst free electrons will be transferred to Fermi level of cathode from LUMO level of acceptor by a hopping or tunneling step [59]. Then they are extracted to external circuit. There is also recombination if there is non-ohmic contact where the HOMO level of the donor and LUMO level of acceptor do not match the Fermi level of anode and cathode, respectively.

2.5 OSC Device Architectures

The three typical device architectures of OSCs as shown in Fig. 2-7 are reviewed in this section. They mainly have two differences. The first one is the exciton dissociation, which takes place at different locations in the active layer. The other one is the sequential charge transport to electrodes. According to the photovoltaic conversion principle in OSCs mentioned above, the exciton dissociation efficiency and charge transport efficiency are key factors that significantly affect the OSC device performance. Therefore, the advantages and disadvantages of these architectures are also discussed.

Figure 2-7 The commonly device structures used in OSCs: (a) Single layer; (b) Bilayer; (c) Bulk heterojunction.

(a) Single layer

The first generation OSCs consist of single organic layer sandwiched between two different electrodes illustrated in Fig. 2-7 (a). The organic layer is usually deposited by vacuum evaporation. The work function difference of these two electrodes or Schottky barrier between the lower work function metal and the organic layer leads to built-in potential which provides a driving force to dissociate the excitons generated in the organic materials. However, only those excitons within the exciton diffusion length (~ 20 nm) from the Schottky contacts can be dissociated and give rise to the photocurrent. Moreover, the mobility of hole and electron in single organic material are different, which limits the short-circuit current of the OSCs. Therefore, this type of OSCs has very low PCE within the range of 0.7% [19].

(b) Bilayer heterojunction

Bilayer heterojunction OSCs shown in Fig. 2-7 (b) have two organic layers (donor and acceptor), which are successively deposited and sandwiched between two electrodes one of which is transparent and conducting. This configuration was pioneered by C. W. Tang in 1986 to demonstrate an OSC device with the efficiency of 0.95% [20]. The bilayer heterojunction concept brought a breakthrough because the large potential drop in the interface between these two layers (CuPc as donor and PTCBI as acceptor) results in an effective field that is sufficient for charge dissociation [22]. Furthermore, free electrons and holes will transport along the electron-transporting acceptor and the hole-transporting donor material respectively after exciton dissociation, which significantly decreases charge carrier recombination. Moreover, two

asymmetric electrodes with different work functions match the donor HOMO and the acceptor LUMO, respectively so that no energy is lost when the photo-generated carriers are extracted at the electrodes. The V_{OC} in the bilayer heterojunction architectures is dependent on the energy levels of organic materials used rather than the work functions of electrodes in a single layer structure. However, due to the exciton diffusion length being smaller than the optical absorption length, a large fraction of the photo-generated excitons will recombine prior to their reaching the dissociation sites at the donor-acceptor interface.

(c) Bulk heterojunction

In order to overcome the limitation of exciton dissociation in both single and bilayer devices, the BHJ structure consisting of an intimate mixture of donor and acceptor was introduced. The phase separation of donor and acceptor is typically on the nanoscale of 10 - 20 nm, and greatly increases the interfacial areas which are of the order of the exciton diffusion length [60]. Ideally, all photo-generated excitons can arrive at the interface for dissociation before recombination. However, BHJ active layer requires the bi-continuous and percolation pathways for the electrons and holes transporting to individual electrodes [29, 61]. Hence, the active layer morphology is very important for the BHJ structure to improve the performance of OSCs [62]. Recently, the highest PCE is around 11% for the BHJ OSCs [14].

2.6 Solar Cell Characterization

2.6.1 Optical Absorption Measurement

The optical absorption measurement can show whether the active layer absorption spectrum matches with the incident irradiance spectrum. The absorptance can be obtained from the reflectance and transmittance by the equation: $absorptance = 1 - reflectance - transmittance$. Reflectance refers to the ratio of the intensity of reflected light to that of incident light on the surface. Transmittance is defined as the ratio of the intensity of transmitted light to that of incident light. The spectrophotometer should be equipped with an integrating sphere which ensures that all light including diffusely reflected and transmitted light was collected.

2.6.2 Equivalent Circuit Model and Current-Voltage Curve Parameters

The equivalent circuit model of a solar cell (Fig. 2-8) is introduced to better understand the photovoltaic properties of a solar cell. Here, the photocurrent generated upon photoexcitation, is represented by a current source while the junction formed between the acceptor and donor is modeled as a diode. In the ideal case, a solar cell can be modeled by a diode connected in parallel with a current source [63]. But in practice, a R_s and a shunt resistance (R_{sh}) should be added to the model.

Figure 2-8 Equivalent circuit model of a solar cell.

When measuring the I - V characteristics of a solar cell, the source meter as the external load (R_L) is connected to the solar cell. The I - V equation from equivalent circuit can be expressed as [64]:

$$J = \frac{1}{1 + \frac{R_s}{R_{sh}}} \left[J_s \left\{ \exp \left(\frac{V - JR_s}{nk_B T / e} \right) - 1 \right\} - \left(J_{ph} - \frac{V}{R_{sh}} \right) \right] \quad (2.1)$$

where k_B is the Boltzmann constant, R_{sh} is the shunt resistance, R_s is the series resistance, T is the temperature in Kelvin, e is electron charge, V is the external bias applied to the diode, n is the ideality factor of the diode and J_s and J are the reverse saturation current density and current density, respectively.

The R_{sh} is ascribed to the current leakage since the trapping and recombination of charge carriers occur when they transport through the cell. The R_s represents the parasitic resistance in the devices, which can be due to interface transfer, low mobility of charge carriers in the bulk transport, and transport through the contact resistance. Ideally, R_{sh} should be large enough to ensure that most of the photocurrent passes through the external load. On the other hand, R_s should be small enough to guarantee that most of the electrical potential is applied to the external load. The R_{sh} and R_s can be extracted from dark I - V curve by taking the inverse slopes at 0 V and at voltage higher than V_{oc}

respectively [64].

$$R_{sh} = \frac{dV}{dI} \bigg|_{V=0} \quad R_s = \frac{dV}{dI} \bigg|_{V \geq V_{oc}} \quad (2.2)$$

The Fig. 2-9 shows the I - V characteristic of typical solar cell in the dark and under illumination. In the dark, the current is almost zero at low applied voltage and increase markedly at high voltage up to V_{oc} . Under illumination, the I - V curve has a similarity to that in the dark. When the applied voltage is zero, the J_{sc} is measured. When the external load resistance is zero, the V_{oc} is measured. Between 0 V and V_{oc} in fourth quadrant, the output power density at one particular point is largest. This point and its associated current density and voltage are called the maximum power point (MPP) and current density and voltage taken at MPP (J_{MPP} and V_{MPP}) respectively [29, 64]. The fill factor (FF) is defined as the power at the MPP divided by the product of V_{oc} and J_{sc} . The PCE of a solar cell is given by [29]:

$$PCE = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \quad FF = \frac{V_{MPP} \times J_{MPP}}{V_{oc} \times J_{sc}} \quad (2.3)$$

Figure 2-9 Typical I - V characteristics in a solar cell.

(a) Short-circuit current density

The J_{sc} is determined by [65]:

$$J_{sc} = q \int_0^{\lambda(h\nu=E_g)} \frac{\eta_{EQE} P(\lambda)}{h\nu} d\lambda \quad (2.4)$$

where η_{EQE} is external quantum efficiency (EQE), q is the electron charge, $P(\lambda)$ is irradiance, E_g is energy band gap, h is planck constant, ν is frequency of light, λ is wavelength of light.

In order to obtain the high J_{sc} , the number of absorbed photons within the active layer should be maximized for photon to electron conversion [65-67]. Moreover, carrier mobility affecting charge transport in the active layer also needs to be improved. Since the charge carrier is undergoing hopping transport via thermal activation in the active layer, carrier mobility is affected by temperature [68, 69]. More importantly, the carrier mobility is also related to the surface morphology of the BHJ active layer [62].

(b) Open circuit voltage

In the original metal-insulator-metal (MIM) model, the V_{OC} is dominated by the work functions difference between cathode and anode [70]. But in recent heterojunction devices such as polymer:fullerene based system, the V_{OC} is decided by the difference between the LUMO of acceptor and the HOMO of donor. The equation of the V_{OC} can be expressed as [33]:

$$V_{OC} = (1/e)(|E_{HOMO,donor}| - |E_{LUMO,PCBM}|) - 0.3V \quad (2.5)$$

where e is the elementary charge and the value of 0.3 V is an empirical factor.

However, the non-ohmic contacts between the active layer and electrodes will lower the V_{OC} in these devices [71]. Thus, the V_{OC} is largely affected by the electrodes, organic materials and their interfaces which play a significant role in

the performance of OSCs.

(c) Fill factor

FF represents the proportion of charge carriers actually reaching the electrodes. It is because some charge carriers may undergo recombination during the charge transport process [72]. Under the built-in electric field (E), the distance d that charge carriers can drift is determined by the mobility μ and lifetime τ [73]:

$$d = \mu \times \tau \times E \quad (2.6)$$

Therefore, the distance d should be long enough to ensure the charge carriers arrive at the electrodes without recombination. The μ can be enhanced by optimizing nanoscale morphology of the BHJ active layer [74]. The R_{sh} and R_s in equivalent circuit model of a solar cell fundamentally impact the FF . In principle, the R_s should be minimized by utilizing the high-conductivity electrodes and ohmic contacts. Meanwhile, the R_{sh} should be maximized, which could be realized by the electrode modification and optimization of the BHJ layer.

In summary, there is a subtle interplay among these parameters, which have to be resolved together to improve the OSC device efficiency.

2.6.3 Quantum Efficiency Measurement

The efficiency of an OSC is mainly limited by the photocurrent, which is obtained by multiplying the total amount of absorbed photons across the irradiance spectrum by the internal quantum efficiency (IQE) of the device [75]. IQE is defined as the fraction (in percent) of collected carriers per absorbed photon [76]. IQE gives insight into both the charge carrier generation and

transport processes in a solar cell. IQE is defined as [77]:

$$\eta_{IQE} = \eta_A \eta_{ED} \eta_{CT} \eta_{CC} \quad (2.7)$$

Considering the light reflection, IPCE or EQE is defined as [77]:

$$\eta_{EQE} = (1 - R) \eta_{IQE} = (1 - R) \eta_A \eta_{ED} \eta_{CT} \eta_{CC} \quad (2.8)$$

where R is reflectivity at the interface between the substrate and air [78]; η_A is the absorption efficiency of light within the active layer of the OSC; η_{ED} is the exciton diffusion efficiency which can be obtained by dividing the number of excitons diffusing to the donor-acceptor interface by the number of photo-generated excitons; η_{CT} is the charge transfer efficiency for exciton dissociation into a free electron and hole at the donor-acceptor interface; η_{CC} is the charge collection efficiency defined as the fraction of collected free carriers at the electrodes after exciton dissociation.

2.7 Efficiency Enhancement for OSCs

The OSCs efficiency can be improved according to the above five aspects (R , η_A , η_E , η_{CT} , η_{CC}). In this section, we will discuss them individually with emphasis on η_A because it is the focus of this thesis.

2.7.1 Reduce the Light Reflectivity

The optical reflection occurs when light is incident at a planar interface between a semiconductor such as silicon or organic materials and a low refractive index (n) medium such as glass or air. Usually, the inorganic semiconductors have higher n than that of organic semiconductor. Therefore, there is a higher reflectivity at the surface of inorganic semiconductors.

The traditional approach to reduce the light reflectivity is through the use of anti-reflection coatings which are based on interference effects [79]. The thickness of the anti-reflection coating is $\lambda/4n$, where λ is the free space wavelength and n is the refractive index of the anti-reflection coating. However, the problem of anti-reflection coating is that the interference effect only works for one or a narrow band of wavelengths and depends on the angle of incidence [80].

2.7.2 Improvement of Absorption Efficiency of Light

The absorption efficiency of light is given by [78]:

$$\eta_A = (1 - e^{-\alpha d}) \quad (2.9)$$

where α is the absorption coefficient or reciprocal of the absorption length and d is the thickness of the active layer.

As mentioned above, the low carrier mobility and short exciton diffusion length of the organic semiconductors necessitate the use of thin active layers. Therefore, it is necessary to increase α for the absorption efficiency enhancement without thickening the active layer. The low α is partially ascribed to the spectral mismatch between the light absorption of some organic semiconductors and incident irradiance spectrum. To overcome the spectral mismatch, the most effective way is to introduce new organic materials. Donor materials should be low band gap materials (<2 eV), which could cover a broad spectral range extending to the infrared range and thus match the solar spectra [81, 82]. For acceptor materials, PC₇₀BM can replace the commonly used PC₆₀BM due to the increased light absorption and higher electron mobility [83].

The transparent spacer layers are used to increase α by maximizing the optical field intensity distribution within the active layer region by the interference effect in the thin-film device [65].

Light trapping is about lengthening the optical path length. Surface texturing is the traditional light trapping approach to enhance the optical path length inside crystalline solar cells. It is based on geometric optic principle and use textured surfaces such as pyramids and random roughness [84, 85]. However, surface texturing is currently only applied to inorganic solar cells with a weak absorption such as silicon. It is because the maximum absorption enhancement of $4n^2$ given by the Yablonovitch theorem could reach ~50X for silicon with a high n ($n = 3.4$) but only can reach ~12X for organic semiconductor with a low n ($n = 1.7$) [86]. In addition, surface texturing needs to form the thick conformal film on the surface and increases the surface recombination, which is not suitable for thin-film OSCs.

Recently, nanophotonic light trapping approaches are being investigated to capture more light in the thin-film OSC device, which go beyond the $4n^2$ limit because light trapping structures such as photonic crystal and period nanostructure are smaller than free space wavelength and based on wave optics principle [87, 88]. However, they need very complicated processing techniques and have processing bottlenecks such as periodic pattern.

The incorporation of metallic NPs has no such processing challenges and thus is attractive nanophotonic light trapping approach for improved light absorption in OSCs [89, 90]. The LSPR of metallic NPs can be excited in the surrounding medium when electromagnetic waves couple to conduction

electrons at the surface of the metal. This contributes to either strong localized electric field or strong light scattering. For the large metallic NPs with the diameter above 100 nm, the light scattering plays an important role in light absorption [91]. For the small metallic NPs within a few tens of nanometers, the enhanced localized electric field is the dominant effect. In the literature, the incorporation of metallic NPs into thin-film silicon solar cell achieves an increase of 33% in photocurrent [92]. There are also many reports on plasmonic OSCs in which single metallic NPs are incorporated into various layers, for examples: the hole transport layer (HTL) [93], the active layer [94] or both [95]. In addition, two different metallic NPs were blended within a single layer [96, 97]. Typically, metallic Au or silver (Ag) NPs are embedded into the anode buffer layer of polymer OSCs. A PCE of 8.67% with the enhancement of 20% has been demonstrated in polymer OSCs by using both Ag and Au NPs to realize dual LSPR plasmonic peaks [97]. Plasmonic OSCs will be discussed in detail in chapter 3.

2.7.3 Improvement of Exciton Diffusion Efficiency

The diffusion efficiency can be expressed as [78]:

$$\eta_{ED} = e^{-d/L_D} \quad (2.10)$$

where L_D is the exciton diffusion length and d is the thickness of the active layer.

From the expression, the smaller the d is, the larger the η_{ED} is. However, the small d limits the light absorption of the active layer. In addition, if the thickness of the active layer is very thin, some of the diffusing excitons could arrive at the opposite interface of metal and organic material. As a result, those

excitons will be quenched by means of heat or other non-radiative relaxations. Therefore, exciton blocking layers (EBL) should be inserted between organic material and metal to prevent the exciton from diffusing to the opposite interfaces. For instance, the bathocuproine (BCP) exhibits good exciton blocking function and electron transporting property. In addition, such EBL can prevent the damage to organic active layer when depositing the metal layer above.

2.7.4 Improvement of Charge Transfer Efficiency

For charge transfer efficiency, it contains the charge transfer process and exciton dissociation process as discussed in section 2.4. The key discovery of ultrafast charge transfer at the donor and acceptor interface is that the charge transfer efficiency in the heterojunction structure is around 100% because there is no decay process for the exciton within the lifetime around 40 - 45 fs [21]. During the exciton dissociation process, the larger the energy level difference between the donor HOMO and acceptor LUMO is, the more efficient the exciton dissociation process is. Therefore, it is important to carefully choose the donor and acceptor, which have sufficient energy level difference between donor HOMO and acceptor LUMO.

2.7.5 Improvement of Charge Collection Efficiency

For charge collection efficiency, it mainly includes charge transport process and charge collection process mentioned in section 2.4. Thus, the improvement of charge collection efficiency is discussed in the following two parts.

(a) Charge transport

The single and bilayer structures limit the exciton dissociation. Therefore, the BHJ structure is widely used to raise the interfacial areas and increase the charge carriers separated. However, due to the low charge carrier mobility in the BHJ, it makes the charge carrier transport difficult in its corresponding layers leading to the carrier recombination. Hence, some modifications and treatments are introduced to improve the carrier transport efficiency of the BHJ. The most efficient approach is to form the interpenetrating and bi-continuous networks in the BHJ by careful optimization of the nanoscale morphology.

