Ultrafast spectroscopic characterization and modelling of hybrid plasmonic organic photovoltaic devices

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**ULTRAFAST SPECTROSCOPIC CHARACTERIZATION
AND MODELLING OF HYBRID PLASMONIC ORGANIC
PHOTOVOLTAIC DEVICES**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2013

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WU BO

School of Physical and Mathematical Sciences

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Summary

Solar energy is one of the most attractive candidates of alternative energy sources to replace the conventional fossil fuels. Among all kinds of solar cells, polymer-based organic solar cells are one that under spotlight in recent years due to some advantages they possess, *e.g.*, low-cost, solution-processed, properties-tunable, flexible, *etc.* With the efficiency of organic solar cells exceeding 10%, their shift from lab to factory will materialize soon.

Further performance improvement of organic solar cell can be achieved by using plasmonic nanostructures as subwavelength antennas or scattering centres. The surface plasmon, which is the collective oscillation of free electrons in the conduction band of some metals such as gold and silver, can yield high-strength local field and scattering when interacting with incident light. However, concomitant issues including energy/charge transfer, morphology disturbance, resistance change, etc can also contribute the performance change when incorporating metallic nanostructures into organic solar cell.

The work explores the integration of different metallic structures into different positions of an organic solar cell and investigates the performance enhancement or loss mechanisms within the plasmonic organic solar cells through ultrafast spectroscopies. It was found that embedding metallic nanostructures (silver nano-triangles, gold/silver nanowires) into the hole transporting layer results in improvement of the performance of an organic solar. Far-field scattering and near-field light coupling contribute to an increased light absorption and exciton/charge generation resulting in an improved short circuit current density. Meanwhile, although

the exciton-surface plasmon interaction is present in polymer only films, it becomes much weaker and negligible in polymer:fullerene blend, indicating exciton dynamics are not strongly affected by the surface plasmon in device. Polaron dynamics were also proven to be negligibly affected by metallic nanostructures well-covered by charge transport layers (e.g. PEDOT: PSS). Thus a good fill factor and open-circuit voltage can be attained while short-circuit current can be increased by incorporating appropriate plasmonic nanostructures in PEDOT: PSS layer.

With silver nanoparticles embedded in the active layer, it was found the performance degrade with increasing silver nanoparticle loading. The loss mechanism is well explained from ultrafast spectroscopy that it is mainly attributed to the charge carrier traps introduced by the silver nanoparticles. The traps can fast trap charges generated near the silver nanoparticle and accelerate the trap-assisted recombination in organic solar cells. The finding correlates well with the electric behaviour of the plasmonic organic solar cells.

Lastly, after realizing that the performance can usually be ameliorated by incorporating plasmonic nanostructures into the hole transporting layer, an academic exercise was also embarked to optimize the ultrathin organic solar cell performance with silver nanodisk array in the hole transporting layer for an ideal structure/scenario. Our finding revealed that the absorption in ultrathin active layer can be significantly boosted using the plasmonic nanodisk and the metal cathode to create cavity-like resonance. A study based on 60 nm thick PCPDTBT: PCBM active layer found that solar light absorption can be increased by 40% through incorporating an appropriate aluminium nanodisk array in the PEDOT:PSS layer. Further improvement of the device performance may also be obtained with silver nanostructure formed cavity.

Publications

1. **Bo Wu**, Xiangyang Wu, Cao Guan, Kong Fai Tai, Edwin Kok Lee Yeow, Hong Jin Fan, Nripan Mathews and Tze Chien Sum, Uncovering Loss Mechanisms in Silver Nanoparticle-Blended Plasmonic Organic Solar Cells, (**Nature Communications** – DOI: 10.1038/ncomms3004 2013)
2. **Bo Wu**, Xinfeng Liu, Than Zaw Oo, Guichuan Xing, Nripan Mathews and Tze Chien Sum, Resonant Aluminum Nanodisk Array for Enhanced Tunable Broadband Light Trapping in Ultra-thin Bulk Heterojunction Organic Photovoltaic Devices, (**Plasmonics** 7, 677 – 684 2012)
3. **Bo Wu**, Than Zaw Oo, Xianglin Li, Xinfeng Liu, Xiangyang Wu, Edwin Kok Lee Yeow, Hong Jin Fan, Nripan Mathews and Tze Chien Sum, Efficiency Enhancement in Bulk-Heterojunction Solar Cells Integrated with Large Area Ag Nano-Triangle Arrays, (**Journal of Physical Chemistry C** 116, 14820 – 14825 2012)
4. Ming Jie Li, Gui Chuan Xing, Guo Zhong Xing, **Bo Wu**, Tom Wu, Xinhai Zhang and Tze Chien Sum, Origin of the Green Emission and the Charge Trapping Dynamics in ZnO Nanowires, (**Physical Review B** 87, 115309 2013)
5. Guichuan Xing, Jingshan Luo, H. Li, **B. Wu**, Xinfeng Liu, Cheng Hon Alfred Huan, Hong Jin Fan, and Tze Chien Sum, Ultrafast Exciton Dynamics and Two-Photon Pumped Lasing from ZnSe Nanowires, (**Advanced Optical Materials** 1, 319–326, 2013)
6. Ming Jie Li, **Bo Wu**, Sandy Adhitia Ekahana, Muhammad Iqbal Bakti Utama, Guichuan Xing, Qihua Xiong, Tze Chien Sum and Xinhai Zhang, Size and Surface Effects on Transient Photoconductivity in CdS Nanobelts probed by Time-Resolved Terahertz Spectroscopy, (**Applied Physics Letters** 101, 091104 2012)
7. Than Zaw Oo, Nripan Mathews, Guichuan Xing, **Bo Wu**, Bengang Xing, Lydia Helena Wong, Tze Chien Sum and Subodh Gautam Mhaisalkar, Ultrafine Au Networks as Plasmonic Antennae in Organic Photovoltaics, (**Journal of Physical Chemistry C** 116, 6453 – 6458 2012)
8. Ankur Solanki, **Bo Wu**, Teddy Salim, Edwin Kok Lee Yeow, Yeng Ming Lam and Tze Chien Sum Performance Improvements in Polymer