The morphology of a BHJ active layer is affected by a number of intrinsic and extrinsic factors. The intrinsic factors refer to the chemical structures of the donor and acceptor which determine their solubility, regioregularity, hydrophobicity, surface energy and surface tension, as well as the miscibility between the two components [40, 62]. The extrinsic factors refer to device fabrication conditions such as solvent, ratio of donor and acceptor, deposition technique, substrate surface energy and post-annealing temperature [98, 99]. The ratio of donor and acceptor blend determines the formation of percolated networks. The solvent is known to influence the phase separation in the BHJ. The thickness of the active layer affects the absorption of the device. On the other hand, the thickness of the buffer layer as an optical spacer affects the interface and changes the light field distribution. The post-annealing temperature will make the morphology coarser and thus form better pathway of the BHJ.

The intrinsic and extrinsic interaction will rely on the specific donor and

acceptor pair. As a result, morphology should be re-optimized when introducing each new component, which is time-consuming and sometimes ineffective due to the incompatibility of donor and acceptor pair [100].

In short, the bi-continuous and nanoscale morphology of the BHJ layer would be desired so as to balance the exciton dissociation and charge transport.

(b) Charge collection

In order to realize high charge collection and V_{OC} for BHJ OSC devices, the ohmic contacts between the active layer and electrodes should be achieved to minimize the carrier loss at the electrodes.

For the anode side, the HOMO of donor and the Fermi level of the anode should be matched. Usually, indium tin oxide (ITO) is treated by O_2 plasma [101], and then an interfacial layer such as PEDOT:PSS, molybdenum trioxide (MoO_3) or tungsten trioxide (WO_3), is spin casted on the ITO surface to facilitate hole transport and hole extraction [102, 103]. For cathode side, the LUMO of acceptor should match with the Fermi level of the cathode. Typically, lithium fluoride (LiF) or calcium (Ca) is used in OSCs to modify the interface while titanium (sub) oxide (TiO_x) and zinc oxide (ZnO) are used for hole blocking [104, 105].

2.8 Lifetime

In order to realize commercial potential of OSCs, the efficiency, cost, fabrication process and lifetime are indispensable. The organic materials are susceptible to photodegradation and photo-oxidation due to sensitivity to the O_2 , moisture and photoexcitation. Therefore, fabrication processes are done inside

glove box and be sealed by glass cover and permeation glue after finishing the device.

Blending of polymer and fullerene can decrease photo-degradation of conjugated polymers due to faster charge transfer from polymer to fullerene, which is more air-stable. The photo-generated excitons are able to reduce O_2 and react with the molecular material, which degrade organic materials. More air-stable polymers and fullerene can be developed to reduce the degradation to the environment. For instance, MDMO-PPV:PCBM blend OSCs is very easy to degrade due to the formation of large crystals [62]. However, P3HT:PCBM blend with better thermal stability gives better performance due to their nanomorphology after the annealing treatments [106]. Finally, electrodes with low work function metals such as aluminum (Al) lead to the formation of metal oxide with high energy barrier when exposed to the air.

Chapter 3 Localized Surface Plasmon Resonance

3.1 Introduction

3.1.1 Brief Review of NPs-based Plasmonic OSCs

Due to a low carrier mobility and limited exciton diffusion length of organic semiconducting materials, the active layer thickness in OSC is normally less than 100 nm, leading to the insufficient light absorption [78]. The metallic NPs were introduced to the OSC devices for improving the light harvesting since metallic NPs upon the excitation of incident light can enhance not only the localized electric field intensity but also scatter light into longer optical path within the active layer [89].

In the literature, metallic NPs can be placed in different layers such as the interfaces between the ITO and the hole transport layer (HTL), the HTL and the active layer [107]. Device parameters of plasmonic OSCs incorporated with metallic NPs in various configurations are listed in Table 3-1. One of the earliest studies on the LSPR effect in OSC device was reported by O. Stenzel et al., who demonstrated the enhanced PCE and photocurrents after incorporation of metal clusters including Ag, Au and Cu at the ITO-CuPc interface [108]. Later, metallic NPs layer with different shapes such as nanodisk and nanoprism at the ITO-PEDOT:PSS interface were also investigated in the P3HT:PC₆₀BM solar cells [109-112]. The increase in the localized electric field leads to the light absorption improvement and consequently more charge generation within the active layer. In 2011, J. -L. Wu et al. as well as D. D. S. Fung et al. incorporated the Au nanospheres with the average diameter less than 50 nm into

the PEDOT:PSS layer of the P3HT:PC₆₀BM solar cells and achieved ~19% and ~13% enhancement in PCE of the devices respectively relative to the reference device due to the enhanced photocurrent and fill factor [93, 113]. Such increased fill factor is ascribed to the reduced R_s . Almost at the same time, D. H. Wang et al. applied the polyvinylpyrrolidone (PVP)-capped Au nanospheres with a diameter around 70 nm into the active layer of the P3HT:PC₇₀BM solar cells and achieved higher PCE improvement by ~23% relative to reference device [91]. The improvement mechanism is attributed to the scattering effect by large-sized Au NPs. The effect of concentration of Au nanospheres within the BHJ layer on the efficiency of the polymer OSC devices was studied by D. D. C. Wang et al. in 2012 [94]. It was observed that at high Au NPs concentration, the device performance declined due to the reduced carrier mobility and enhanced surface roughness of the active layer comprising poly[2,7-(9,9-dioctylfluorene)-*alt*-2-((4-(diphenylamino)phenyl)thiophen-2-yl)-malononitrile]:PC₆₀BM (PFSDCN:PC₆₀BM).

In addition, the incorporation of different types of metallic NPs into the same layer in an OSC was also explored [96, 97]. A combination of metallic NPs with different shapes involving Ag nanospheres and Ag nanoprisms in the active layer was proposed by X. Li et al. to broaden the spectral range of light absorption [96]. A high PCE up to 8.67% has been achieved by incorporating the mixed Ag and Au nanospheres into the buffer layer of polymer BHJ solar cells [97].

Table 3-1 Device parameters of plasmonic OSCs incorporated with NPs in various configurations.

Geometry	NPs	Active layer	PCE(%)	Ref.
Interface between the ITO and PEDOT:PSS				
ITO-PEDOT:PSS interface	1 nm Ag NPs film	P3HT:PC ₆₀ BM	2.2%	[110]
ITO-PEDOT:PSS interface	13 nm Ag NPs	P3HT:PC ₆₀ BM	3.7%	[111]
ITO-PEDOT:PSS interface	47 nm Ag nanodisks	P3HT:PC ₆₀ BM	3.5%	[112]
Into the HTL layer				
PEDOT:PSS layer	45 nm Au NPs	P3HT:PC ₆₀ BM	4.2%	[93]
PEDOT:PSS layer	18 nm Au NPs	P3HT:PC ₆₀ BM	3.5%	[114]
PEDOT:PSS layer	30-40 nm Au NPs	P3HT:PC ₆₀ BM	4.2%	[114]
Interface between the HTL and active layer				
PEDOT:PSS-BHJ interface	50 nm Ag NPs	PTB7:PC ₇₀ BM	8.9%	[115]
Into the active layer				
BHJ layer	70 nm Au NPs	P3HT:PC ₇₀ BM	4.4%	[91]
BHJ layer	18 nm Au NPs	PFSDCN:PC ₆₀ BM	2.2%	[94]
BHJ layer	110 nm Au nanowires	P3HT:PC ₆₀ BM	3.9%	[116]
BHJ layer	40 nm Ag cluster	PCDTBT:PC ₇₀ BM	7.1%	[117]
Combinations				
Both HTL and BHJ layers	18 and 35 nm Au NPs	P3HT:PC ₆₀ BM	3.9%	[95]
PEDOT:PSS layer	Both Au and Ag NPs	PTB7:PC ₇₀ BM	8.7%	[97]
BHJ layer	Ag NPs and nanoprisms	P3HT:PC ₆₀ BM	4.3%	[96]

3.1.2 LSPR Effect

The mechanism of enhancement in these plasmonic OSCs is the LSPR effect induced by the metallic NPs. We first introduce the concept of surface plasmon resonance (SPR) which refers to the collective oscillation of electrons in a solid when excited by incident light. This phenomenon was first discovered by R. W. Wood in 1902 [118, 119]. The theoretical explanation of this phenomenon was initiated by Lord Rayleigh in 1907 [120], and completely interpreted by A. Otto [121] as well as E. Kretschmann and H. Raether [122] who almost at the same time reported the optical excitation of surface plasmons. Here, we should first distinguish the SPR at the planar metal/dielectric interface from that at the surface of metallic NPs whose dimension must be comparable to or smaller than the free space wavelength of light. For the former, surface plasmons refer to the electron dilatational wave propagation along the metal

surface which is resulting from the interaction of the conduction electrons and the electromagnetic field at the metal/dielectric interface. For the latter, when the dimensions of this metallic surface are reduced to subwavelength size, the electrons in the metallic NPs will resonate at the characteristic resonance frequency. The collective oscillation of conduction electrons in the nanoparticles which are excited by light is called LSPR. This is because only electrons near the surface are involved in the LSPR. When incident light arrives at a planar metallic film, its electromagnetic wave can only penetrate into the metal with a certain depth and exponentially decay. This distance is commonly termed as the skin depth δ which can be expressed as [123]:

$$\delta = 1 / \sqrt{f \pi \mu \sigma} \quad (3.1)$$

where f is the frequency of light, μ is permeability and σ is conductivity.

In the case of Au, the value of δ at 500 nm is ~30 nm. At optical frequencies, only the surface conduction electrons of a metal can oscillate with the electric field of the incident light.

Although the LSPR in metallic NPs, are very useful in the biosensing [124], nanophotonics [125], optical data processing [126, 127], and optical data storage [128], we solely focus on the photovoltaic application of the LSPR in metallic NPs in the following discussion. The conditions required for observing the LSPR in metallic NPs are [129]: 1) a negative value for the real part of the complex dielectric function ($\epsilon(\omega)$) at the wavelength of the application and 2) the dimensions of the particle must be less than the free space wavelength of the incident light. In addition, a low value for the imaginary part of $\epsilon(\omega)$ is desirable but not essential. It is because the imaginary part of $\epsilon(\omega)$ accounts for

energy losses due to the carrier scattering within the metal [130].

The LSPR in metallic NPs has two important properties [131]:

1) Electric fields near the surface of the NPs have great enhancement but decay quickly with the increase of distance from the surface.

2) The LSPR of metallic NPs depends on the dielectric constant of the surrounding medium (ϵ_m). For noble metallic NPs such as Ag or Au, the LSPR occurs typically at visible wavelengths.

The origin of these properties of the LSPR will be explained in the following sections.

3.2 Complex Dielectric Function of Metals

Metals have unique electrical and optical properties, originating from their outer shell valence electrons which can move freely through the crystal structure. When a metal is placed in a time-harmonic electromagnetic wave characterized by the electric field ($\vec{E}_0(\vec{r}, \omega)$), the electron cloud (plasma) of the metal is displaced and this creates a polarization ($\vec{P}$) and executes the back-and-forth oscillation against the restoring force of positive nuclei over time. The polarization can be defined as [129]:

$$\vec{P} = -\frac{e^2 N}{m\omega^2} \vec{E}_0(\vec{r}, \omega) \quad (3.2)$$

where N is the electron density, m is electron mass, e is the free electron charge, ω is the angular frequency, $\vec{r}$ is position vector and E_0 is the amplitude of the applied $\vec{E}_0(\vec{r}, \omega)$ field.

This polarization is generated because the applied $\vec{E}_0(\vec{r}, \omega)$ field

stimulates the negative electrons to be displaced from the positive charge and thus induces the dipole moment. This displacement of electrons relative to atom cores results in a depolarization field ($\vec{E}'(\vec{r}, \omega)$). The sum of $\vec{E}_0(\vec{r}, \omega)$ and $\vec{E}'(\vec{r}, \omega)$ is the displacement field $\vec{D}(\vec{r}, \omega)$, which is related to the $\vec{E}_0(\vec{r}, \omega)$ field by the complex and frequency-dependent permittivity or complex dielectric function $\varepsilon(\omega)$ [139]:

$$\vec{D}(\vec{r}, \omega) = \varepsilon_0 \varepsilon(\omega) \vec{E}_0(\vec{r}, \omega) \quad (3.3)$$

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (3.4)$$

where $\varepsilon_1(\omega)$ describes the strength of the polarization induced by $\vec{E}_0(\vec{r}, \omega)$, $\varepsilon_2(\omega)$ describes the energy losses in polarizing the material and $i = \sqrt{-1}$.

The Drude model is the simplest model to describe this polarization and oscillation of the electrons in a metal and was proposed in 1900 by Paul Drude [132, 133]. The equation of motion for electrons using the Drude model can be written as follows [129]:

$$m_e \frac{d^2 \vec{r}}{dt^2} + \gamma m_e \frac{d\vec{r}}{dt} = e \vec{E}_0 e^{-i\omega t} \quad (3.5)$$

where m_e is the effective free electron mass, e is the free electron charge, ω is the angular frequency, γ is the damping constant.

By assuming $\vec{r} = \vec{r}_0 e^{-i\omega t}$, the Drude dielectric function can be directly derived from above equation [139]:

$$\varepsilon_{Drude}(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \quad (3.6)$$

The real and imaginary parts of $\varepsilon_{Drude}(\omega)$ are [129]:

$$\varepsilon_1(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + \gamma^2} \quad (3.7)$$

$$\varepsilon_2(\omega) = \frac{\omega_p^2 \gamma}{\omega(\omega^2 + \gamma^2)} \quad (3.8)$$

$$\omega_p^2 = \frac{e^2 N}{\varepsilon_0 m_e} \quad (3.9)$$

here, ω_p is the bulk plasma frequency of the metal, N is the electron density and ε_∞ is the ionic background in the metal. Since N_{Au} is equal to $5.90 \times 10^{22} \text{ cm}^{-3}$, the calculated value of ω_p is $2.16 \times 10^{15} \text{ Hz}$.

The Drude dielectric function can be normally approximated as $\varepsilon_{\text{Drude}} = 1 - \omega_p^2 / \omega^2$ by neglecting the γ and ε_∞ . Therefore, ε_1 is negative if $\omega < \omega_p$ while ε_1 is positive if $\omega > \omega_p$. When ε_1 at a certain frequency range is negative, $\vec{P}$ has the opposite direction to the $\vec{E}_0(\vec{r}, \omega)$ and this leads to the $\vec{E}'(\vec{r}, \omega)$ with same direction as $\vec{E}_0(\vec{r}, \omega)$ as shown in Fig. 3-1. As a result, the total electric field $\vec{E}_0(\vec{r}, \omega) + \vec{E}'(\vec{r}, \omega)$ is enhanced, which explains why metal with negative $\varepsilon_1(\omega)$ can have intense fields upon the excitation of incident light. In an analogous way, the positive $\varepsilon_1(\omega)$ results in the attenuation of the applied field $\vec{E}_0(\vec{r}, \omega)$. The ω_p of the noble metals such as Au and Ag lies in the ultraviolet region. This explains why Au and Ag are usually utilized in the LSPR studies and application in photovoltaics.

Figure 3-1 The spherical NPs with negative permittivity under the external electric field.

However, the Drude model can be inaccurate outside the visible near IR frequency range because it only takes the free electrons (intraband transitions) into account and completely ignores the bound electrons (interband transitions) which play a vital role for Au. The Drude model corroborates with the accurate measurement of the complex refractive index for Au as reported by Johnson and Christy in 1972 [134]. A more accurate dielectric function model for Au has been proposed by P. G. Etchegoin [135]. The complex refractive indexes at different wavelengths are tabulated for calculation of the ε_1 and ε_2 . The relation between the complex dielectric function $\varepsilon(\omega)$ and complex refractive index ($\tilde{n}(\omega)$) can be expressed as [139]:

$$\varepsilon(\omega) = \tilde{n}^2(\omega) = (n + ik)^2 = n^2 - k^2 + 2nki \quad (3.10)$$

$$\varepsilon_1(\omega) = n^2 - k^2; \quad \varepsilon_2(\omega) = 2nk \quad (3.11)$$

where n is refractive index, k is extinction coefficient.

Fig. 3-2 illustrates the complex dielectric function of Au calculated from ref. [134] using the equation above. It is observed that the ε_1 is negative for

wavelength from 500 nm to 1900 nm. In addition, there is small energy loss within the range of 600 - 1000 nm. Therefore, it explains why Au NPs are usually used in the LSPR studies and application in the OSCs for light trapping.

Figure 3-2 The real and imaginary parts of the complex dielectric function for Au.

3.3 Mie Theory

In a 1908 review paper, Gustav Mie first computed the light scattering by spherical Au particles and explained the colour of Au colloids varying with the size of the Au spheres [136]. In this paper, he gave the exact solution of Maxwell's equation for an electromagnetic field interacting with Au spheres, which was named as Mie theory. The electromagnetic field can be expressed by multipole expansion and expansion coefficients depend on the boundary conditions. Due to the limit of small size of metallic NPs (<60 nm), only first term in the multipole expansion is considered which is called dipolar approximation or quasi-static approximation. The quasi-static approximation assumes that the electromagnetic field does not change much with position inside the Au NPs and the conduction electrons are in phase with the field by

neglecting all retardation effects. Therefore, at any instant, the field looks like a static field even though it is time varying field. The solution of the Laplace equation of metallic NPs is outlined in the following for better understanding the principle of LSPR. Extensive literature about Mie theory can be found in form of the articles, reviews and classic textbooks such as those by M. Born [137] and C. F. Bohren [138].

Let us consider analytical solutions or plasmon modes in a metallic sphere with a radius of a under the excitation of incident electromagnetic field (Fig. 3-3). Electric field should obey the Laplace equation [129]:

$$\nabla^2 V = 0 \quad (3.12)$$

where V is the electrical potential linked to the electric field by [129] :

$$\vec{E} = -\vec{\nabla} V \quad (3.13)$$

Figure 3-3 The spherical NPs under the external electric field.

The electric potentials inside and outside the metallic sphere can be written as V^+ and V respectively. They should satisfy the following boundary conditions [129]:

$$\left. \frac{\partial V^+}{\partial r} \right|_{r=0} = 0 \quad \text{exists} \quad (3.14)$$

$$V^-(\infty) = 0 \quad (3.15)$$

$$\varepsilon \frac{\partial V^+}{\partial r} \Big|_{r=a} = \varepsilon_0 \frac{\partial V^-}{\partial r} \Big|_{r=a} \quad (3.16)$$

$$V^+ \Big|_{r=a} = V^- \Big|_{r=a} \quad (3.17)$$

The product solutions of the Laplace equation are plasmon modes which can be expressed as [129]:

$$V_{nm}^+(r, \theta, \phi) = A_{nm}^+ r^n Y_n^m(\theta, \phi), \quad (m = 0, \pm 1, \dots, \pm n) \quad (3.18)$$

$$V_{nm}^-(r, \theta, \phi) = A_{nm}^- r^{-n-1} Y_n^m(\theta, \phi), \quad (m = 0, \pm 1, \dots, \pm n) \quad (3.19)$$

$$Y_n^m(\theta, \phi) \equiv (-1)^m \sqrt{\frac{2n+1}{4\pi} \frac{(n-m)!}{(n+m)!}} P_n^m(\cos \theta) e^{im\phi} \quad (3.20)$$

where r , θ and ϕ correspond to radial distance, polar angle and azimuth angle of the spherical coordinate system for three-dimensional (3D) space respectively. $Y_n^m(\theta, \phi)$ is spherical harmonics. $P_n^m(\cos \theta)$ is Legendre function.

These product solutions can be realized only for such special values (ε_n) of dielectric permittivity of metallic sphere [129]:

$$A_{nm}^- = A_{nm}^+ a^{2n+1} \quad (3.21)$$

$$\varepsilon_n = -\varepsilon_0 \frac{n+1}{n} \quad (3.22)$$

There are $(2n + 1)$ plasmon modes for each ε_n . From Eq. 3.18 and Eq. 3.19, it is obvious that with the increase of n , plasmon modes is highly oscillatory and concentrated near the spherical boundary and then decrease quicker in the radial direction. This phenomenon explains why the intense field is limited to the surface of spherical boundary. Under the dipolar approximation, we only

need to consider $n = 1$. The value of m can equal to 0 and ± 1 . However, according to the boundary conditions (Eq. 3.14 - 3.17), the solution of V^- (Eq. 3.18 - 3.21), only has non-zero coefficient A_{10}^- because the coefficients A_{11}^- and $A_{1,-1}^-$ are both zero. The spherical harmonic $Y_1^0(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta$ is independent of ϕ according to Eq. 3.20. Therefore, the solution of V^- only has two coordinates (r and θ).

Once the solutions of V^- are obtained, the electric field outside of metallic sphere ($\vec{E}^-$) can be deduced from Eq. 3.13. The electric field is a sum of the applied field and depolarization field produced by metallic sphere as discussed in section 3.2. Here, $\vec{E}^-$ also consider only two coordinates (r and θ) which can be written as follow [139]:

$$\vec{E}^- = \vec{E}_0 - \alpha E_0 \left[-2 \frac{\cos \theta}{r^3} \vec{r} - \frac{\sin \theta}{r^3} \vec{\theta} \right] \quad (3.23)$$

where $\vec{r}$ and $\vec{\theta}$ are vector of r and θ , α is the sphere polarizability which can be expressed as [139]:

$$\alpha = 4\pi\epsilon_0 a^3 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \quad (3.24)$$

From Eq. 3.23, the electric field outside sphere will reach a maximum when the α is maximized. Therefore, the α can reach maximum when the following condition is satisfied [139]:

$$|\epsilon + 2\epsilon_m| \text{ is a minimum} \quad (3.25)$$

The ϵ_m of the surrounding medium is usually a real constant. The above Eq. 3.25 can be rewritten as $\epsilon_1(\omega) + 2\epsilon_m = 0$. We can conclude that the LSPR is

strongly affected by the surrounding environment close to the surface of the particle. Take Au nanospheres in water for example, $\epsilon_{\text{diel}} = 1.77$, $\epsilon_1(\omega) = -2\epsilon_m = -3.54$. According to the plot of $\epsilon(\omega)$ in Fig. 3-2, we can find that $\epsilon_1(\omega)$ equals to -3.54 at 520 nm. Therefore, the LSPR occurs at 520 nm in Au nanospheres in water which is consistent with the following result in chapter 4.

Upon the incident light interacting with homogenous particle, light will be absorbed or scattered. Here, light is considered as a wave rather than a static electric field. Absorption cross section ($C_{\text{abs}}(\lambda)$) and scattering cross section ($C_{\text{sca}}(\lambda)$) for Au nanospheres can be calculated by Mie theory [140]. The extinction cross section ($C_{\text{ext}}(\lambda)$) is a sum of $C_{\text{abs}}(\lambda)$ and $C_{\text{sca}}(\lambda)$. The corresponding extinction efficiency ($Q_{\text{ext}}(\lambda)$), absorption efficiency ($Q_{\text{abs}}(\lambda)$) and scattering efficiency ($Q_{\text{sca}}(\lambda)$) can be obtained by dividing $C_{\text{ext}}(\lambda)$, $C_{\text{abs}}(\lambda)$ and $C_{\text{sca}}(\lambda)$ by cross sectional area (πa^2) of the sphere. The relation of three cross sections is given as [139]:

$$C_{\text{ext}}(\lambda) = C_{\text{abs}}(\lambda) + C_{\text{sca}}(\lambda) \quad (3.26)$$

For spherical particle with a diameter less than 60 nm, the calculation of $C_{\text{ext}}(\lambda)$ can be simplified by only considering dipole oscillation and ignoring the high order terms [141]. The equations of $C_{\text{ext}}(\lambda)$ and $C_{\text{sca}}(\lambda)$ are linked to the sphere polarizability as described above and can be given as [139]:

$$C_{\text{ext}}(\lambda) = 3 \frac{2\pi}{\lambda} \sqrt{\epsilon_m} \text{Im}(\alpha) = 9 \frac{2\pi}{\lambda} \epsilon_m^{3/2} V \frac{\text{Im}(\epsilon)}{|\epsilon + 2\epsilon_m|^2} \quad (3.27)$$

$$C_{\text{sca}}(\lambda) = 3 \frac{(2\pi)^3}{\lambda^4} \epsilon_m^2 |\alpha|^2 = 3 \frac{(2\pi)^3}{\lambda^4} \epsilon_m^2 V^2 \left| \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \right|^2 \quad (3.28)$$

This description is acceptable for small spherical particle of which

scattering is negligible. A proper calculation for Au NPs with different size and shape by Discrete Dipole Approximation (DDA) method was proposed by El-Sayed et al. [142]. Fig. 3-4 shows that the $Q_{\text{sca}}(\lambda)$ is almost zero for 20 nm Au nanospheres but is equivalent to the $Q_{\text{abs}}(\lambda)$ for 80 nm Au nanospheres. The scattering induced by NPs is very important to enhance the optical path length and thereby absorption within the BHJ layer of OSC device. Therefore, metallic NPs with a large size are more appropriate for plasmonic OSC device.

Figure 3-4 Comparison of the $Q_{\text{ext}}(\lambda)$ (solid line), $Q_{\text{abs}}(\lambda)$ (red dashed) and $Q_{\text{sca}}(\lambda)$ (black dotted) for Au nanospheres with the diameter of (a) 20 nm, (b) 40 nm and (c) 80 nm [142].

3.4 Gans Theory

For spherical particles, Mie theory is an efficient approach to describe their optical response. However, for non-spherical particles, exact solutions cannot be derived from Mie theory. In 1912, Gans theory as the extension of Mie theory was proposed by R. Gans for the case of Au spheroids [143]. In Gans theory, it gives the extinction characteristics for both prolate (lemon-like) ellipsoid and oblate (pumpkin-like) ellipsoid. There is more than one LSPR peak because the polarizabilities along x, y and z axis are different due to the different value of the depolarization factor, which will be discussed below.

Later, this theory was further extended to cover the particles with other shapes [144]. Gans theory for Au nanorods is briefly reviewed below [145].

In order to demonstrate the rationale behind our choice of Au nanorods for incorporation into the active layer of OSC devices, we first outline the plasmonic properties of metallic nanorods. As with the nanosphere, a collective oscillation of the surface conduction electrons can be excited when the frequency of incident light matches the characteristic LSPR frequencies of the nanorod. By extending the Mie theory, originally developed for an isolated sphere, Gans showed that the $C_{\text{ext}}(\lambda)$ for a metallic nanorod under the dipolar approximation is given by [146]:

$$C_{\text{ext}}(\lambda) = \frac{2\pi NV \varepsilon_m^{3/2}}{3\lambda} \sum_j \frac{(1/P_j^2) \varepsilon_2}{\left(\varepsilon_1 + \frac{1-P_j}{P_j} \varepsilon_m \right)^2 + \varepsilon_2^2} \quad (3.29)$$

In Eq. 3.4, ε_1 and ε_2 are the frequency dependent real and imaginary parts of the dielectric function of the nanorod material respectively; ε_m is the dielectric constant of the surrounding medium; N is the concentration of nanorods and V is the volume of each nanorod. P_j ($j = A, B, C$) in the summation represent the depolarization factors for the three Cartesian axes. Assuming the length of the nanorod, A parallel to the z axis is greater than the radius B and C along the x and y directions respectively [146]:

$$P_A = \frac{1-e^2}{e^2} \left[\frac{1}{2e} \ln \left(\frac{1+e}{1-e} \right) - 1 \right] \quad (3.30)$$

$$P_B = P_C = \frac{1}{2e^2} \left\{ 1 - \left(\frac{1-e^2}{2e} \right) \ln \left(\frac{1+e}{1-e} \right) \right\} \quad (3.31)$$

where,

$$e = \sqrt{1 - \left(\frac{B}{A}\right)^2} \quad (3.32)$$

For a given aspect ratio (A/B), the three depolarization factors can be found by substituting Eq. 3.32 into Eq. 3.30 and Eq. 3.31. The $C_{\text{ext}}(\lambda)$ can then be calculated by substituting the complex dielectric function spectrum for Au and the dielectric constant of the surrounding medium. As shown by Link et al. [146], the theoretical $C_{\text{ext}}(\lambda)$ spectrum of Au nanorods consists of two peaks in the visible region. The peak at shorter wavelengths (around 520 nm) is due to a transverse LSPR mode and the peak at longer wavelengths is due to a longitudinal LSPR mode. The peak positions of both the transverse and longitudinal modes are dependent on the aspect ratio [147].

Figure 3-5 Comparison of the $Q_{\text{ext}}(\lambda)$ (black line), $Q_{\text{abs}}(\lambda)$ (red line) and $Q_{\text{sca}}(\lambda)$ (blue line) for Au nanorods with equal volume but with different aspect ratios: (a) $R = 1.0$, (b) $R = 2.0$, (c) $R = 2.6$ and (d) $R = 3.4$ [148].

As the aspect ratio increases, the transverse mode blue shifts while the

longitudinal mode red shifts as depicted in Fig. 3-5 [148]. The extent of the shift for the longitudinal mode is significantly greater than that of the transverse mode. Hence, the great advantage of using Au nanorods is that the two extinction peaks can be readily tuned to match the absorption spectrum of a particular BHJ blend. This tuning property is not available with the Au nanosphere because for a sphere, the LSPR peak position is not a sensitive function of the sphere radius. Since a metallic surface has high surface recombination velocity and can potentially lead to loss of photo-generated carriers, we coat the surface of the Au nanorod core with a thin silica shell to render it more suitable for incorporation into the active layer.

3.5 Application of Au NPs in OSCs

Since metals with nanoscale feature have interesting optical properties which can excite the LSPR when exposure to incident light, the noble metals commonly including the Ag, Cu, Al and Au, are used as plasmonic materials [149]. In this thesis, Au is chosen as the plasmonic metal due to its unique advantages. The first and most important is that Au has excellent corrosion resistance in a nanoscale form under the ambient condition. Most other metals such as Ag, Cu and Al have surface oxidation in air, which will compromise their plasmonic properties. Second, Au can effectively use the solar light whose spectrum distribute mainly from 400 nm to 800 nm. Furthermore, the choice of metal also needs to consider the band gap of organic semiconducting materials. It should maximize the overlap of spectrum between light absorption of organic semiconductors and the LSPR of the metal within the incident irradiance

spectrum. Au NPs with rod shape have a longer wavelength beyond 700 nm which match well with low band gap organic materials. In addition, Au has a relatively low absorption loss within the metal although it is expensive than Cu and Al. Finally, the synthesis methods of Au NPs started very early and have developed rapidly in the past ten years. In summary, Au NPs is considered as a promising plasmonic metal due to stability, small loss, mature synthesis technique and the spectral match within the solar spectrum.

Chapter 4 Conventional Polymer OSCs

Enhanced by Au-Silica Nanorods

4.1 Introduction

Due to the solution processing capability in ambient conditions and potentially low cost, OSC is a highly promising thin film photovoltaic technology [32]. However, it is still limited by insufficient PCE of OSC devices since the active layer has to be very thin because of the short exciton diffusion length in the organic BHJ and low carrier mobility in organic semiconductors [150]. The typical active layer thickness of an OSC device is of order 100 nm [78]. As a result, the amount of light that can be absorbed in a solution deposited active layer is somewhat limited. In the open literature, the highest reported PCE for a BHJ OSC devices is approaching 11% [14]. For commercial application, a PCE above 15% is needed. An effective approach to enhance the PCE is to increase the optical absorption in the active layer of the OSC device.

In recent years, there has been intense interest in applying the plasmonic properties of metallic NPs to enhance the performance of OSC devices [91, 94, 107, 112, 151, 152] (Table 3-1). The absorption of light in the thin active layer of the OSC can be increased by the LSPR effect in noble metal NPs such as Au or Ag because, as explained in chapter 3, the LSPR peaks of these metals lie in the visible region of the electromagnetic spectrum. Typically, metallic Au or Ag NPs are embedded into the anode buffer layer of the polymer OSCs [93, 97, 113]. However, the direct incorporation of the metallic NPs with the insulating

shell into a BHJ is more favorable because the excitation of LSPR occurs within the light absorption layer while carrier recombination at the metal surface is inhibited by the insulating shell [153]. In addition, most existing plasmonic materials for improved light absorption in the OSC are focused on spherical NPs [93, 113]. The absorption spectrum of spherical NPs is narrow and extends only up to 600 nm with one peak. Therefore, it does not match the absorption spectrum of the low bandgap polymer or other potential donors with broad absorption spectrum at longer absorption wavelength. Moreover, the scattering cross section area of spherical particles varies with the sixth power of the particle radius [148]. As a result, these NPs contribute negligible scattering to enhance the optical path length (Fig. 3-5). In previous studies, the metallic NPs have diameter less than 50 nm [107]. Due to the limitation of small size of NPs, the NPs have negligible scattering effect to increase the optical path length (Fig. 3-4). On the other hand, for large metallic NPs (~100 nm) with rod shape within the BHJ layer, the incident photons can be scattered more strongly by the metallic NPs into a longer propagation path in the active layer [91].

Thus far, only a few reports studied the metallic nanorods with larger size which have a wide absorption spectrum enhancement up to 700 nm [107]. These nanorods can give rise to both enhanced localized electric field intensity and increased light scattering. In this chapter, we report the positive effect of incorporating Au-silica core-shell nanorods into the active layer of the BHJ OSC devices comprising solution processed regioregular P3HT and PC₆₀BM. This chapter is partially based on our paper published in journal of Organic Electronics [154]. Detailed study of mechanism is deferred to chapter 5.

4.2 Experimental

4.2.1 Synthesis of Au-Silica Core-Shell Nanorods

Au nanorods were synthesized by a seed-mediated method [155, 156]. First, the Au seed solution was prepared by borohydride reduction of 0.25mM HAuCl_4 in an aqueous hexadecyltrimethylammonium bromide (CTAB) solution (10 ml, 0.1 M). For the synthesis of the Au nanorods, 10 μL of seed solution was added to an aqueous solution of HAuCl_4 (0.01 M, 2 mL), AgNO_3 (0.01 M, 0.4 mL), CTAB (0.1 M, 40 mL), ascorbic acid (0.1 M, 0.32 mL) and HCl (1.0 M, 0.8 mL). After mixing by gentle inversion for 10 s, the reaction solution was left undisturbed for 16 hrs. The Au nanorods were obtained by centrifugation and re-dispersed in 26.7 ml of deionized water.