Nanofiber:Fullerene Solar Cells with External Electric Field Treatment,
(Submitted to **Journal of Physical Chemistry C**)

9. Xinfeng Liu, **Bo Wu**, Qing Zhang, Jing Ngei Yip, Guannan Yu, Qihua Xiong, Nripan Mathews, and Tze Chien Sum Observing the Surface Plasmonic Effects of Single Silver Nanowire on the Performance Improvement of Organic Solar Cells, (In preparation)

CHAPTER 1. Introduction

1.1 Organic Photovoltaics: Background

In the last four decades, tremendous efforts have been exerted on the development of organic photovoltaic (OPV) devices. Organic solar cells (OSCs) offer us advantages over their inorganic counterparts such as low cost, ease-of-fabrication, flexibility, lightweight as well as the ability to tune the optoelectronic characteristics through synthesis. In 1973 a report using tetracene as the active layer yielded a power conversion efficiency of less than $10^{-4}\%$ was published. This is possibly the earliest literature report of OPV.^{1,2} After that, numerous reports followed and the efficiency of OSCs drastically increased year by year,²⁻⁶ among which polymer-fullerene solar cells based on composites of an electron-donating conjugated polymer and an electron-accepting fullerene have gained the most successes so far. The architectures of polymer-based OSCs have evolved from initial single layer type to bilayer,⁴ and then to the present bulkheterojunction (BHJ) type, leading to significant boost in efficiencies. The BHJ concept was introduced due to the short exciton diffusion length ($\sim 10\text{nm}$) in organic materials that limits the OPV performance. It is achieved by blending the polymer and fullerene in solution and forming a bicontinuous network of both materials after spincoating on substrates (**Figure 1.1**). Tandem cells formed by stacking several bulkheterojunction layers have also been developed.⁷ New polymers have been synthesized to better match the solar irradiation spectrum and they also possess a better charge transport ability that results in a higher performance. The popular polymers are 2-methoxy-5-(2-ethylhexyloxy)-polyphenylenevinylene (MEH-PPV),⁸ poly(3-hexylthiophene) (P3HT),⁹ low band-gap poly[2,6-(4,4-bis-(2-

ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT),¹⁰ poly[N-9''-hepta-decanyl-2,7-carbazole- alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT)¹¹ and thieno[3,4-b]thiophene-alt-benzodithiophene copolymer (PTB7).¹² Presently, the efficiencies of polymer-based OSCs beyond 10% have been reported.^{6,7,13} Meanwhile, the stability of polymer-based OSCs has been continuously improving with new organic materials,^{14,15} new electrodes/ transporting layer,^{16,17} processing methods,¹⁸ inverted architecture,¹⁹ and improved encapsulation technique.²⁰ All of these efforts and success lead to a common belief the commercially available OSCs are not far away.

Figure 1.1 Typical device structure of a BHJ organic solar cell

1.2 Operation Principle and Physical Insights

Generally, organic solar cells convert the solar irradiation to electric power through four steps: (1) light absorption and mainly exciton formation; (2) exciton diffusion to heterojunction where charge transfer (CT) states form; (3) CT excitons dissociation into free charge carriers; (4) charge carriers extraction to the respective electrodes.

(Figure 1.2)

Figure 1.2 The basic steps of OPV operation. (a) Light absorption and exciton formation (b) CT exciton formation (c) Free charge carrier formation (d) Charge extraction.

(1) *Light absorption and exciton formation.* Light absorption by the active layer organic materials creates electrically-bound electron hole pairs (excitons), rather than free charges as in an inorganic semiconductor. The bound charges located on the same chain, are more specifically termed as intrachain singlet excitons. It is formed along the polymer chain due to the low dielectric constant in organic semiconductors which does not significantly screen the Coulombic attraction of the charges. The exciton is usually regarded as Frenkel-type as their binding energy is of the order ~ 1 eV.