Au-silica core-shell nanorods were synthesized according to a previously published procedure [157]. NaOH solution (0.1 M) was added to 2 ml of Au nanorod solution until the pH value was adjusted to 10-11. A 60 μL of 20 vol% solution of tetraethylorthosilicate (TEOS) in methanol was then added into Au nanorod solution. After stirring for 12 hrs, Au-silica core-shell nanorods were obtained by centrifugation, and re-dispersed in 3 ml ethanol. Finally, 50 μL of hexadecyltrimethoxysilane was added to obtain the core-shell solution. After stirring for 18 hrs at 60 $^{\circ}\text{C}$, the hydrophobic core-shell nanostructures were obtained by centrifugation and re-dispersed in CB or DCB. The reason for dispersing the Au nanorods in two separate solvents is to avoid possible co-solvent effects during fabrication of the polymer OSC devices. Fig. 4-1 shows the TEM image of the solution-processed Au-silica core-shell nanorods. The length and diameter of the Au core are 92.5 ± 8.0 nm and 34.3 ± 4.0 nm,

respectively, and the thickness of the silica shell is 17.1 nm.

Figure 4-1 TEM image of the Au-silica nanorods. The scale bar represents 50 nm.

4.2.2 Device Fabrication

The OSC devices fabricated for this study all have a conventional architecture of the ITO/PEDOT:PSS/P3HT:PC₆₀BM/Ca/Al, which has the cathode at the top and is illuminated via the bottom substrate. A standard cleaning procedure was followed to prepare the surface of the ITO glass with a sheet resistance 15 Ohm/square. The ITO glass was cleaned for 15 min respectively in de-ionized water, acetone, and isopropyl alcohol with ultra-sonication and was blown dry using N₂ gas. The ITO surface was then treated with O₂ plasma for 3 min. Next, a 40 nm thick layer of PEDOT:PSS (Baytron P 4083) was spin coated at 3000 rpm for 1 min onto the ITO. The thickness of the PEDOT:PSS was measured by profilometry. The ITO coated glass substrate with the PEDOT:PSS layer was then preheated on a hotplate at 150 °C for 20 min in air.

The P3HT:PC₆₀BM solution was prepared by adding a 1:0.8 mass ratio of P3HT (Rieke Metals, Inc.) and PC₆₀BM (American Dye Sources, Inc.) with a combined mass of 40 mg to 1ml of DCB. This corresponds to a concentration

of 40 mg/ml of DCB. For the P3HT:PC₆₀BM device with Au-silica nanorods, DCB solutions with the Au-silica nanorod concentrations of 0.2 mg/ml, 0.4 mg/ml and 0.8 mg/ml are prepared by diluting the Au-silica nanorods solution with different amount of DCB. The 40 mg blends of P3HT and PC₆₀BM with a weight ratio of 1:0.8 are similarly added to 1 ml of these DCB solutions to give the P3HT:PC₆₀BM blend with 0.5 wt%, 1 wt%, and 2 wt% concentrations of Au-silica nanorods, respectively. The P3HT:PC₆₀BM solutions with and without Au-silica nanorods were spin coated at same coating condition, namely 500 rpm for the first 18 s and 1000 rpm for the next 10 s onto the PEDOT:PSS layer. The layer thickness of the P3HT:PC₆₀BM and P3HT:PC₆₀BM blended with 1 wt% of Au-silica nanorods were measured by profilometry to be 101 nm and 102 nm, respectively.

Figure 4-2 Photographs of (a) glove box, (b) thermal evaporator and (c) full view of device fabrication system.

The P3HT:PC₆₀BM films were dried naturally and then annealed at 140°C for 10 min inside the glove box filled with N₂ (H₂O < 0.1ppm and O₂ < 0.1ppm). As shown in Fig. 4-2, the evaporator system is connected with the

glove box, to prevent the devices exposure to the air during the transferring. Finally, a Ca (13 nm) /Al (200 nm) bilayer top electrode was subsequently vacuum-deposited at a pressure of 1×10^{-4} Pa onto the active layer. All devices had an active area of $3 \times 3 \text{ mm}^2$ as illustrated in Fig. 4-3. They were encapsulated using epoxy and cover glass before taking out from the glove box.

Figure 4-3 Photograph of the fabricated OSC devices with four samples on transparent ITO glass substrate.

4.2.3 Device Characterization

Transmission electron microscope (TEM) of the Au-silica nanorods was acquired using a JEOL 1400 TEM with an accelerating voltage at 100 kV. The thickness of the active layer and PEDOT:PSS layer of the devices was measured using a KLA-Tencor P-10 surface profiler. A thin line was scratched on either the BHJ film or PEDOT:PSS film. The tip of the surface profiler will then scan the film surfaces across the scratched line. The depth of the profile across the line was measured as the thickness of the film.

The J - V characteristics of the OSC devices were acquired in air using a Keithley 2400 source measure unit (Fig. 4-4 (a)). For the J - V characteristics under illumination, a solar simulator (Solar Light Ltd) with a simulated AM1.5G spectrum and irradiance of 100 mW/cm^2 was used. The irradiance was calibrated using an oriel reference silicon solar cell and power meter. Optical absorption spectra were measured using a Perkin Elmer Lambda 950 UV/Vis/near-IR spectrophotometer equipped with a 150 mm diameter integrating sphere (Fig. 4-4 (b)). The absorbance was obtained from the reflectance and transmittance by the equation: $absorbance = 1 - reflectance - transmittance$. The IPCE spectra were measured using a Bentham PVE 300 system equipped with a xenon lamp, monochromator, light chopper and lock-in amplifier and a calibrated silicon photodetector (Fig. 4-4 (c)).

The steady state PL spectrum of the P3HT film was recorded in air under ambient conditions by a RF-5301PC fluorescence spectrometer. A 150W Xenon lamp (530 nm) was used as the excitation source and the photodetector had a spectral range from 300 nm to 900 nm.

Figure 4-4 Photographs of (a) current density-voltage measurement system, (b) Perkin Elmer Lambda 950 UV/Vis/near-IR spectrophotometer and (c) EQE measurement system.

4.3 Results and Discussion

The extinction spectrum of the Au-silica nanorods solution in CB is shown in Fig. 4-5. The Au-silica nanorods solution in the quartz cuvette was put inside the Perkin Elmer Lambda 950 spectrophotometer equipped with the integrating sphere. Light transmitted through the sample and light scattered by sample was collected by integrating sphere and measured by detector. Therefore, the extinction spectrum was obtained by measuring both of the absorption and

scattering. There are two LSPR peaks where localized surface plasmons are excited in Au-silica nanorods. The major peak is located at about 720 nm and minor peak is at about 530 nm. As demonstrated by Gan's theory in chapter 3 [158], the wavelength of the major peak is tunable through the aspect ratio of the nanorod and thus provides a greater degree of design freedom relative to the nanosphere. The major and minor LSPR peaks originate from the longitudinal and transverse oscillations of surface electrons respectively due to the rod shape of Au-silica nanorods.

Figure 4-5 Extinction spectrum of the Au-silica nanorods solution in CB with the LSPR peaks at ~530 nm and ~720 nm.

The effect of Au-silica nanorods with transverse LSPR at 520 nm was first studied in P3HT:PC₆₀BM solar cells. The device structure as described in section 4.2.2 and the molecular structures of P3HT and PC₆₀BM are shown in Fig. 4-6. Fig. 4-7 shows the UV-Vis absorption spectra of the P3HT:PC₆₀BM BHJ films with and without the concentration of 1 wt% Au-silica nanorods with the same thickness. The absorption spectrum of the P3HT:PC₆₀BM film without NPs ranges from 300 to 650 nm. Shorter wavelengths of light from 300 to 400 nm are mainly absorbed by the fullerene and longer wavelengths from 400 to

650 nm are primarily absorbed by the polymer. There is a “shoulder” at wavelength of 600 nm due to the weak vibronic structure. After incorporation of Au-silica nanorods, the P3HT:PC₆₀BM film with Au-silica nanorods has more light absorption than plain P3HT:PC₆₀BM film in the spectral range of 300 nm to 600 nm. The 11% of maximum absorption enhancement in the P3HT:PC₆₀BM film with Au-silica nanorods occurs at 520 nm, which coincides with the minor LSPR peak of Au-silica nanorods.

Figure 4-6 Device structure of conventional polymer OSC with Au-silica nanorods in the P3HT:PC₆₀BM layer and molecular structures of P3HT and PC₆₀BM.

Figure 4-7 UV-Vis absorption spectra of P3HT:PC₆₀BM BHJ films with and without 1 wt% of Au-silica nanorods.

To verify the light absorption enhancement originated from the LSPR of Au-silica nanorods, we conducted the J - V characteristics and IPCE measurement of the OSCs. Fig. 4-8 (a) shows the J - V characteristics of OSCs with and without Au-silica nanorods in P3HT:PC₆₀BM blend under 100 mW/cm² illumination. The average photovoltaic parameters from ten identical devices for each type are listed in Table 4-1. For the optimized device without Au-silica nanorods, the V_{oc} , the J_{sc} , the FF and the PCE are 0.62 ± 0.01 V, 7.89 ± 0.12 mA/cm², $63.8 \pm 0.32\%$ and $3.1 \pm 0.03\%$, respectively. For the device with the optimized Au-silica nanorod concentration of 1 wt%, the V_{oc} remains unchanged. The J_{sc} , FF and PCE of the polymer OSC increase to 8.66 ± 0.09 mA/cm², $65.4 \pm 0.56\%$ and $3.5 \pm 0.06\%$ respectively. As a result, the overall efficiency enhancement induced by Au-silica nanorods in polymer OSCs based on P3HT:PC₆₀BM blend is 13%. This improvement in efficiency was repeatable. When the concentration of the Au-silica nanorods increases to 2 wt%, the V_{oc} remains the same while the J_{sc} and FF decrease to 8.55 ± 0.10 mA/cm² and $59.7 \pm 0.74\%$ respectively.

Figure 4-8 (a) J - V characteristics of conventional P3HT:PC₆₀BM devices with and without Au-silica nanorods; (b) IPCE spectra of conventional P3HT:PC₆₀BM devices with and without Au-silica nanorods.

Fig. 4-8 (b) shows that the IPCE spectrum of the P3HT:PC₆₀BM device with 1 wt% of Au-silica nanorods is increased with respect to the reference device spectrum within the wavelength range from 480 nm to 600 nm. Outside this range, the two spectra are essentially overlapping. The wavelength range 480 nm - 600 nm coincides with the transverse LSPR peak of the Au-silica nanorods. Since both devices have similar absorber thickness, Fig. 4-8 shows that the improvement in photocurrent is due to the incorporation of Au-silica nanorods.

Table 4-1 Device performance parameters of polymer OSCs based on P3HT:PC₆₀BM with different Au-silica nanorod concentrations under 100 mW/cm² AM1.5G simulated solar irradiation.

Au NPs concentration (wt%)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE(%)
0	0.62 ± 0.01	7.89 ± 0.12	63.8 ± 0.32	3.1 ± 0.03
0.5 wt%	0.62 ± 0.01	8.56 ± 0.13	64.2 ± 0.21	3.4 ± 0.05
1 wt%	0.62 ± 0.01	8.66 ± 0.09	65.4 ± 0.56	3.5 ± 0.06
2 wt%	0.61 ± 0.01	8.55 ± 0.10	59.7 ± 0.74	3.1 ± 0.09

PL spectrum measurements of the pure P3HT film with and without Au-silica nanorods were conducted to better understand the origin of the improved J_{sc} . Fig. 4-9 presents the PL emission spectrum of a spin-coated P3HT film and a P3HT film with 1 wt% Au-silica nanorods. The excitation wavelength used for both spectra was 530 nm. The PL emission peak at 650 nm for the P3HT film with nanorods is enhanced with respect to the P3HT film by a factor of 1.22. Since the excitation wavelength corresponds to the transverse

LSPR peak of Au-silica nanorods, these NPs can cause an increase in the density of photo-generated excitons in the P3HT, thereby increasing the PL intensity.

Figure 4-9 PL spectra of pure P3HT film and P3HT film with 1 wt% Au-silica nanorod concentration using an excitation source wavelength of 530 nm.

The experimental results show that the incorporation of the Au-silica nanorods causes the light absorption enhancement in the P3HT:PC₆₀BM device. The main mechanisms of light absorption enhancement in the plasmonic device are the LSPR effect and scattering effect. Upon the excitation of incident light metallic NPs can enhance not only the localized electric field intensity but also scatter light into longer optical path length within the active layer. These mechanisms will be further studied in the next three chapters. The improved light absorption enhances the generation rate of excitons in the organic active layer. Furthermore, the interplay between excitons and the electromagnetic field of metallic NPs facilitates the exciton dissociation [93]. As a result, the photocurrent and PCE of the P3HT:PC₆₀BM device were enhanced.

4.4 Summary

We demonstrate the improved the PCE of conventional P3HT:PC₆₀BM device by incorporation of Au-silica nanorods into the BHJ active layer. At the optimized concentration of 1 wt% Au-silica nanorods, the PCE of the P3HT:PC₆₀BM device incorporating Au-silica nanorods is enhanced by 13% from 3.1% to 3.5%. Absorption spectra, *J-V* characteristics, IPCE and PL measurements verify that the addition of Au-silica nanorods into OSCs leads to increased light absorption of the active layer. This architecture inhibits the carrier recombination at the metal/polymer interface and effectively exploits light absorption at the LSPR wavelengths of the Au-silica nanorods. However, the enhancement in the P3HT:PC₆₀BM device is moderate because only the transverse LSPR peak is able to enhance the absorption.

Chapter 5 Low Bandgap Polymer OSCs

Enhanced by Au-Silica Nanorods

5.1 Introduction

The low bandgap polymers provide an effective way to increase the light absorption in the OSC by harvesting more light at longer wavelength [24, 46, 159, 160]. The Au-silica nanorods in chapter 4 have two plasmon resonance peaks which match with the absorption spectrum of the low bandgap polymer (PCPDTBT), and leads to greater plasmonic effects. In this chapter, we employed PCPDTBT to construct a solar cell and investigate the effect of Au-silica core-shell nanorods on polymer OSCs based on the blend of PCPDTBT:PC₇₀BM. The Au-silica nanorods were blended directly into the BHJ solution with different concentrations. We demonstrate that Au-silica nanorods have a greater effect on polymer OSCs based on low bandgap polymer PCPDTBT than polymer OSCs based on P3HT. Compared with the P3HT:PC₆₀BM device with Au-silica nanorods, the PCPDTBT:PC₇₀BM device with 1 wt% Au-silica nanorod concentration has a higher efficiency of 4.4% with an increase of 25% relative to the reference device. This chapter is partially based on our paper published in journal of Organic Electronics [154].

5.2 Experimental

5.2.1 Device Fabrication

ITO-coated glass substrates (15 Ohm/square) were sequentially cleaned in detergent, de-ionized water, acetone and isopropyl alcohol under sonication for 15 min each. The substrates were then dried under a flow of N₂ and treated with O₂ plasma for 3 min. PEDOT:PSS was spin coated onto the ITO electrode with a thickness of around 40 nm and then preheated on a hotplate at 150 °C for 20 min in air. For the preparation of the PCPDTBT:PC₇₀BM blend, 10 mg of 1,8 octanedithiol (DIO) was added to 1 ml of a CB dispersion of Au-silica nanorods with varying concentration. The DIO was found to be critical to improve the phase separation of the PCPDTBT:PC₇₀BM blend. A 40 mg blend of 1:3 mass ratio PCPDTBT:PC₇₀BM was then added to the CB solution containing DIO and Au-silica nanorods. The final solutions consisted of PCPDTBT (average molecular weight 30,000 g/mol; polydispersity 2.2, 1-material, Inc.) and PC₇₀BM (Ossila, Inc.) and Au-silica nanorods with weight ratio of 0 wt%, 0.5 wt%, 1 wt% and 2 wt%. These solutions were spin-coated on top of the PEDOT:PSS layer at 3000 rpm for 50 s. The thicknesses of the active layers with and without Au-silica nanorods were around 110 nm. Finally, a cathode consisting of 13 nm Ca and 200 nm Al were deposited on the BHJ layer under vacuum condition of 1×10^{-4} Pa in a thermal evaporator. The active area of all devices is 9 mm² and the devices were taken out from the glove box after the encapsulation.

5.2.2 Characterization

TEM of the Au-silica nanorods was performed using a JEOL 1400 TEM with an accelerating voltage at 100 kV. Absorption spectra were measured using an UV/vis/near-IR spectrophotometer (Perkin Elmer Lambda 950) equipped with a 150 mm diameter integrating sphere. In a total transmission measurement, the sample was mounted at the transmittance port of the integrating sphere and the sample reflectance port opposite was covered by a white diffuse reflector. This ensures that all light that passed through the sample was collected. For the total reflection measurement, the sample was mounted at the reflectance port with the sample normal titled at 8° with respect to the incident beam direction. The specular exclusion port was covered by a white diffuse reflector. In addition, diffuse (off-specular) transmission and reflection measurements were performed in order to obtain the haze factor. For diffuse transmission and diffuse reflection measurements, the sample reflectance and specular exclusion ports were left respectively open. In addition, scanning electron microscope (SEM) of the polymer blend film was imaged by a JEOL 7001F field emission (FE) SEM at an accelerating voltage of 5.0 kV. For cross sectional SEM, the polymer blend film was spin coated onto a silicon wafer to avoid sample charging. Atomic force microscopy (AFM) (MFP-3D, Asylum Research) in the tapping mode was used to analyze the surface roughness of the films. The film thickness was determined by a surface profiler (KLA-Tencor P-10). The J - V measurement of the devices was conducted with a Keithley 2400 source meter unit under simulated 100 mW cm^{-2} (AM1.5G) irradiation from a solar simulator (Solar Light Co. Inc.). The IPCE measurement system

(PVE 300, Bentham) comprised a xenon lamp, a monochromator, a chopper, a lock-in amplifier and a calibrated silicon photodetector. The PL spectrum of the PCPDTBT solution in a spectral range from 300 nm to 900 nm was measured by a RF-5301PC fluorescence spectrometer under excitation of 150W Xenon lamp at 720 nm.

5.3 Results and Discussion

The same Au-silica nanorods were incorporated into PCPDTBT:PC₇₀BM film and their TEM image of are the same as those in chapter 4. The absorption spectrum of PCPDTBT:PC₇₀BM film shown in Fig. 5-1 is broader than that of P3HT:PC₆₀BM film and ranges from 300 to 850 nm with a maximum absorption peak at 780 nm. Since this matches the longitudinal LSPR peak of Au-silica nanorods, Au-silica nanorods were mixed with PCPDTBT:PC₇₀BM solution to fabricate standard polymer OSCs. The molecular structures of PCPDTBT and PC₇₀BM are shown in Fig. 5-2.

Figure 5-1 UV/Vis absorption spectra of P3HT:PC₆₀BM film (~100 nm) and PCPDTBT:PC₇₀BM film (~110 nm).

Figure 5-2 Molecular structures of PCPDTBT and PC₇₀BM.

Fig. 5-3 shows the plan view secondary electron SEM image of a nanorod embedded in a spin-coated PCPDTBT:PC₇₀BM film with 1 wt% Au-silica nanorods. Due to the short range of secondary electrons, this particular nanorod should be located near the surface of the PCPDTBT:PC₇₀BM film. The diameter and length measured from the SEM image are around 35 nm and 88 nm, which are smaller than that measured from the TEM image. It is because the Au-silica nanorod is tilted with respect to the surface the PCPDTBT:PC₇₀BM film and part of the Au-silica nanorod is embedded within the film. In general, it is difficult to image the Au-silica nanorods using SEM as large areas of the sample surface are devoid of nanorods. Fig. 5-3 (b) shows a cross section SEM image of the ~110 nm thick PCPDTBT:PC₇₀BM film with a probable embedded Au-silica nanorod highlighted by the circle. The SEM results are consistent with AFM topographic images. Fig. 5-4 (a), (b) and (c) show the surface morphology scans of PCPDTBT:PC₇₀BM films with 0 wt%, 1 wt% and 2 wt% of Au-silica nanorods respectively. The nanorods are not apparent on the surface and the root mean square (RMS) surface roughnesses for Fig. 5-4 (a), (b) and (c) are 1.13 nm, 0.934 nm and 1.147 nm respectively.

Figure 5-3 (a) Plan view SEM image of a PCPDTBT:PC₇₀BM film with 1 wt% Au-silica nanorod showing a nanorod near the surface; (b) Cross sectional SEM image of a PCPDTBT:PC₇₀BM:Au-silica nanorods film; The white scale bars in (a) and (b) represent 100 nm.

Figure 5-4 AFM height images of (a) the PCPDTBT:PC₇₀BM film without Au-silica nanorods, (b) the PCPDTBT:PC₇₀BM film with 1 wt% Au-silica nanorods and (c) the PCPDTBT:PC₇₀BM film with 2 wt% Au-silica nanorod.

Fig. 5-5 (a) presents the J - V characteristics of the polymer OSCs with and without Au-silica nanorods in the PCPDTBT:PC₇₀BM blend. The average photovoltaic parameters calculated from ten devices for each weight percentage

are listed in Table 5-1. For the device without Au-silica nanorods, V_{oc} , J_{sc} , FF and PCE are 0.60 ± 0.01 V, 11.1 ± 0.37 mA/cm², $51.2 \pm 0.44\%$ and $3.4 \pm 0.10\%$, respectively (Table 5.1). For the device with 1 wt% Au-silica nanorod concentration, the V_{oc} is 0.60 ± 0.01 V which is the same as the reference device. The J_{sc} , FF and PCE increase to 12.48 ± 0.33 mA/cm², $57.9 \pm 0.37\%$, and $4.4 \pm 0.11\%$, respectively. The FF has the largest enhancement by 14% at this concentration and the series resistance of the OSC device reduced from 2.75Ω cm² to 1.32Ω cm². When the Au-silica nanorod concentration increases to 2 wt%, the FF decreases from $57.9 \pm 0.37\%$ to $47.2 \pm 0.47\%$ due to increase in series resistance and decrease in shunt resistance. The J_{sc} does not show any further increase. Fig. 5-5 (b) presents the IPCE spectra of the reference PCPDTBT:PC₇₀BM device and the devices incorporated with different Au-silica nanorod concentrations. The IPCE spectra of the devices with Au-silica nanorods increase relative to the reference device spectrum over a broad wavelength range from about 500 nm to 800 nm. The largest increase is seen for the device with 1 wt% of nanorods. Outside this range, the spectra are overlapping. The spectral region of enhanced IPCE is in good agreement with the transverse and longitudinal LSPR peaks of the Au-silica nanorods referred to Fig. 4-5 in chapter 4. Since these devices have similar absorber thickness, the Au-silica nanorods should account for the improvement in the photocurrent.

Figure 5-5 (a) J - V characteristics of PCPDTBT:PC₇₀BM devices with and without Au-silica nanorods; (b) IPCE spectra of PCPDTBT:PC₇₀BM device with and without Au-silica nanorods.

Table 5-1 Device performance parameters of polymer OSCs based on PCPDTBT:PC₇₀BM with different Au-silica nanorod concentrations under 100 mW/cm² AM1.5G simulated solar irradiation.

Au NPs concentration (wt%)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE(%)
0	0.60 ± 0.01	11.10 ± 0.37	51.2 ± 0.44	3.4 ± 0.10
0.5 wt%	0.60 ± 0.01	12.00 ± 0.26	56.6 ± 0.52	4.1 ± 0.12
1 wt%	0.60 ± 0.01	12.48 ± 0.33	57.9 ± 0.37	4.4 ± 0.11
2 wt%	0.59 ± 0.01	12.02 ± 0.29	47.2 ± 0.47	3.4 ± 0.10

The PL spectra of the PCPDTBT and the PCPDTBT with 0.1 mg/ml of Au-silica nanorods dissolved in CB are shown in Fig. 5-6 (a). Fig. 5-6 (a) shows that the PL intensity of the PCPDTBT solution with Au-silica nanorods is enhanced with respect to the reference PCPDTBT solution from 825 nm to 850 nm when excited at 720 nm. For the low bandgap polymer PCPDTBT, PL spectrum of PCPDTBT solution had to be performed instead of PL spectrum of PCPDTBT film. This is because our PL system has the limited spectral range of

the detector from 300 nm to 900 nm and only can operate under room temperature while the PL spectrum of PCPDTBT film has the wavelength range from 850 nm to 1100 nm which needs cryostat for low temperature recording of spectrum [46]. This confirms that the density of photo-generated excitons is increased when Au-silica nanorods are present in the PCPDTBT solution. Fig. 5-6 (b) shows that the PCPDTBT:PC₇₀BM film with 1 wt% Au-silica nanorods has greater optical absorption than the plain PCPDTBT:PC₇₀BM film within the spectral range from 500 nm to 800 nm. Both layers have a thickness of 110 nm. For wavelengths below 500 nm and above 830 nm, the absorption is the same. This shows that the Au-silica nanorods increase the optical absorption of the PCPDTBT:PC₇₀BM film over the spectral range spanning the two LSPR peaks.

Figure 5-6 (a) Solution PL spectra of PCPDTBT and PCPDTBT with 0.1 mg/ml Au-silica nanorod concentration in CB using an excitation source wavelengths of 720 nm; (b) UV/Vis absorption spectra of plain PCPDTBT:PC₇₀BM film and BHJ film with 1 wt% Au-silica nanorods concentration. The thickness of both film layers is 110 nm.

The main mechanisms of absorption enhancement in photovoltaic devices incorporated with metallic NPs are: (i) enhanced localized electric fields at the LSPR and (ii) increased scattering of light [90]. The latter effect is analogous to an anti-reflection coating if the NPs are located at the surface. In order to

identify the main enhancement mechanism in our OSC with embedded Au-silica nanorods, we performed additional haze factor measurement for diffuse transmission and reflection on the PCPDTBT:PC₇₀BM films [161]. Fig. 5-7 (a) shows the spectrum of the haze factor for transmission (H_T) defined as the ratio between the diffuse transmission and the total transmission for PCPDTBT:PC₇₀BM films with and without 1 wt% Au-silica nanorods. It can be seen that for the PCPDTBT:PC₇₀BM film with nanorods, the H_T ranges between 20% - 25% from 300 nm - 850 nm which is higher than that of the reference sample (8% - 10%). This shows that the sample with nanorods has significantly more diffuse transmission than the reference sample. The slight increase in the H_T from 500 nm to 800 nm could be due to increased light scattering near the two LSPR peaks of the Au-silica nanorods. Fig. 5-7 (b) shows the spectrum of the haze factor for reflection (H_R) defined as the ratio between the diffuse reflection and the total reflection for PCPDTBT:PC₇₀BM films with and without 1 wt% Au-silica nanorods. For the sample with nanorods, the H_R ranges between 10% - 20% from 300 nm to 850 nm. The corresponding range for the reference sample is 5% - 7.5%. Taken together, these results for the H_T and H_R show that increased light scattering by the nanorods can account for the observed performance enhancement in the PCPDTBT:PC₇₀BM devices with blended nanorods. This conclusion is consistent with the theoretical calculations of the scattering and absorption efficiencies of Au nanorods by Lee and El-Sayed [148]. For an aspect ratio of 3 similar to the Au-silica nanorods used in this chapter, they found that the scattering efficiency is larger than the absorption efficiency at the longitudinal plasmon resonance peak.

Figure 5-7 (a) Transmission haze factor spectrum for PCPDTBT:PC₇₀BM film with and without 1 wt% of Au-silica nanorods; (b) Reflection haze factor spectrum for PCPDTBT:PC₇₀BM film with and without 1 wt% of Au-silica nanorods.

In the experimental study by Brown et al., spherical Au-silica NPs with a shell thickness of 3 - 8 nm was found to increase absorption in the active layer of a DSSC by enhanced localized electric fields or resonant energy transfer. Reduction of the shell thickness of the Au-silica nanorods in this work to this range may therefore be beneficial because both light scattering and enhanced localized fields could then be effective. The details will be discussed in chapter 6.

5.4 Summary

Au-silica core-shell nanorods were randomly blended into active layers of a low bandgap polymer system (PCPDTBT:PC₇₀BM) to enhance the PCE. The device based on PCPDTBT:PC₇₀BM blend with a Au-silica nanorod concentration of 1 wt% has a higher efficiency improvement (25% from 3.4% to 4.4%) than the devices based on P3HT:PC₆₀BM blend in chapter 4 with the optimized Au-silica nanorod concentration. This is because the absorption spectrum of PCPDTBT:PC₇₀BM film is wide and its absorption peak matches

the primary LSPR peak of Au-silica nanorods, resulting in much stronger plasmonic effects. IPCE, PL and absorption spectra confirm that incorporation of Au-silica nanorods into the BHJ film enhances light absorption at the surface plasmon resonances of Au-silica nanorods. From diffuse transmission and reflection measurements, we deduced that increased light scattering by Au-silica nanorods can result in enhanced light absorption by polymer OSCs.

Chapter 6 Solution-Processed Small-Molecule OSCs Enhanced by Dual Plasmonic Au-Silica Nanorods

6.1 Introduction

Recently, solution-processed SM donors have stimulated much interest as a viable alternative to the widely studied conjugated polymers for organic BHJ solar cells [50, 162]. Solution-processed SM donors have the advantage that the donor molecules are monodisperse and are therefore more uniform than conjugated polymer-based devices and higher levels of material purity can be realized. This unique property and evolution of molecular design (from initial work of oligothiophenes and polycyclic acenes to push-pull type chromophores) [163-168] has resulted in improved device performance relative to polymer OSCs. SM BHJ solar cells based on p-DTS(FBTTh₂)₂:PC₇₀BM was initially reported to have a PCE of 7% [50]. p-DTS(FBTTh₂)₂ exhibits broad and strong light absorption up to 750 nm, similar to that of low band gap conjugated polymers [47]. In addition, the well-balanced and high charge carrier mobilities ($\sim 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$) of p-DTS(FBTTh₂)₂ is superior to other polymer systems, such as P3HT, PCPDTBT and PTB7 systems [169]. For these polymer systems, the electron and hole mobilities are lower than p-DTS(FBTTh₂)₂ and may be unbalanced. Therefore, p-DTS(FBTTh₂)₂ fulfils the requirements of a wide absorption range, high charge generation rate, and well-balanced charge carrier mobilities.

Similar to polymer BHJ solar cells, SM OSCs are limited by insufficient sunlight absorption because the active layer of SM BHJ should be very thin (~100 nm) due to low carrier mobility and short exciton diffusion length [78]. In order to enhance light harvesting, there is a need to capture more light without increase the thickness of the SM BHJ layer beyond the limited optical path length. In chapter 4 and chapter 5, metallic NPs have been introduced into the polymer OSCs for enhanced light harvesting induced by the plasmonic effect of metallic NPs [148]. We have demonstrated the PCE of 3.5% with 13% enhancement in P3HT:PC₆₀BM solar cells and PCE of 4.4% with 25% enhancement in PCPDTBT:PC₇₀BM solar cells respectively by incorporation of Au-silica nanorods in the active layer [154]. There has been no report on the plasmonic effect of metallic NPs in solution-processed SM OSCs. In addition, the mechanism of the Au-silica nanorods has not been explored in sufficient detail for polymer BHJ solar cells. In particular, the localized electric field enhancement around the nanorod at the dual plasmonic peaks is seldom reported.

In this chapter, it reveals for the first time, the introduction of plasmonic effect of metallic NPs into solution processed SM OSCs rather than the widely studied polymeric counterparts. A high PCE of 8.29% with 27% enhancement has been achieved by incorporation of Au-silica nanorods into the BHJ of p-DTS(FBTTh₂)₂:PC₇₀BM. Both J_{SC} and FF were relatively high because the dual plasmonic peaks of Au-silica nanorods are within the absorption spectrum range of p-DTS(FBTTh₂)₂ and the carrier mobility of p-DTS(FBTTh₂)₂:PC₇₀BM BHJ is relatively high and well-balanced. We use

electromagnetic field simulation to investigate the contribution of localized electric field in the enhancement mechanism at the dual plasmonic peaks for three silica shell thickness. The FDTD simulation [170] showed that the localized electric field intensity is enhanced for both the 520 nm and 680 nm peaks at the surface of the Au core and the field intensity at the interface of the silica shell and the organic layer decreased with increasing shell thickness. As a result, both increased localized electric field intensity and increased light scattering were involved in the PCE enhancement of the OSCs for a shell thickness of 5 nm. In addition, charge recombination at the surface of metallic nanorods can be suppressed by the silica shell, which is demonstrated by light intensity dependence study. Furthermore, the factors that influence the optimum nanorod concentration were determined by the carrier mobility and surface roughness of the active layers at various nanorod concentrations. Finally, the lifetime studies of the SM OSCs show that the addition of Au-silica nanorods does not affect the stability of device.

6.2 Experimental

6.2.1 Nanorod and Device Fabrication

We synthesized Au-silica core-shell nanorods using the seed-mediated method as discussed previously [155]. After the Au nanorods solution was prepared, it was divided into four parts into which the different amounts of TEOS [171] were added to tune the thicknesses of the silica shell. The silica shell thicknesses of nanorods are 0 nm, 5 nm, 7 nm and 10 nm, respectively. SM BHJ solar cells with Au-silica nanorods were fabricated by the following

process. ITO-coated glass substrates were cleaned by detergent, de-ionized water, acetone and isopropyl alcohol sequentially using an ultrasonic bath. Each substrate was blow dried by N₂ and treated with O₂ plasma for 10 min to reform the ITO surface. PEDOT:PSS was spin-coated at 5000 rpm for 40 s on the ITO glass to obtain a thickness of 30 nm. The PEDOT:PSS film was then annealed on a hotplate at 150 °C for 20 min in the air. The p-DTS(FBTTh₂)₂:PC₇₀BM blend and Au-silica nanorods were mixed in CB with 0.4 v/v% DIO processing additive to form uniform solution and were dissolved at 60 °C overnight. The final solutions consisted of p-DTS(FBTTh₂)₂ (21 mg/mL, 1-material, Inc.) and PC₇₀BM (14 mg/mL, Nano-C, Inc.) and Au-silica nanorods with weight ratios of 0 wt%, 0.5 wt%, 1 wt%, 2 wt% and 5 wt% of the weight of p-DTS(FBTTh₂)₂:PC₇₀BM blend. Before spin-casting the BHJ active layer, the prepared solutions were heated at 90 °C for 15 min. For all devices, the solutions were spin-coated at 2000 rpm for 45 s in a glove box. The BHJ film coated sample was immediately transferred back to the hotplate and then thermally annealed at 80 °C for 10 min to remove residual solvent. The thicknesses of the active layer of all BHJ devices were determined by a surface profiler to be 100 ± 2 nm. Finally, 20 nm Ca and 80 nm Ag were thermally deposited sequentially under vacuum condition of 1 × 10⁻⁴ Pa. All fabricated devices had the structure ITO/PEDOT:PSS/p-DTS(FBTTh₂)₂:PC₇₀BM/Ca/Ag and an active area of 8 mm². They were encapsulated using epoxy and cover glass before removal from the glove box.