The concept of interchain exciton was also proposed in the lamellar structure.^{21,22} It means the exciton does not form on a single polymer chain, instead, it forms across two or more chains, with the electron locating on one chain while the

hole on the other. Interchain excitons are expected to be more delocalized and long-lived compared to intrachain excitons.²¹ Direct photogeneration of free charges were also frequently reported in well-ordered film such as P3HT.²³⁻²⁵ In fact, in organic materials, charges are not absolutely free; instead, they have strong interaction with phonons. The strong interaction between electron/hole and phonon leads to rapid self-localization of the charge excitations. When an electron move through the lattices, it is always surrounded and affected by the lattice distortion and polarization around it. This forms a type of quasiparticles known as polarons. Polarons are a form of charge carriers in OSCs and are directly related to the output of the current in OSCs. However, the exact mechanism of the direct generation of polarons is still unclear. Guo *et al.* suggests the prompt formation of polarons, after photoexcitation is due to dissociation of hot excitons generated at the interface of donor-acceptor within a time scale of <100 fs.²⁶ Furthermore in the absence of an acceptor, direct generation of polarons are also observed in regioregular P3HT, with a generation efficiency as high as 30% being reported.²⁴ It has been proposed that the phenomenon results from the formation of microcrystalline lamellar stacking.²³ In regioregular P3HT, neighbouring polymer chains tend to form lamellar structure and have strong coupling. Banerji *et al.* even suspected the primary excitation in PCDTBT is mobile electrons and holes through studies using fs-resolved fluorescence up-conversion spectroscopy.²⁷ The singlet excitons are only formed after the mobile charges self-localize (<100 fs) and evolve to a bound exciton state (<1 ps). There is an ongoing debate on the species of initial photoexcitation and how they are formed in organic systems.

(2) *Exciton Diffusion and Dissociation.* Excitons diffuse to the donor-acceptor interface and dissociate into charge-transfer states. These states are a result of the interfacial electronic interactions at the heterojunction. Wavefunction overlapping

between an acceptor and donor molecule yield such hybrid states with the electron residing at the LUMO of electron acceptor while the hole located at the HOMO of the electron donor.²⁸ The electron and hole are still bound together by the electrostatic force. This complex is referred to the charge transfer exciton (CT exciton), exciplex, bound polaron pairs, interfacial charge pairs, *etc.* in reports. The binding energy is considered in the range of 0.1-0.5 eV.²⁹ In terms of electric characteristics, CT states strongly determine the photocurrent dependence on the voltage and the open circuit voltage.

The existence of CT states and their role in exciton dissociation into free charges are obvious. The first evidence of CT states is from the appearance of additional absorbing states that are not present in either the donor or acceptor materials. Besides, in polymer-polymer blends, where the radiative coupling between CT states and ground state is strong, photoluminescence of the CT states are also found.^{28,30} Typical charge transfer exciton (CTE) PL is broad and redshift compared to the singlet exciton PL. Theoretical calculation estimated a separation energy of around 100 meV distance between CTE emission and singlet exciton emission.³¹ Typical lifetime of CT PL is around several nanoseconds. Electroluminescence spectroscopy can provide stronger evidence of the existence of CT states since EL mainly comes from the electron-hole recombination at the lowest excited state of blend system, i.e., the CT states.^{32,33}

(3) *CT states to charges.* CT excitons mediate the charge transfer efficiency. They can either dissociate into free charge carriers or relax to the ground state. One important factor limiting the efficiency of OSCs is the charge transfer efficiency.

How the CT states mediate the exciton dissociation and charge generation in polymer: fullerene systems remains an open question. Several mechanisms have been proposed to explain how these CT states work in OSCs. The first model, Onsager-Braun model considers that when a hot CT state is created after exciton quenching, it will soon relax to the lowest CT state (~ 100 fs scale). The relaxed CT exciton then either recombine geminately or dissociate into spatially separate free charges.³⁴ This model can successfully describe the current-voltage characteristics in various polymer-fullerene devices. However, it fails to explain the temperature and electric field- independent behaviour of charge generation as frequently reported.^{35,36} Furthermore, the theoretically calculated CT state lifetime using this model is around $\sim \mu\text{s}$,³⁷ which is several orders larger than the experimentally observed values ($\sim \text{ns}$).³⁸ A second model, the hot CT model, suggests that spatially separated charges can be directly generated from the hot CT excitons, while hot CT excitons can also undergo relaxation to the lowest CT state where germinate recombination may take place. This results in one loss pathway for OSCs.^{39,40} It is recently found that the hot CT states in many polymer-fullerene systems are so highly delocalized that it can very easily split into free charges. In other systems, such as in polymer:polymer systems, they are more localized and their charge separation efficiency is not as high as in the polymer:fullerene system.⁴¹ Another report studied the well-mixed PCPDTBT:PCBM system and also reached similar conclusions that the hot CT states are more delocalized than thermally-relaxed ones and can facilitate charge generation within the first 200 fs.⁴² Hence, the delocalization of the hot CT states is therefore key to exciton dissociation and internal quantum efficiency in OSCs.