For the charge transport studies, hole-only devices are fabricated with the structure of the ITO/MoO₃/p-DTS(FBTTh₂)₂:PC₇₀BM/MoO₃/Ag. The second

layer of MoO_3 blocks the injection of electrons from the Ag electrode. Electron-only devices have the structure of ITO/Al/p-DTS(FBTTh₂)₂:PC₇₀BM/Ca/Al. The first layer of Al blocks the injection of holes from the ITO electrode.

6.2.2 Device Characterization

The dimensions of the Au NPs and the morphology of the p-DTS(FBTTh₂)₂:PC₇₀BM films were characterized using TEM and AFM respectively. A JEOL 1400 TEM with an accelerating voltage of 100 kV was used to obtain bright field images of the NPs from which their diameter, length and aspect ratio was measured. The height and phase AFM images of the films with and without nanorods were scanned in the tapping mode using a Cypher S AFM (Asylum Research).

Optical absorption spectra of the thin film samples were measured using a UV/Vis/near-IR spectrophotometer (Perkin Elmer Lambda 950) fitted with an integrating sphere with a diameter of 150 mm. For absorbance measurement, the reflectance and specular exclusion ports of the integrating sphere are blocked by white standard plates. By unblocking these two ports consecutively, the ratio of diffuse scattering to total scattering or the haze factor could also be measured. Prior to absorption measurements, the film thickness of all layers was measured by a KLA-Tencor P-10 surface profiler to ensure the thicknesses are the same.

For solar cell characterization, a Keithley 2400 source meter unit was used to obtain the *J-V* characteristics under dark and illuminated conditions. A solar simulator (Solar Light Inc.) provides simulated sunlight with AM1.5G spectrum

and irradiance of 100 mW/cm^2 . The oriel reference silicon solar cell and power meter are used for solar simulator calibration. The light intensity dependence of J_{sc} was studied by tuning the light intensity using neutral density filters. The EQE or IPCE spectrum was measured by a Bentham PVE 300 system consisting of a xenon lamp, monochromator, chopper wheel, lock-in amplifier and a calibrated silicon photodiode.

6.2.3 Electromagnetic Field Simulation

The FDTD method was used to calculate the 3D electric field intensity distribution in the silica shell and adjacent spatial region of the Au silica nanorods. The simulation region in the x, y and z directions are all perfect matched layer (PML) boundary condition. A total field scattered field (TFSF) light source was used as the excitation for a single core shell Au-silica nanorod in the electric field simulation. In order to achieve higher accuracy, a mesh size of 1.0 nm was set in the active layer region. A 3D power monitor was used to obtain the spatial distribution of electric field at 680 nm and 520 nm for Au-silica nanorods with the different shell thicknesses.

6.3 Results and Discussion

6.3.1 Effect of Shell Thickness

Four types of Au nanorods with silica shell thicknesses of 0 nm, 5 nm, 7 nm and 10 nm, respectively, were prepared. The thickness of the silica shell was increased by increasing the amount of TEOS. The TEM images as shown in Fig. 6-1 display that the average length and diameter of these Au nanorods core are approximately 87 nm and 34 nm, respectively. The normalized

extinction spectrum (Fig. 6-2 (a)) reveals that Au-silica nanorods with 5 nm of silica shell in CB have a broad spectrum with dual LSPR peaks at 520 nm and 680 nm. The extinction spectra of the nanorods with other silica shell thickness were also plotted in Fig. 6-2 (a). These extinction spectra almost overlap since the extinction spectrum shifts only two to three nanometers when shell thickness changes from 5 nm to 10 nm. The major LSPR peak of nanorods at 680 nm is also well-matched with the absorption peak of p-DTS(FBTTh₂)₂ donor which has wide and strong absorption spectrum from 400 to 700 nm (Fig. 6-2 (b)). Therefore, we fabricate a p-DTS(FBTTh₂)₂ solar cell with Au nanorods embedded in the active layer. The molecular structures of p-DTS(FBTTh₂)₂ and PC₇₀BM, and device structure are shown in Fig. 6-3.

Figure 6-1 TEM images of Au-silica nanorods with silica shell thickness of (a) 0 nm, (b) 5 nm, (c) 7 nm and (d) 10 nm. The scale bars represent 50 nm.

Figure 6-2 (a) Normalized extinction spectra of Au-silica nanorods with various silica shell thicknesses in CB solvent. a. u., arbitrary units; (b) Normalized absorption spectrum of p-DTS(FBTTh₂)₂ donor.

Figure 6-3 The device structure of SM BHJ solar cell and chemical structures of the p-DTS(FBTTh₂)₂ and PC₇₀BM.

Before the reference device without Au NPs was compared with plasmonic device with Au NPs, the effect of the p-DTS(FBTTh₂)₂:PC₇₀BM film thickness on the reference device was first studied. The film thickness is varied by adjusting the spin coating speed. Fig. 6-4 represents the *J-V* characteristics of the p-DTS(FBTTh₂)₂:PC₇₀BM devices with various BHJ film thicknesses under AM1.5G irradiation at 100 mW/cm². The photovoltaic parameters for each thickness are listed in Table 6-1. With the increase of p-DTS(FBTTh₂)₂:PC₇₀BM film thickness from 70 nm to 100 nm, the *J*_{SC} increased by 12% which is faster than the rate of decrease in *FF* while the *V*_{OC}

remains the same. The PCE in the device with the thickness of 100 nm reaches 6.52%. However, when the BHJ film thickness further increased from 100 nm to 200 nm, the PCE began to decrease since the FF declined faster than the rate of the increase in the J_{SC} while the V_{OC} remains the same. Finally, it is found that the reference device with thickness of 100 nm can obtain the best performance. In this thesis, the highest PCE reference device with a thickness of 100 nm was used to compare with plasmonic device with Au NPs.

Figure 6-4 J - V characteristics of PCPDTBT:PC₇₀BM solar cells with various BHJ film thicknesses.

Table 6-1 Photovoltaic device parameters of SM BHJ devices based on p-DTS(FBTTh₂)₂:PC₇₀BM with various BHJ film thicknesses under 100 mW/cm² AM1.5G simulated solar irradiation.

BHJ film thickness (nm)	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
70 nm	0.77	10.8	72.8	6.05
80 nm	0.77	11.2	71.9	6.20
100 nm	0.77	12.1	69.9	6.52
120 nm	0.77	12.2	67.3	6.31
150 nm	0.77	12.3	65.4	6.19
200 nm	0.76	12.4	61.6	5.80

Fig. 6-5 represents the J - V characteristics of the p-DTS(FBTTh₂)₂:PC₇₀BM devices with and without 1 wt% of Au nanorods with various silica shell thicknesses under AM1.5G irradiation at 100 mW/cm². The concentrations of Au-silica nanorods are optimized at 1 wt% (section 6.3.2). The average photovoltaic parameters calculated from ten devices for each type are listed in Table 6-2. The reference device has an average PCE of $6.5 \pm 0.14\%$ with the V_{OC} of 0.77 ± 0.01 V, J_{SC} of 12.01 ± 0.27 mA/cm² and FF of $70.2 \pm 0.32\%$. After incorporation of 1 wt% bare Au nanorods, the average V_{OC} , J_{SC} , FF and PCE are decreased to 0.72 ± 0.01 V, 11.73 ± 0.13 mA/cm², $63.5 \pm 0.49\%$ and $5.4 \pm 0.05\%$, respectively. It is assumed that there is the carrier recombination at the surface of the bare Au nanorods which creates the internal short-circuits throughout the BHJ active layer [153]. Upon incorporation of Au-silica nanorods with 5 nm, 7 nm and 10 nm silica shell, the V_{OC} and FF remain the same while the J_{SC} increases to 15.14 ± 0.35 mA/cm², 14.53 ± 0.26 mA/cm² and 14.12 ± 0.23 mA/cm², respectively. The unchanged V_{OC} and FF suggest that incorporation of Au-silica nanorods does not induce charge recombination with protect of silica shell, which will be demonstrated later. In addition, the improved J_{SC} indicates that light absorption is enhanced by incorporation of Au-silica nanorods, which is confirmed by absorption spectra in Fig. 6-6. The value of J_{SC} decreases somewhat with the increase of silica shell thickness although there are similar enhancement in absorption for four types of Au nanorods embedded in the p-DTS(FBTTh₂)₂:PC₇₀BM film. These results show the importance of having a silica shell around the Au nanorods.

Figure 6-5 J - V characteristics of p-DTS(FBTTh₂)₂:PC₇₀BM BHJ solar cells with and without 1 wt% of Au-silica nanorods with silica shell thickness of 0 nm, 5 nm, 7 nm and 10 nm.

Figure 6-6 UV/Vis absorption spectra of p-DTS(FBTTh₂)₂:PC₇₀BM BHJ films with and without 1 wt% of Au-silica nanorods with shell thickness of 0 nm, 5 nm, 7 nm and 10 nm.

Table 6-2 Photovoltaic device parameters of SM BHJ devices based on p-DTS(FBTTh₂)₂:PC₇₀BM with and without 1 wt% of Au nanorods with various silica shell thicknesses under 100 mW/cm² AM1.5G simulated solar irradiation.

Au NPs shell thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
No NPs	0.77 ± 0.01	12.01 ± 0.27	70.2 ± 0.32	6.5 ± 0.14
0 nm	0.72 ± 0.01	11.73 ± 0.13	63.5 ± 0.49	5.4 ± 0.05
5 nm	0.77 ± 0.01	15.14 ± 0.35	70.4 ± 0.61	8.2 ± 0.12
7 nm	0.77 ± 0.01	14.53 ± 0.26	70.3 ± 0.43	7.8 ± 0.12
10 nm	0.77 ± 0.01	14.12 ± 0.23	70.2 ± 0.41	7.6 ± 0.10

In order to study the effect of silica shell on the enhanced photocurrent in the p-DTS(FBTTh₂)₂:PC₇₀BM devices, the enhancement mechanisms including the LSPR effect and light scattering were investigated. Localized electric field intensity distributions within the active layer embedded with Au-silica nanorods are simulated by FDTD method. In this simulation, it is assumed that the incident light is incident from the top and electric field is polarized parallel to the longitudinal axis of Au-silica nanorods. The electric field intensity distribution of the Au-silica nanorod surrounded with CB is also simulated as a reference. The simulation results in CB are consistent with the experimental absorption spectrum of Au-silica nanorods in CB that light absorption at 680 nm is higher than that at 520 nm (Fig. 6-7). The electric field intensity distributions in the active layer embedded with Au-silica nanorod at 520 nm and 680 nm are shown in Fig. 6-8 for different silica shell thickness from 5 nm to 10 nm. From the simulation, for the same thickness, strong electric field localization is observed which is due to LSPR excited by Au-silica nanorod. The electric field intensities are also enhanced around the Au-silica nanorod at both 520 nm and 680 nm. The electric field intensity is the strongest at the surface of Au core and decays within silica shell at both of the two wavelengths respectively. The highly localized electric field corresponds to the broadband light absorption enhancement in the active layer.

Figure 6-7 Electric field intensity distributions of Au-silica nanorods with 5 nm silica shell at 520 nm and 680 nm in CB solution.

For the 5 nm shell thickness illustrated in Fig. 6-8 (a), there is significant enhancement of electric field intensity at the interface of the silica shell and in the nearby organic medium (white dotted line). Here, the enhancement of electric field intensity at 520 nm is larger than that at 680 nm due to the different dielectric constant of organic medium from CB. For the 7 nm shell thickness, the enhancement pattern in Fig. 6-8 (b) is basically similar to that of Fig. 6-8 (a) for both 520 nm and 680 nm. However, at the surface of the silica shell, the electric field intensity enhancement is slightly reduced, which is consistent with the reduced J_{SC} in Fig. 6-5. When the shell thickness is increased to 10 nm (Fig. 6-8 (c)), the electric field intensity distribution at the surface of the Au core is still similar to that of Fig. 6-8 (a) and Fig. 6-8 (b) but the electric field intensity enhancement at the surface of the silica shell is greatly reduced. Therefore, the electric field intensity at the surface of the 5 nm

silica shell is higher and contributes to more light absorption by organic medium.

Figure 6-8 Electric field intensity distribution of Au-silica nanorods at 520 nm and 680 nm for (a) 5 nm silica shell; (b) 7 nm silica shell and (c) 10 nm silica shell.

Haze factor measurement was performed to examine the scattering effects of Au nanorods with various shell thicknesses in the SM OSCs. Fig. 6-9 (a) and 6-9 (b) show the H_T and H_R for p-DTS(FBTTh₂)₂:PC₇₀BM film with and without Au-silica nanorods. Upon incorporating the Au-silica nanorods, there are similar enhancements in H_T and H_R for Au nanorods with 0 nm, 5 nm, 7 nm and 10 nm. The H_T for plasmonic samples ranges between 7% and 17% from 400 to 800 nm which is higher than that of reference sample with range between 3% and 8%. Similarly, the H_R for plasmonic samples increased to the range between 8% and 18% compared to that of reference sample with range

between 3% and 9%. Such enhancements show that the light scattering is increased in the active layer when incorporating the Au-silica nanorods. Taken together, it can be concluded that both LSPR effect and the scattering effects excited by Au-silica nanorods with 5 nm attribute to the light absorption enhancement. This also suggests that for shell thickness of 10 nm or more, the electric field intensity enhancement in the vicinity of the nanorod is negligible and enhancement is dominated by scattering consistent with our prior results in chapter 5.

Figure 6-9 (a) H_T spectra for p-DTS(FBTTh₂)₂:PC₇₀BM films with and without 1 wt% Au-silica nanorods with silica shell thickness of 0 nm, 5 nm, 7 nm and 10 nm; (b) H_R spectra for p-DTS(FBTTh₂)₂:PC₇₀BM films with and without 1 wt% Au-silica nanorods with silica shell thickness of 0 nm, 5 nm, 7 nm and 10 nm.

As mentioned above, the J_{SC} , V_{OC} and FF decreased after incorporation of bare Au nanorods while the J_{SC} increased and V_{OC} and FF remained unchanged for silica coating Au nanorods. In order to further understanding the effect of silica shell of the nanorods on the device performance, we studied the recombination mechanisms of Au nanorods with and without silica shell by measuring the J_{SC} at various light intensities. Generally, J_{SC} of OSC device is power law dependence on light intensity, which can be written as [72, 172]:

$$J_{SC} \propto P^S \quad (6.1)$$

where P is light intensity and S is the exponential factor.

From Fig. 6-10, the value of $S = 0.913$ and $S = 0.944$ for bare Au nanorods and Au nanorods with 5 nm silica shell respectively were determined by fitting the data with Eq. 6-1. Usually, when the value of S is equal to 1, it means that there is no bimolecular recombination and space-limited charges for ideal material without defects. The values of S for bare Au nanorods and Au nanorods with 5 nm silica shell are both less than 1, which means that there is bimolecular recombination in both devices. However, the enhanced S for the Au nanorods with 5 nm silica shell indicated that there is less bimolecular recombination for the device with silica coating Au nanorods. Such enhancement is consistent with the increase in J_{SC} and FF by coating the Au nanorods with silica.

Figure 6-10 The value of J_{SC} as a function of light intensity for bare Au nanorods and Au nanorods with 5 nm silica shell. Short dash lines are fitted by Eq. 6-1.

6.3.2 Effect of Au-silica Nanorod Concentration

Fig. 6-11 represents the J - V characteristics of the devices with the weight ratios of 0 wt%, 0.5 wt%, 1 wt%, 2 wt% and 5 wt% of Au-silica nanorods with 5 nm silica shell under AM1.5G irradiation at 100 mW/cm². The average photovoltaic parameters calculated from ten devices for each weight percentage are listed in Table 6-3. The reference device has average PCE of $6.5 \pm 0.14\%$ with the V_{OC} of 0.77 ± 0.01 V, J_{SC} of 12.04 ± 0.27 mA/cm² and a FF of $70.2 \pm 0.65\%$. After incorporation of Au-silica nanorods, the PCE increases with higher concentration of Au-silica nanorods and reaches a maximum at 1 wt%. A high PCE of $8.2 \pm 0.12\%$ (with the maximum value of 8.29%) was achieved. The improvement in PCE is mainly due to J_{SC} which increases to 15.14 ± 0.35 mA/cm². Despite significant changes in J_{SC} , V_{OC} remains at 0.77 V, implying that Au-silica nanorods do not change the nature of the electrode and the BHJ layer interface and the energy offsets between the respective HOMO and LUMO of p-DTS(FBTTh₂)₂ and PC₇₀BM. The similar FF also suggests that Au-silica nanorods do not adversely affect the charge collection/recombination and carrier transport in the device. At the highest Au-silica nanorod concentration of 5 wt%, however, the PCE of the devices declined because of decrease in J_{SC} and FF .

Figure 6-11 J - V characteristics of p-DTS(FBTTh₂)₂:PC₇₀BM BHJ solar cells with Au-silica nanorod concentrations of 0 wt%, 0.5 wt%, 1 wt%, 2 wt% and 5 wt%.

Table 6-3 Photovoltaic device parameters of SM BHJ devices based on p-DTS(FBTTh₂)₂:PC₇₀BM with different Au-silica nanorod concentrations under 100 mW/cm² AM1.5G simulated solar irradiation.

Au NPs concentration (wt%)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE(%)
No NPs	0.77 ± 0.01	12.04 ± 0.27	70.2 ± 0.65	6.5 ± 0.14
0.5 wt%	0.77 ± 0.01	13.62 ± 0.30	70.5 ± 0.84	7.4 ± 0.15
1 wt%	0.77 ± 0.01	15.14 ± 0.35	70.4 ± 0.61	8.2 ± 0.12
2 wt%	0.77 ± 0.01	13.93 ± 0.40	68.4 ± 0.80	7.3 ± 0.24
5 wt%	0.76 ± 0.01	12.08 ± 0.34	65.8 ± 0.88	6.0 ± 0.17

Fig. 6-12 depicts the EQE spectra of the reference device and plasmonic devices with the Au-silica nanorods with 5 nm silica shell. For the device with the optimized Au-silica nanorod concentration, the EQE increases the most within the wavelength range from 450 nm to 700 nm. The IQE spectrum was calculated by dividing the EQE spectrum by the absorption spectrum [173]. Fig. 6-13 shows that the plasmonic device with 1 wt% Au-silica nanorods has

remarkably high IQE values near or above 90% from 480 nm to 670 nm, which is well-matched with the broad absorption range of dual plasmonic Au-silica nanorods.

Figure 6-12 EQE spectra of p-DTS(FBTTh₂)₂:PC₇₀BM BHJ solar cells with Au-silica nanorod concentrations of 0 wt%, 0.5 wt%, 1 wt%, 2 wt% and 5 wt%.

Figure 6-13 IQE spectrum of p-DTS(FBTTh₂)₂:PC₇₀BM BHJ solar cells with 1 wt% Au-silica nanorods with 5 nm silica shell.

The mobility of charge carriers is important for organic photovoltaic device performance because it needs to be high enough to give a high J_{sc} and PCE [172]. When nanorods are blended into the active layer, there may be increased carrier scattering resulting in reduced mobility. It is therefore

important to study the effect of nanorod concentration on the carrier transport in the active layer. The theory of space-charge limited current (SCLC) in a semiconductor was first given by Mott and Gurney [44, 174]. It can be seen in wide bandgap semiconductors and insulators with low charge carrier mobility. Under bias, the space-charge effect occurs when the injected carrier concentrations is larger than its equilibrium concentration and the doping concentration. Here, the space-charge and electric field distribution in the semiconductor are controlled by the injected carriers. In the presence of a space-charge effect, the current through the space charge region is dominated by the drift current of the carriers while the drift current is determined mainly by the electric field the space-charge generated. Therefore, the current through the space charge region is limited by the space-charge in the semiconductor, which is called SCLC. In case of electron injection, current density can be written as $J = qnv$, where v is drift-velocity of the carrier, q is electric charge, n is electron concentration which is determined by the applied voltage and the capacitance of the device. When a low electric field is applied, the drift-velocity is related to the mobility ($v = \mu E$), where μ is carrier mobility and E is electric field. In this case, the current density should be proportional to the square of the applied voltage (Mott-Gurney law). It should be noted that the equation derived from Mott-Gurney law is based on the following assumption: there is only one type of charge carrier present. By using electrodes which suppress either electrons or holes, we measured dark J - V characteristics of hole-only and electron-only devices and numerically fit the results using the SCLC model [44,

174]. The Mott-Gurney law that includes a field dependent carrier mobility, is given by [44]:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 \frac{V^2}{L^3} \exp\left(\beta \sqrt{\frac{V}{L}}\right) \quad (6.2)$$

where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the SM and fullerene blend; μ_0 is the zero-field mobility; V is the voltage drop across the BHJ layer which is the applied voltage V_{applied} compensated by the built-in voltage (V_{BI}) and the voltage across the contacts (V_{RS}); i.e., $V = V_{\text{applied}} - V_{\text{BI}} - V_{\text{RS}}$. L is the thickness of the active layer and β is the field activation factor.

The dark J - V curves of hole-only and electron-only devices with Au-silica nanorod concentrations of 0 wt%, 1 wt%, 2 wt% and 5 wt% are shown in Fig. 6-14 (a) and Fig. 6-14 (b) respectively. The extracted zero-field hole and electron mobilities (Table 6-4) of reference device from these curves are $1.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $1.5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Upon the incorporation of 1 wt% Au-silica nanorods with 5 nm silica shell, the zero-field hole and electron mobilities slightly increase to $2.4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $2.5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The values of β are almost same in those devices. The ratio between electron mobility and hole mobility in p-DTS(FBTTh₂)₂:PC₇₀BM blend are observed to decrease from 1.2 to 1.06, indicating both higher and more balanced carrier mobilities in p-DTS(FBTTh₂)₂:PC₇₀BM solar cell after incorporating 1 wt% Au-silica nanorods. Hence, the incorporation of 1 wt% Au-silica nanorods does not adversely affect the charge transport in the active layer. However, at 2 wt% Au-silica concentration, the zero-field hole and electron mobilities decline to $1.6 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $1.7 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. When Au-silica concentration continued to rise to 5 wt%, the

zero-field hole and electron mobilities decrease to $8.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $9.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, which correspond to the decreased performance of SM OSCs with 5 wt% Au-silica nanorods.

Figure 6-14 The dark J - V characteristics of (a) hole-only device (b) and electron-only device with Au-silica nanorod concentrations of 0 wt%, 1 wt%, 2 wt% and 5 wt%. The solid lines represent the best fitting using the SCLC model.

Table 6-4 Zero-field hole and electron mobilities of reference device and plasmonic devices extracted from dark J - V curves.

Au NPs concentration (wt%)	Zero-field hole mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	Zero-field electron mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)
No NPs	1.2×10^{-3}	1.5×10^{-3}
1 wt% nanorods	2.4×10^{-3}	2.5×10^{-3}
2 wt% nanorods	1.6×10^{-3}	1.7×10^{-3}
5 wt% nanorods	8.5×10^{-4}	9.0×10^{-4}

Carrier mobility of these SM devices might be affected by the changed nanoscale morphology of the BHJ film after incorporation of Au-silica nanorods with 5 nm silica shell. AFM height and AFM phase images of the films with various concentrations of Au-silica nanorods (0 wt%, 0.5 wt%, 1 wt% and 5 wt%) are shown in Fig. 6-15. At low Au-silica nanorods, the RMS

roughness of the BHJ film are 2.112 nm, 2.393 nm and 2.477 nm for films with 0 wt%, 0.5 wt% and 1 wt% Au-silica nanorods, respectively and no obvious difference in phase separation can be observed. AFM images suggest that we can add the Au-silica nanorods as high as 1 wt% without affecting the morphology of the BHJ film. However, the RMS roughness drastically increases to 12.487 nm when the concentration is increased to 5 wt%. Such change in morphology induced by high nanorod concentration affects the charge transport process and thus degrades both hole mobility and electron mobility in SM devices, which agree well with the above results as shown in Fig. 6-14.

Figure 6-15 AFM height images for p-DTS(FBTTh₂)₂:PC₇₀BM film with (a) 0 wt%, (c) 0.5 wt%, (e) 1 wt% and (g) 5 wt% Au-silica nanorods with 5 nm silica shell; AFM phase images for p-DTS(FBTTh₂)₂:PC₇₀BM film with (b) 0 wt%, (d) 0.5 wt%, (f) 1 wt% and (h) 5 wt% Au-silica nanorods with 5 nm silica shell.

6.3.3 Study of the Stability

Finally, we studied the stability of reference and plasmonic devices because the stability or degradation characteristics is as important as the efficiency and we have to ensure that Au-silica nanorods used for efficiency enhancement should not have negative impact on the stability of the device. Furthermore, the influence of plasmonic metallic NPs on the device stability has never been reported before. Due to the nature of the organic active layer and interfacial layers, OSCs typically degrade rapidly when exposed to O₂ and moisture at ambient condition [175, 176]. Therefore, we used a simple encapsulation scheme using epoxy and cover glass to test the effect of Au-silica nanorods on the stability of the solution-processed SM BHJ solar cells. Fig. 6-16 (a) shows the normalized PCE of the devices as a function of storage time in air for the encapsulated reference device and plasmonic device with 1 wt% nanorods. The PCE in both the devices with and without 1 wt% nanorods gradually declined during the first 20 days and then dropped rapidly to zero in the last few days because the O₂ and moisture in air have penetrated into the

devices and thus caused the rapid degradation of the device performance. Before the onset of rapid degradation, the normalized PCE of reference and plasmonic devices showed similar trends and finally decreased to 35.5% and 37.9% of the initial PCE values in the 20 days, respectively. The 3.11% decline per day in plasmonic devices is slightly slower than the 3.23% decline per day in reference devices, which indicates that incorporation of Au-silica nanorods into the device has no adverse effect on the stability of SM solar cells. The changes in the normalized V_{OC} , J_{SC} and FF of plasmonic device are shown in Fig. 6-16 (b). V_{OC} has a slight decrease from 0.774 V to 0.746 V whereas both the normalized J_{SC} and FF have a large decrease to 53.0% and 74.3% of initial values, respectively, in the first 20 days. On day 23, the PCE became unmeasurable. The detailed J - V characteristics of SM BHJ solar cells with and without 1 wt% Au-silica nanorods with simple encapsulation over a period of 22 days stored in air are shown in Fig. 6-16 (c) and Fig. 6-16 (d).

Figure 6-16 (a) The normalize PCE versus storage time of reference device and plasmonic device with 1 wt% Au-silica nanorods stored in ambient air with simple encapsulation. a. u., arbitrary units. (b) The normalized V_{oc} , J_{sc} and FF of plasmonic device with 1 wt% Au-silica nanorods as a function of storage time in ambient air. a. u., arbitrary units. (c) J - V characteristics of SM BHJ solar cell with 1 wt% Au-silica nanorods with simple encapsulation over a period of 22 days stored in air. (d) J - V characteristics of reference SM BHJ solar cell with simple encapsulation over a period of 22 days stored in air.

6.4 Summary

We improved the PCE of the solution-processed SM OSCs by incorporation of Au-silica nanorods into the p-DTS(FBTTh₂)₂:PC₇₀BM active layer. At the optimized concentration of 1 wt% Au-silica nanorods with 5 nm silica shell, J_{sc} and PCE increased by ~25% and ~27%, respectively. Theoretical calculation reveals that shell thickness should be thin to get sufficient localized electric field intensity outside silica shell. Hence, the PCE

enhancements in SM BHJ solar cells incorporated with nanorods with 5 nm silica shell is originated from both LSPR and scattering effect. Carrier mobility and AFM measurements confirm that carrier mobility is high and balanced and surface roughness has negligible change in the blend system at 1 wt% concentration of Au-silica nanorods.

Chapter 7 Incorporation of Nanospheres and Nanorods into Organic Layers of OSCs

7.1 Introduction

In the literature, there have been reports on plasmonic OSC in which single metallic NPs are incorporated into various layers (Table 3-1), for example: the HTL [93], active layer [91] or both [95]. In addition, two different metallic NPs had been blended within a single layer [96, 97]. In these plasmonic devices, the configuration that incorporates metallic NPs into the HTL layer [95] and the active layer results in better hole transport and improved light absorption while the configuration that combines different shapes of NPs in the active layer achieved a broadband absorption enhancement [96]. However, embedding NPs with two different shapes into the HTL layer and the active layer, respectively, in order to leverage advantages of both configurations, has not been reported yet.

In this chapter, we report high-performance solution-processed SM OSCs by incorporation of Au nanospheres into the PEDOT:PSS layer and Au-silica nanorods into the p-DTS(FBTTh₂)₂:PC₇₀BM layer, simultaneously. A combination of Au nanospheres and Au-silica nanorods in organic layers achieves a broader optical absorption enhancement and better hole transport. As a result, significantly improved PCE is realized by incorporating dual Au NPs. The OSC device reported in this chapter has the highest PCE in this thesis. This chapter is partially based on our paper published in journal of Chemical

Communication [177].

7.2 Experimental

7.2.1 Synthesis of Au Nanospheres and Au-silica Nanorods

Au nanospheres were synthesized by rapid injection of 20 ml of 38.8 mM sodium citrate into a boiling growth solution of HAuCl_4 (200 ml, 1 mM) under vigorous stirring. After boiling for 15 min, the solution was allowed to cool to room temperature. The Au nanospheres solution (20 ml) was added to the mixed solution of CTAB (20 ml, 0.2 M) and HCl (0.8 ml, 1 M) under vigorous stirring at 30 °C. After the solution was kept for 24 hrs, CTAB-coated Au nanospheres were obtained. After a further 12 hrs at 0 °C, the CTAB was removed by centrifugation. Finally, the Au nanospheres were dispersed into water. The syntheses of Au-silica nanorods followed the seed-mediated method as discussed in chapter 4.

7.2.2 Device Fabrication

The fabrication process of the p-DTS(FBTTh₂)₂ solar cells is exactly same to that in chapter 6 except for the PEDOT:PSS buffer layer. For preparation of the buffer layers, a Au nanospheres solution was doped into PEDOT:PSS. The PEDOT:PSS solutions with weight ratio of 0 wt%, 1.5 wt%, 0.3 wt% and 0.6 wt% Au nanospheres were spin-coated at 5000 rpm for 40 s on ITO substrates and annealed at 150 °C in air for 20 min. The thicknesses of PEDOT:PSS films were all about 30 nm determined by a surface profiler, indicating that incorporation of Au nanospheres does not change the PEDOT:PSS film thickness.

To determine the effect of Au NPs incorporated into different layers on hole mobility, we fabricated the hole-only devices with the structures of ITO/PEODOT:PSS (with and without Au nanospheres)/p-DTS(FBTTh₂)₂:PC₇₀BM (with and without Au-silica nanorods)/MoO₃ (10 nm)/Ag (100 nm). Dark *J-V* characteristics of the hole-only devices were measured and then fitted using SCLC model and the Mott-Gurney law that includes field-dependent mobility.

7.3 Results and Discussion

Fig. 7-1 (a) and (b) show the TEM images of Au nanospheres and Au-silica nanorods, respectively. Au nanospheres synthesized using the seed-mediated method [155] had an average diameter of about 10 nm. Au-silica nanorods are completely and uniformly coated by 6 nm silica shell and have an average length and diameter of 89 nm and 34 nm, respectively. The normalized extinction spectra of the Au nanospheres in water and Au-silica nanorods in CB were measured. Fig. 7-2 shows that the maximum extinction peaks of Au nanospheres and Au-silica nanorods were at 521 and 681 nm, respectively. Here, four types of SM OSCs as illustrated in Fig. 7-3 were fabricated (Device A: reference device without NPs; B: Au nanospheres in PEDOT:PSS only; C: Au-silica nanorods in the active layer only; D: NPs in both PEDOT:PSS and the active layers).

Figure 7-1 TEM images of (a) Au nanospheres and (b) Au-silica nanorods. The white scale bars in (a) and (b) represents 10 nm and 20 nm respectively.

Figure 7-2 The normalized extinction spectra of Au nanospheres in water and Au-silica nanorods in CB, a. u., arbitrary units.

The AFM height images of the PEDOT:PSS layer in Fig. 7-4 show that the RMS roughness of PEDOT:PSS films increases from 0.872 nm to 0.899 nm after incorporation of 0.3 wt% concentration of Au nanospheres. The AFM images in Fig. 6-15 suggest that the incorporation of 1 wt% concentration of Au-silica nanorods has negligible effect on the morphology of the BHJ film. The almost unchanged RMS roughness confirm that all the NPs are embedded within PEDOT:PSS layer and the active layer and would not affect their morphologies.

Figure 7-3 Device configurations of (a) reference device without NPs; (b) Device with Au nanospheres in PEDOT:PSS only; (c) Device with Au-silica nanorods in the active layer only; (d) Device with NPs in both PEDOT:PSS and the active layers.

Figure 7-4 AFM height images for the PEDOT:PSS films with (a) and without (b) Au nanospheres.

The J - V characteristics of the four devices with Au NPs incorporated into different layers are shown in Fig. 7-5. The average photovoltaic parameters from ten identical devices for each type are listed in Table 7-1. We first investigate the impact of Au NPs concentration incorporated in single organic

layer of SM OSC, either in the HTL or the active layer at a time. The corresponding J - V curves as shown in Fig. 7-6 illustrate that the optimum concentration of Au nanospheres in PEDOT:PSS layer and Au-silica nanorods in the BHJ layer are 0.3 wt% and 1 wt% respectively. Then, we studied the effect of Au NPs incorporated in both HTL and active layer simultaneously. The reference device has average PCE of $6.5 \pm 0.15\%$ with the V_{OC} of 0.77 ± 0.01 V, J_{SC} of 12.17 ± 0.32 mA cm⁻² and a FF of $69.7 \pm 0.65\%$. After incorporation of the Au nanospheres only in the PEDOT:PSS layer, the V_{OC} of the plasmonic device remained the same, J_{SC} and FF both increased to 13.53 ± 0.36 mA cm⁻² and $71.2 \pm 0.79\%$, respectively, leading to an average PCE of $7.4 \pm 0.22\%$. Besides, the R_s of plasmonic device, extracted from the dark J - V curve, reduced from 2.75 to 2.04 Ω cm² which contributes to an increase of FF . When only Au-silica nanorods are incorporated in the active layer, V_{OC} and R_s remained the same and FF increased slightly to $70.6 \pm 0.44\%$. In contrast, J_{SC} has a larger enhancement to 14.96 ± 0.30 mA cm⁻² than previous plasmonic device, which is due to the broader absorption spectrum of Au-silica nanorods that extends to longer wavelengths relative to Au nanospheres. When doping Au NPs into both the PEDOT:PSS layer and the active layer, J_{SC} and FF further improved to 15.56 ± 0.37 mA cm⁻² and $71.5 \pm 0.75\%$ while the V_{OC} remain unchanged, resulting in a much better PCE of $8.5 \pm 0.22\%$ (with the maximum value of 8.72%).