(4) *Charge Recombination and Extraction.* Charges move to the respective electrode driven by electric field and extracted by the external circuit while

undergoing recombination with each other. The competition between carrier sweep-out and recombination is another important factor that limits the efficiency of OSCs. Recombinations such as Langevin type recombination and/or Shockley-Read-Hall (SRH) like trap-assisted recombination were frequently reported in OSCs. In the classic Langevin recombination, two opposite free charges are annihilated when they collide and the recombination is bimolecular. This is however not the case in many OSCs, with a much reduced recombination rate and a higher order (usually around 3) of recombination.⁴³⁻⁴⁵ It can be interpreted as due to the disordered nature and/or phase segregation in the polymer-fullerene films.⁴⁶ The energetic disorder in the density of states (DOS) in organic semiconductor blends leads to the thermally activated charge carriers hopping that can be described by multiple-trapping-and-release (MTR) approach. Under this scenario, carrier mobility will be highly dependent on carrier concentration, resulting in a recombination order higher than two.^{46,47} Besides, due to phase segregation in the blend, recombination can only happen at the interface, thereby limiting the amount of carriers located deep inside a domain to undergo the non-germinate recombination.⁴³

In addition to the Langevin process, recombination via traps was also proposed.⁴⁸⁻⁵⁰ When one free carrier is trapped and become immobilized, it will undergo recombination when another opposite free carrier meets it. The trap-assisted recombination process is highly plausible in organic blends due to their intrinsically disordered nature. Recombination via traps is usually regarded as Shockley-Read-Hall (SRH) process which has a monomolecular decay order.⁵⁰ Identifying the recombination type in OSCs is a highly controversial task that either Langevin or trap-assisted recombination process was supported.^{48,51,52} It is highly plausible that both processes co-exist. Depending on the light intensity, the nature of the organic

film and the bias voltage, the Langevin process may compete with the trap-assisted process and complicate the recombination process in OSCs.^{53,54}

1.3 The use of plasmonics for improving the PCE of OPV

To improve the efficiency of OSCs to $\geq 10\%$, one has to reduce the recombinations in OSCs. One approach is to synthesize new electron donor and acceptors that are better optimized and can reach higher efficiencies. Another approach is to use additives, or employ light trapping strategies. Light trapping in OSCs is a promising strategy to improve the performance of OSCs. Generally, due to the low charge carrier mobilities in OSCs, the active film of OSCs cannot be too thick otherwise charge collection efficiency will be very poor; on the other hand, the active layer cannot be too thin otherwise much of sunlight will be not absorbed and used to create charges. Light trapping allow one to trap more light in the active layer so that the active layer can absorb light as much as possible while keeping the thickness thin enough for charge extraction. Use of optical strategies like photonic structures,⁵⁵⁻⁵⁸ microlenses array,⁵⁹ diffraction gratings,⁶⁰ and metallic nanostructures⁶¹⁻⁶³ were theoretically or experimentally demonstrated to increase the light absorption in a PV cell, among them metallic nanostructures utilizing plasmonic effects is the most widely studied approach.

Surface plasmon resonance (SPR) is the collective oscillations of free electrons founded in noble metals (Au, Ag, Cu, *etc*) when excited by an electromagnetic (EM) wave. Resonance happens when the frequency of the EM wave matches that of the natural oscillation of surface electrons. It propagates at the interface of metal and dielectric/semiconductor materials when interacting with EM wave and possesses the

behavior of both plasmon and EM wave, which is termed as surface plasmon polaritons (SPPs). In nanometer-sized metallic particles, the oscillation however is strongly localized, and is therefore often referred to localized surface plasmon resonance (LSPR) (see **Figure 1.3**). Due to the confinement of the EM wave, SPR can generate very high local EM field; besides, the strong oscillation near resonance also leads to strong scattering of the EM wave.

Figure 1.3 *Schematic of localized surface plasmon resonance*

Atwater and Polman outlined three approaches that plasmonic nanostructures can be employed to enhance the absorption of solar cells⁶³: (1) Plasmonic nanostructures can be used as subwavelength scattering center to couple and trap light into absorbing layer. The enhancement of absorption usually comes from high-angle and/or multiple scattering. (2) The strong near field around the resonance can also be used to improve the absorption of an active layer when it is located near the plasmonic nanostructures which serve as subwavelength antennae. (3) Light can be coupled at the interface of metal/active layer interface as SPPs or photonic modes. SPPs travel parallel to the active layer and has a long optical length which can be fully utilized for light absorption (see **Figure 1.4**).

Figure 1.4 Plasmonic light-trapping geometries for thin-film solar cells. (a) metal nanoparticles as subwavelength scattering center; (b) metal nanoparticles as subwavelength antenna; and (c) corrugated metal back surface as light coupler into SPP or photonic modes.⁶³

Experimentally, plasmonic nanostructures can be embedded either external to or within the active layer. When they are located outside the active layer, for example, deposited on ITO,⁶⁴⁻⁶⁶ over-coated with PEDOT:PSS hole transporting layer,⁶⁷⁻⁶⁹ or lying between active layer and Al electrode.⁶⁹ They can also serve as electrodes. In this case, plasmonic nanostructures are either used to replace ITO anode,⁷⁰⁻⁷² or the metal electrodes are patterned into gratings to bring in improved performance for OSCs.⁷³⁻⁷⁵ By placing the plasmonic nanostructures outside of the active layer, one may not fully capitalize on the advantages of the plasmonic effects since these effects decay exponentially with distance. To exploit the strong confined EM field and capture more scattering, nanostructures have also been embedded inside the active layers.⁷⁵⁻⁸¹

Although there is no doubt that plasmonics can provide a promising solution to improving the performance of OSCs, it is still unclear which factors leads to performance improvement. Apart from plasmonic effects (i.e., strong local field, strong scattering), it is well known that these metallic nanostructures may reduce device resistance by facilitating charge transport or by doping;^{78,82} they may also

simultaneously increase the exciton dissociation efficiency.^{67,68} Fung *et al.* argued that metallic nanoparticles embedded in PEDOT:PSS layer have minor contribution to the absorption of active layer, they only help to increase hole collection efficiency by enlarging the interfacial area between PEDOT:PSS and the active layer. Kim *et al.* considered AgNPs inside the PEDOT: PSS layer can redistribute and concentrate the photon field near the active layer and it is the hole transporting layer that will benefit the hole transport and collection. Since the holes usually have lower mobilities than the electrons in OSCs, it will eventually lead to higher photocurrent and fill factor.⁸³ Paci *et al.* proved that small AgNPs can improve the structural stability and reduce the photo-degradation rate of the P3HT:PCBM based OPV, providing possible new way of the utilization of metallic particles.⁸⁰ Besides, numerous problems have arose when incorporating metallic nanostructures into OSCs, such as morphology change,⁸⁴ excitation quenching,⁸⁴⁻⁸⁶ increased charge recombination,⁸⁴ *etc.* These effects may contribute to the loss mechanisms and degrade the performance of OSCs. In sum, the effects of metallic nanoparticles on the OSCs are still not fully understood. Further investigation is urgently needed to clarify these issues.

1.4 Motivation and Objectives

At the start of my graduate study in 2010, the plasmonic approach in OPV is fledging. To trap light in the ultra-thin organic active layer using metallic nanostructure was thought to highly promising solution for increasing the PCE of the under-performed OPV devices to beyond the 10% barrier. However, there are also many open questions highlighted earlier such as the origin of enhancement or detracting in OPV performance.

Fabrication of new metallic nanostructures, incorporating them into different OPV devices and testing the performance of the systems are the primary experimental works that need to be implemented to fulfil the above mentioned goals. Besides the frequently used metallic nanoparticles, other nanostructures such as prisms, cuboids, rods may be more useful in boosting the OPV performance. Incorporation of metallic nanostructures into OPV devices introduces new challenges to the fabrication process. This includes issues such as morphology change, shunting problems, etc.

Besides, experimentally incorporating metallic nanostructures into OPV devices and recursively optimizing the performance, proper design of light trapping strategies using plasmonic structures should also be embarked. From optical simulations, the parameters of the metallic nanostructures including their material, shape, size, position, and period can be optimized to improve the light absorption in OPV devices. A combination of optical and electrical simulations would give a theoretical upper limit to the performance of the plasmonic OPV devices.

Albeit its advantages, the published device performances of the plasmonic OPV are often confusing because of the various above mentioned challenges.⁸⁷ Few research works delve deep into the gain or loss mechanisms in plasmonic OPVs. It is of great importance to unveil the physical mechanisms of plasmonic OPV devices exploring both their improvements and losses. Ultrafast spectroscopy provides a window to these charge carrier dynamics and charge transfer mechanisms in OPV system. Using a combination of ultrafast spectroscopy and electric characterization, a clear picture of the underlying physics can be uncovered and many of the open questions can be resolved.

All these challenges give me the motivation to embark on this field. Besides these motivations, my study will focus on several topics: (1) Fabrication of plasmonic nanostructures and embedding them into the hole transporting layer and examining electric and optic properties. (2) Incorporating plasmonic nanostructures into the active layer and investigate electric, optic properties (3) Design a novel light trapping strategy using aluminum nanostructures, optimizing the light absorption in the organic active layer and modeling the device performance via a combination of optical and electrical models.

1.5 Thesis Outline

The thesis consists of seven chapters. Chapter 1 is an introduction chapter that provides an overview of the research. It includes the background, operating mechanisms of OPV devices and a literature review on using plasmonics to improve the performance of OPV. In chapter 2, the experimental and simulation techniques frequently used in the thesis are explained. In chapter 3, the approach by embedding plasmonic nanostructures in the hole transporting PEDOT:PSS layer is investigated and the findings are discussed. Several different plasmonic nanostructures are incorporated into PEDOT:PSS layer and device performance are improved. Detailed enhancement mechanisms and interaction between surface plasmon and excitation species in OPV are investigated and the findings are discussed. In chapter 4, oleylamine-capped silver nanoparticles are blended into P3HT:PCBM active layer and the device performance drops; transient optical spectroscopies are utilized to investigate the loss mechanisms of the plasmonic OPV films and devices. In Chapter 5, a novel light trapping strategy, namely, plasmonic cavity resonance is proposed and aluminium nanodisks are used to form the cavity for strong light trapping. The

mechanism of this light trapping strategy is discussed in detail. A combination of optical and electrical simulation gives a much better performance for the plasmonic OPV based on the new concept. The last chapter gives the conclusion of the studies and ongoing or proposed future work.