Figure 7-5 J - V characteristics of p-DTS(FBTTh₂)₂:PC₇₀BM BHJ solar cells with and without the optimized concentration of NPs.

Table 7-1 Photovoltaic parameters of p-DTS(FBTTh₂)₂:PC₇₀BM BHJ devices with Au NPs in different layers under AM1.5G illumination at 100 mW cm⁻². (Device A: reference device without NPs; B: Au nanospheres in PEDOT:PSS only; C: Au-silica nanorods in the active layer only; D: NPs in both PEDOT:PSS and the active layers).

Device	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF (%)	PCE (%)
A	12.17 ± 0.32	0.77 ± 0.01	69.7 ± 0.65	6.5 ± 0.15
B	13.53 ± 0.36	0.77 ± 0.01	71.2 ± 0.79	7.4 ± 0.22
C	14.96 ± 0.30	0.77 ± 0.01	70.6 ± 0.44	8.1 ± 0.17
D	15.56 ± 0.37	0.77 ± 0.01	71.5 ± 0.75	8.5 ± 0.22

Figure 7-6 (a) J - V characteristics of p-DTS(FBTTh₂)₂:PC₇₀BM BHJ solar cells with Au nanospheres concentrations of 0 wt%, 0.15 wt%, 0.3 wt% and 0.6 wt% in PEDOT:PSS layer; (b) J - V characteristics of p-DTS(FBTTh₂)₂:PC₇₀BM BHJ solar cells with Au-silica nanorod concentrations of 0 wt%, 0.5 wt%, 1 wt%, 2 wt% and 5 wt% in the active layer.

To verify that the improved J_{SC} is due to optical effect of Au NPs, we performed the IPCE and the UV-vis absorption measurements. Fig. 7-7 (a) and (b) show that the IPCE and absorption spectra of the active layer are both enhanced in the spectral region of 420 to 550 nm after incorporation of Au nanospheres only in PEDOT:PSS layer, and further improvement in the spectral range of 460 to 720 nm are evident after incorporation of Au-silica nanorods only in the active layer. In addition, the broader IPCE and light absorption spectra covering from 420 to 720 nm are achieved when combining dual Au NPs in the devices. Such enhanced IPCE and absorption spectra are well matched with the plasmonic resonance region of Au nanospheres and Au-silica nanorods.

Figure 7-7 (a) IPCE spectra of p-DTS(FBTTh₂)₂:PC₇₀BM solar cells with and without NPs; (b) UV-Vis absorption spectra of p-DTS(FBTTh₂)₂:PC₇₀BM BHJ films with and without NPs; (c) Photocurrent density (J_{ph}) versus internal voltage (V_{int}) characteristics of the reference device and dual NPs device.

To further confirm the effect of Au NPs on the optical absorption of the SM OSC, we determined the maximum photoinduced carrier generation rate ($G_{\max}$) in the devices with and without dual NPs [172, 178, 179]. Fig. 7-7 (c) reveals the dependence of the photocurrent density (J_{ph}) on the internal voltage (V_{int}) for reference and plasmonic devices. J_{ph} is determined as $J_{\text{ph}} = J_{\text{L}} - J_{\text{D}}$, where J_{L} and J_{D} are the current density under illumination and in the dark, respectively. V_{int} is calculated as $V_{\text{int}} = V_0 - V_{\text{a}}$, where V_0 is the voltage at which $J_{\text{ph}} = 0$ and V_{a} is the applied voltage [178]. Fig. 7-7 (c) shows that J_{ph} increases linearly at low V_{int} and saturates at a high V_{int} (2 V and above), which is large enough to dissociate all the photo-generated excitons into free charge carriers and collect them at the electrodes. Thus, at a high V_{int} , saturation current density (J_{sat}) is only limited by the total number of absorbed photons. $G_{\max}$ could be calculated from $J_{\text{sat}} = qLG_{\max}$, where q is the electronic charge and L is the thickness of active layer [179]. The value of $G_{\max}$ for the reference device and plasmonic device are $8.4 \times 10^{27} \text{ m}^{-3} \text{ s}^{-1}$ ($J_{\text{sat}} = 135 \text{ A m}^{-2}$) and $1.1 \times 10^{28} \text{ m}^{-3} \text{ s}^{-1}$ ($J_{\text{sat}} = 172 \text{ A m}^{-2}$), respectively. A significant enhancement of $G_{\max}$ occurred after incorporating dual Au NPs. Since $G_{\max}$ corresponds to the maximum number of absorbed photons, such enhancement demonstrates increased light absorption in the device with dual NPs. This is consistent with the optical absorption data.

The mechanisms of enhanced light absorption by Au NPs are studied by FDTD method [180] and diffuse scattering measurements [161]. Fig. 7-8 shows the distribution of electric field intensity around the Au-silica nanorods at 680 nm in side view and front view. It is found that the electric field intensity is

increased by a factor of 2 relative to the incident light outside the silica shell which will increase absorption within the active layer. Moreover, the haze factor spectra for H_T and H_R are measured by dividing the diffuse transmission/reflection by the total transmission/reflection. Fig. 7-9 shows the increase in both H_T and H_R upon incorporating the Au-silica nanorods, suggesting that NPs scatter more light to increase the optical path. Therefore, both plasmonic and scattering effects excited by NPs contribute to light absorption in SM OSC.

Figure 7-8 Electric field intensity distribution around Au-silica nanorods at 680 nm in side view and front view.

Figure 7-9 H_T and H_R spectra for p-DTS(FBTTh₂)₂:PC₇₀BM film with and without 1 wt% of Au nanorods.

Fig. 7-10 (a) shows the charge collection probability (P_C) versus internal voltage (V_{int}). The P_C could be obtained by normalizing J_{ph} by J_{sat} [172]. The P_C under short-circuit condition ($V_a = 0$ V) increases from 88.1% to 91.3% by adding dual Au NPs, indicating that the incorporation of Au NPs has a positive influence on the charge collection by electrodes. The value of P_C is higher than polymer OSCs and it decreased slowly from short-circuit condition to open-circuit condition compared to sharp increase of some polymers [47]. This indicates that there is less recombination and thus result in high photocurrent and FF in p-DTS(FBTTh₂)₂:PC₇₀BM device.

Figure 7-10 (a) Charge collection probability (P_C) versus internal voltage (V_{int}) characteristics of the reference device and dual NPs device; (b) The dark J - V characteristics of hole-only devices with and without Au NPs.

Since carrier mobility is an important factor for charge transport [178], the value of carrier mobility should be obtained to show the effect of incorporation of Au NPs on the performance of OSC device. However, electron-only device has a structure of ITO/Al/p-DTS(FBTTh₂)₂:PC₇₀BM/Ca/Al and thus can not reflect the changes of electron mobility after incorporation of Au nanospheres into PEDOT:PSS layer. Therefore, only hole-only devices were fabricated to determine the hole mobility. The dark J - V characteristics of hole-only devices

are measured and fitted using SCLC model and the Mott-Gurney law that includes field-dependent mobility, as shown in Fig. 7-10 (b). Upon incorporation of Au NPs in the PEOdT:PSS layer only, the active layer only and both layers, the zero-field hole mobility slightly increased from $1.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $1.4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $2.1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $2.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively. The hole mobility of the device with NPs in the active layer is increased more because Au NPs can introduce dopant states within the active layer which can provide hopping sites for holes and thus enhance the mobility [94]. An increase in the hole mobilities indicate that the incorporation of the Au NPs does not adversely affect the charge transport in the active layer.

7.4 Summary

We demonstrate the maximum PCE of 8.72% with a relative performance increase of 31% in solution-processed SM OSC by incorporation of Au nanospheres and Au-silica nanorods into the organic layers of the OSCs. Absorption spectra, IPCE spectra and G_{max} confirm that the combination of Au NPs with two different shapes realized a broadband absorption improvement in the SM OSCs. The studied mechanisms of enhanced light absorption ascribe to both plasmonic and scattering effects by Au NPs. Enhanced carrier collection and carrier transport properties ensure the good performance of the in plasmonic device. Therefore, apart from contributing to the light absorption within the active layer, the Au nanospheres in PEDOT:PSS layer can facilitate the hole collection and Au-silica nanorods in the active layer can avoid the carrier recombination at the metal surface by insulating silica shell.

Chapter 8 Conclusion and Future Work

8.1 Conclusion

In order to enhance the PCE of OSC devices, this thesis has investigated the plasmonic OSC devices for improving light trapping. The Au-silica nanorods were embedded into the active layers comprising conventional polymer fullerene blend, low bandgap polymer fullerene bend and solution-processed SM fullerene blend, respectively. The improved performances of all of these devices have been demonstrated and the enhancement mechanisms have also been studied in detail. Furthermore, a combination of two different types of Au NPs into the HTL and the active layer of the SM OSCs, respectively, has been proposed to further improve efficiency.

The first type of Au-silica nanorods with thick shell has major absorption peak at ~720 nm and silica shell thickness of ~17 nm. They were blended into both the P3HT:PC₆₀BM BHJ and the PCPDTBT:PC₇₀BM BHJ layers. As a result, the PCE of optimized plasmonic P3HT:PC₆₀BM and PCPDTBT:PC₇₀BM devices were enhanced by ~13% (to 3.5%) and ~25% (to 4.4%), respectively. It was observed that there was greater enhancement in plasmonic PCPDTBT:PC₇₀BM device than plasmonic P3HT:PC₆₀BM. This is because of the better absorption spectrum matching of PCPDTBT and Au-silica nanorods in the wavelength range from 500 nm to 800 nm. In addition, the enhanced light scattering played an important role in improving light absorption upon incorporation of large-sized nanorods within the PCPDTBT:PC₇₀BM BHJ layer, which was confirmed by diffusion scattering measurements.

This study demonstrated, for the first time, the introduction of plasmonic effect of metallic NPs into the solution-processed SM OSCs rather than widely studied polymeric counterparts. The second type of Au-silica nanorods with major absorption peak at ~680 nm and thinner shell were incorporated in the p-DTS(FBTTh₂)₂:PC₇₀BM BHJ layer of OSC devices. Here, the effect of silica shell thickness on the performance of the devices was explored by FDTD simulation, diffusing scattering measurements and light intensity dependence of J_{SC} . The results show that the localized electric field intensity in vicinity of Au-silica nanorods is increased with the decrease of the shell thickness while the light scattering almost remained unchanged. In addition, Au-silica nanorods in the active layer prevents the carrier recombination at the metal surface by insulating silica shell. Therefore, the incorporation of Au-silica nanorods with 5 nm silica shell can result in a better PCE of 8.29% with 27% enhancement relative to other shell thicknesses. Moreover, the effect of nanorods concentration in the SM device was also studied. At optimum concentration, the carrier mobility reached the maximum and there was almost no change with surface roughness of SM BHJ layer.

Finally, the highest efficiency of 8.72% with an increase of 31% in this thesis has been achieved by adopting a new device architecture which is different from that in Table 3-1. Here, bare Au nanospheres and Au-silica nanorods were blended into the anode buffer layer and the active layer of the device, respectively. As shown in chapter 7, apart from contributing to broadband light absorption within the active layer, Au nanospheres in the anode buffer layer can facilitate the hole collection due to reduced R_s .

8.2 Future Work

For solar cells, efficiency, life time and fabrication technology are three most important factors for commercialization [37]. Therefore, the ultimate aim is to realize roll-to-roll manufacturing of large-sized OSC device with good device stability and high efficiency.

In this thesis, significantly enhanced photocurrent of the OSC devices has been demonstrated by the incorporation of Au NPs. However, the value of V_{OC} and FF remain unchanged. Therefore, it is necessary to enhance the V_{OC} and FF for further improvement in PCE by interlayer modification methods. Recently, poly [(9,9-bis(3'-(*N,N*-dimethylamino) propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN) was reported to enhance the J_{SC} , V_{OC} and FF of polymer OSCs simultaneously by Y. Cao's group [44]. The J_{SC} , V_{OC} and FF for polymer OSCs based on PCDTBT increased to 12.1 mA/cm² from 11.4 mA/cm², 0.9 V from 0.7 V and 62% from 49%, respectively.

In addition, all fabricated devices in this study were based on the conventional device structure which has the drawback in device stability since the buffer layer such as Ca and cathode with low work function such as Al is air-sensitive. O₂ can diffuse via pinholes into the active layer and Al cathode grain boundaries, leading to the degradation of the active layer and thus device instability in air [174, 181]. In addition, ITO/PEDOT:PSS interface will degrade, which is inevitable due to the strong acidic nature of PEDOT:PSS. As a result, inverted structure of ITO/ZnO/BHJ layer/MoO₃/Ag was proposed to solve this issue, where holes transport through the BHJ layer and MoO₃ layer to the less air sensitive Ag anode and electrons transport through the BHJ layer and

ZnO layer to the ITO cathode [182]. In this way, ITO/PEDOT:PSS interface, Ca buffer layer and Al electrode can be circumvented.

Most of reported high efficiency OSC devices are usually fabricated by spin coating and thermal evaporation methods, leading to small active area and material waste. Recently, inkjet printing and other printing technology is considered as a promising alternative due to its unique advantages: easy and fast deposition over large area, accurate and direct patterning without mask and waste of materials, compatibility to flexible substrates due to no direct contact [183, 184]. One of the applications for inkjet printing of electronic devices is radio-frequency identification (RFID) tag for baggage identification at airport. In past years, there are lots of studies on the mechanism of inkjet printing and its application in OSC devices [184-186]. In the literature, the inkjet printing of ZnO layer [187], PEDOT:PSS layer [188], electrode contact [31, 189] and polymer: fullerene blends [190] have been reported. In our preliminary study, the inkjet printing of high conductive PEDOT:PSS and Ag electrode layers have been demonstrated and presented in the international conferences [191].

Finally, inkjet printing of inverted OSC device embedded with Au NPs could achieve a larger area, better stability and higher efficiency simultaneously.

List of Publications

Journal

1. X. Xu, A. K. K. Kyaw, B. Peng, Q. Xiong, Y. Wang, H. V. Demir, T. K. S. Wong, and X. W. Sun, "Influence of gold-silica nanoparticles on the performance of small-molecule bulk heterojunction solar cells," *Organic Electronics*, vol. 22, pp. 20-28, 2015.
2. X. Xu, Q. Du, B. Peng, Q. Xiong, L. Hong, H. V. Demir, T. K. S. Wong, A. K. K. Kyaw and X. W. Sun, "Effect of shell thickness on small-molecule solar cells enhanced by dual plasmonic gold-silica nanorods," *Applied Physics Letters*, vol. 105, pp. 113306, 2014. (Web of Science: 1 Citation)
3. X. Xu, A. K. K. Kyaw, B. Peng, Q. Du, L. Hong, H. V. Demir, T. K. S. Wong, Q. Xiong and X. W. Sun, "Enhanced efficiency of solution-processed small-molecule solar cells by incorporating gold nanospheres and nanorods into organic layers," *Chemical Communications*, vol. 50, pp. 4451-4454, 2014. (Web of Science: 3 Citations)
4. X. Xu, A. K. K. Kyaw, B. Peng, D. Zhao, T. K. S. Wong, Q. Xiong, X. W. Sun and A. J. Heeger, "A plasmonically enhanced polymer solar cell with gold-silica core-shell nanorods," *Organic Electronics*, vol. 14, pp. 2360-2368, 2013. (Web of Science: 17 Citations)
5. L. Hong, Rusli, X. Wang, H. Zheng, L. He, H. Wang, X. Xu and H. Yu, "Light Trapping in hybrid nanopyramid and nanohole structure silicon solar cell beyond the Lambertian limit," *Journal of Applied Physics*, vol. 116, pp. 074310, 2014.
6. L. Hong, Rusli, X. Wang, H. Zheng, L. He, X. Xu, H. Wang and H. Yu, "Design principles for plasmonic thin film GaAs solar cells with high

absorption enhancement,” *Journal of Applied Physics*, vol. 112, pp. 054326, 2012.

Conference

1. X. Xu, A. K. K. Kyaw, B. Peng, T. K. S. Wong, Q. Xiong and X. W. Sun, “Enhancement of power conversion efficiency in solution processed organic photovoltaic devices by embedded plasmonic gold-silica core-shell nanorods,” *Proc. SPIE, Organic Photonics VI*, vol. 9137; doi: 10.1117/12.2051717, 2014. (Poster Presentation)
2. X. Xu, K. I. Chin, H. Gardner, J. Zhang and T. K. S. Wong, “Inkjet printing of PEDOT:PSS electrode layers for organic photovoltaic devices,” *International Conference on “Frontiers in Materials Science, Chemistry & Physics”*, 2012. (Poster Presentation)
3. X. Xu and T. K. S. Wong, “Inkjet printing of high conductivity Poly(2,4-ethylene-dioxythiophene): Poly(Styrenesulphonate) (HC PEDOT:PSS) anode layers for all organic photovoltaic devices”, *International Conference on Materials for Advanced Technologies, Symposium R: Organic, flexible and printed electronics, Singapore*, 26 Jun-1 Jul 2011 (Oral Presentation).

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