CHAPTER 2. Experimental and Simulation Techniques

2.1 Introduction

In this chapter, I will give a brief description of the experimental techniques and the simulation packages used in this thesis. The principles and setup of spectroscopies used will be firstly introduced, including steady-state and transient absorption spectroscopies, photoluminescence and time-resolved photoluminescence spectroscopies, and spatially-resolved spectroscopy. Following that, electrical characterization techniques will be explained. Current-voltage and incident-photon-to-current efficiency measurements are the basic ones for solar cell efficiency characterizations and will be described. Lastly, electromagnetic simulation package used in this thesis will be shown.

2.2 Steady-state and Transient Absorption Spectroscopies

Steady-state absorption occurs when there are interaction between light and the sample, for example, light-induced electronic, vibrational and torsional transitions. Absorption coefficient is usually evaluated by the Lambert-Beer law. It states that the absorbance of a solution is directly proportional to the concentration of absorbing molecules and the path length:

$$T = \frac{I}{I_0} = 10^{-aL} = 10^{-\varepsilon cL} \quad (\text{Eq. 2.1})$$

while in Physics, it is expressed as:

$$T = \frac{I}{I_0} = e^{-\alpha' L} = 10^{-\sigma L N} \quad (\text{Eq. 2.2})$$

where I_0 and I correspond to the incident and transmitted light intensities, respectively. ε is a molar absorptivity, c is the molar concentration of absorbing species. σ is cross section of light absorption by a single particle and N is the density of absorbing molecules. α (α') is the absorption coefficient. Steady-state absorption spectroscopy is the technique measuring samples' ground-state absorption of light as a function of frequency. The setup we used in this thesis for measuring steady-state absorption is the Shimadzu UV-3600 UV-Vis-NIR spectrophotometer that can perform high-sensitivity measurements of light absorption ranging from 185 to 3300 nm wavelength. Three detectors are equipped in such a system: a PMT detector (photomultiplier tube) for the ultraviolet and visible regions, and InGaAs and PbS detectors for near infrared region. With <0.00003 Abs noise at 1500 nm, it is claimed to have the world's lowest noise level.

Transient absorption spectroscopy (TAS) is a fundamental and versatile technique to probe and characterize excitation dynamic in many photo-sensitive chemical, physical and biological systems. In this technique, two ultrashort pulses are required (See **Figure 2.1**), namely pump and probe pulses. The pump beam is used to promote a fraction of molecules to electronic excited states. The probe beam that passes through the sample with a delay Δt with respect to the pump is used to probe the perturbation effect by the pump beam on the sample. The probe beam should be much weaker than the pump beam so as to avoid multi-photon/multistep excitations during probing. By means of measuring the difference of the light transmission (ΔT) in transmission geometry or the reflection (ΔR) in reflection geometry with and without pumping, one can determine the difference in light absorption (ΔA) between the excited sample and that in equilibrium. Through varying the delay time Δt and

recording the ΔT or ΔR at each delay time, the temporal profile of the dynamics can be gained. By choosing different wavelengths λ , the spectral profile of the dynamics can also be acquired. In general, there are several sources that contribute to the transient absorption signals.

Figure 2.1 Schematic of pump-probe operation

Ground State Bleaching (GSB). When the system is excited with a high fluence pump pulse, a fraction of molecules (0.1% to 10%) will be promoted from the ground state to excited states.⁸⁸ As a result, there will be less molecules in the ground state compared to that without pumping. The excited molecules will gradually decay to the ground state and the system will recover back to thermal equilibrium eventually (**Figure 2.2 Process 1**). After excitation and before the recovery of thermal equilibrium, at delay time Δt , the probe beam passes through the sample and will be partly absorbed. For the probe beam at certain frequencies, it will be less absorbed due to the fact that less molecules reside in the ground state and the transmission (T) will be increased ($\Delta A < 0$, $\Delta T > 0$).

Photo-induced Absorption (PIA). Upon excitation with the pump, optical transitions from excited state (populated after pumping) to even higher excited state may exist in certain frequency regions. The probe beam will be absorbed when its

frequency satisfies the optical transitions, resulting in decreased transmission ($\Delta A > 0$, $\Delta T < 0$) (**Figure 2.2 Process 2**).

Stimulated Emission (SE). Upon population of the excited state, the emission of excited state molecules to ground state will occur following optically-allowed transitions. When the probe beam passes through the sample, it causes the stimulated emission of the excitations at the same direction of the probe beam. The emission frequencies generally are coincident with that of the fluorescence of the excited states, i.e., they have a Stokes shift with respect to the ground state bleaching.⁸⁹ Stimulated emission will bring in additional light detected by the detector, i.e., $\Delta T > 0$, $\Delta A < 0$ (**Figure 2.2 Process 3**).

Absorption by New Species. In photobiological or photochemical systems, reaction may occur after photoexcitation. The product will have its new absorption that yields a $\Delta A > 0$ and $\Delta T < 0$ at corresponding frequencies. For example, in organic solar cell, the photoexcitation will yield charge (polaron) states after exciton undergoes charge transfer. Charges will have their corresponding absorption which does not happen at equilibrium condition. (**Figure 2.2 Process 4**)

Figure 2.2 Schematic of possible processes contributing to TAS signal. Process 1-4 represents physic process of GSB, PIA, SE and absorption from new species, respectively.

In the fs-TAS setup of our lab (**Figure 2.3**), the pump pulses are generated from an optical parametric amplifier (OPA) (Light Conversion TOPASTM) that is pumped by a 1 kHz regenerative amplifier (Coherent LegendTM; center wavelength: 800 nm; pulse width: 150 fs; power: 1 mJ per pulse). A Q-switched pump laser (Coherent EvolutionTM) is used to pump the regenerative amplifier. OPA can produce a tunable pumping wavelength range from 230-3100 nm. The probe beam is generated from a sapphire crystal using the 800 nm fs pulses. A spectrum region from 450 nm to around 1200 nm can be acquired using adequate thick sapphire crystal.

Figure 2.3 *Schematic of the femtosecond laser system.*

The probe delay in fs-TAS is tuned by a mechanical delay line. Schematic of fs-TAS setup is shown **Figure 2.4**. A motor-controlled reflection is set up on the delay line that can move with high resolution steps to change the probe beam optical

path so that the time with respect to the pump is altered. $\Delta t = \frac{\Delta L}{c}$, where ΔL is the difference of optic path between the probe and pump beam, c is the light speed in the air. Pump induced probe transmittance change ($\Delta T/T$) is monitored using either a monochromator/PMT configuration (for visible probe range) or a IR-monochromator/CCD configuration (for NIR probe range).

Figure 2.4 Schematic of the white-light pump-probe setup in our lab.

The fs-TAS in our lab has a high temporal resolution of around 150 fs, however it is limited to the time window it can measure, for example, for a 1 m delay line, a maximum time window of around 6 ns can only be measured, which is not sufficient to probe long-lived photoexcitation species. To probe the dynamics in a longer time region, electronically delayed TAS must be used.

Nanosecond transient absorption spectroscopy (ns-TAS) setup presented here (Applied Photophysics LKS.60 Nanosecond Laser Flash Photolysis Spectrometer) can measure the temporal evolution of excitation dynamics from nanoseconds to milliseconds. The pump pulse is generated from a seed Nd:YAG, Q-switched laser (532 nm, 7 ns pulse width). The probe light is a strong flash of the pulsed xenon lamp (150 W) that is sufficiently stable over the measured time region. Once the sample is

photoexcited by the pump pulse (ns laser) triggered at a preset time, transient species of the transmission of the probe light is created. Following which, the time dependent transmission change is recorded that enable us to monitor the change of the optical density (ΔOD) and therefore the dynamics of photo-excited species. The data is collected in transmission geometry with the sample positioned at 45° with respect to both the excitation source and the probe light.

2.3 Time-integrated Photoluminescence and Time-resolved

Photoluminescence

Photoluminescence (PL) is the light emission from any system after light absorption. Photoluminescence can be divided into fluorescence and phosphorescence depending on the nature of the excited state.⁹⁰ As seen from the Jablonski diagram in **Figure 2.5**, light absorption populates a singlet excited state (S_1 or S_2) that fast relax to the lowest vibrational level of S_1 . The optical transition between S_1 and ground state S_0 is allowed and the fast radiative recombination is called fluorescence. A typical fluorescence lifetime is several hundred ps to around 10 ns. Excitation can also undergo an intersystem crossing to a triplet state (T_1) where the transition to the ground state is forbidden. The emission is termed as phosphorescence and the rate is very slow. A typical lifetime of milliseconds to seconds can be found for phosphorescence.

Figure 2.5 Jablonski diagram of the physic process of photoluminescence.⁹⁰

Time-integrated photoluminescence (TIPL) simply measures an integrated PL over time duration much longer than the emission lifetime. For example, for a nanoseconds lifetime emission species, the integration time is usually milliseconds to seconds, which is much longer than that of the emission time and can provide accurate average of PL for this emission species. To trace the temporal evolution of PL over its lifetime, Time-resolved photoluminescence (TRPL) is performed. TRPL can be realized using different methods, such as : time-correlated single photon counting (TCSPC), phase-modulation, and streak camera detection, *etc.*⁹¹

Figure 2.6 (a) Schematic of TRPL setup. (b) A typical image of the TRPL of a P3HT film.

The setup in our lab employs a streak camera system which has very high time resolution and light sensitivity to detect ultra-fast phenomena down to single photon processes (**Figure 2.6(a)**). **Figure 2.6(b)** provides a typical image of a P3HT film TPRL. It has an ultimate system temporal resolution of 6 ps and can measure light events from picoseconds to milliseconds. A schematic picture of the operation principle of the streak camera is shown in **Figure 2.7**. Light being measured is projected onto the slit and forms an image on the photocathode by the optics. The photocathode converts photons to electrons proportional to the incident photon intensity. The stream of electrons then passes through the sweep electrode. A time-

varying voltage is applied to the sweep electrode so that the electrons can reach different position on the phosphor screen depending on their time arriving at the sweep electrode. Through these steps, the temporal profile of the light pulse can be turned into a spatial distribution. A monochromator is also placed before the streak camera to permit wavelength-resolved detection in TRPL. Eventually we can acquire a 2D image of the emission with one dimension representing the wavelength and the other representing the time.

Figure 2.7 Principle of streak camera operation.⁹²

2.4 Spatially Resolved Spectroscopy

The combination of ultrafast spectroscopy with spatially resolved measurement provides us with versatile approach to characterize excitation dynamics in micro-size region. The optical properties of structures such as nanowires can be studied individually, therefore phenomena obscured in ensemble measurements of the nanostructures may be revealed.

Spatially resolved or microscopic femtosecond transient absorption spectroscopy (μ -TAS) was performed in a non-degenerate pump-probe configuration

(**Figure 2.8**). The collinear pump and probe beams were focused onto the sample using a microscope objective. Then the probe signal was coupled out by another objective. Pump-induced probe transmittance change (relative DT, $\Delta T/T$) was monitored using either a monochromator/PMT configuration (for visible probe) or a IR-monochromator/ InGaAs photodetector configuration (for NIR probe). Microscopic time-resolved photoluminescence (μ -TRPL) measurements were performed using excitation pulses from a Mira 900 fs laser system with output wavelength 800 nm and repetition rate of 80 MHz. Typically, the samples were photoexcited with a pump fluence of $1.5 \mu\text{J cm}^{-2}$ at 400 nm which is generated using a BBO crystal, and the TRPL signals were collected in a conventional backscattering geometry through microscope objective. The luminescence signal was dispersed by a DK240 1/4-m monochromator with 300 g mm^{-1} grating, and the temporal evolution of the PL was resolved by an Optronis Optoscope streak camera system, which has an ultimate temporal resolution of ~ 6 ps when operated with the fast synchroscan unit. Microscopic steady-state absorption and scattering spectra were collected using a home-made confocal microscope system (the setup seen in **Figure 2.9**) with spatial resolution of around 200 nm. For samples with strong scattering, e.g., plasmonic nanostructure, a resolution of several tens of nm can be acquired.

Figure 2.8 Schematic of micro-transient absorption spectroscopy setup.

Figure 2.9 Schematic of home-made microscopic absorption, scattering, PL and TRPL setup.

2.5 *I-V* measurement

Investigating the current-voltage (*I-V*) characteristics of a solar cell in the dark and under illumination permits evaluation of most photovoltaic performances and the electric behaviour of a solar cell. A typical *I-V* characteristic of a solar cell under illumination is shown in Fig. 2.10. The short circuit current density (J_{SC}) indicates the current density collected under short circuit condition (Bias $V=0$), while open-circuit voltage (V_{OC}) is the bias voltage needed to keep there is no current flow ($J=0$) in the cell. Ideally, a cell can yield an output of power $P = V_{OC} \times J_{SC}$. In real cells, however, due to thermostatic limit and recombination, the maximum power output is less than P , and the fill factor (FF) is used to determine such losses:

$$FF = \frac{P_{MPP}}{V_{OC} \times J_{SC}} = \frac{V_{MPP} \times J_{MPP}}{V_{OC} \times J_{SC}}, \quad (\text{Eq. 2.3})$$

where MPP is the maximum power point.

Figure 2.10 A typical *I-V* curve of a solar cell.

I-V measurements performed in Energy Research Institute at Nanyang Technological University (ERI@N) were recorded with a HP 4155 semiconductor analyzer. The cells were illuminated by an Air Mass 1.5 Global (AM 1.5 G) solar simulator (San-ei XES-300, AAA rating) with an irradiation intensity of 100 mW/cm². The light intensity of the solar simulator was calibrated using a solarimeter with a reference silicon solar cell certified by National Renewable Energy Lab (NREL).

2.6 IPCE measurement

Internal photon to current efficiency (IPCE) measurement displays wavelength-dependent photovoltaic conversion efficiency:

$$\text{IPCE} = \frac{J_{\text{sc}}}{G \times \lambda} \times \frac{hc}{e}, \quad (\text{Eq. 2.4})$$

Where G is the illumination power, λ is the wavelength, h is Boltzmann constant, c and e is light speed and elementary charge, respectively. The external quantum efficiency (EQE) is defined as the ratio of the maximum electric power extracted to the illumination G multiply by the surface S of the module:

$$\text{EQE} = \frac{P_{\text{max}}}{G \times S} \quad (\text{Eq. 2.5})$$

The IPCE spectra were recorded using a Merlin radiometry system, where the light source is provided by a 150 W Newport-Oriel Xenon lamp, spectrally resolved using a Cornerstone 260 ¼ m monochromator and chopped at 60 Hz by an optical chopper. The light power-density was calibrated with a Hamamatsu silicon photodiode. All the device tests were performed in an inert nitrogen atmosphere.

2.7 Simulations

In organic solar cells, the manipulation of light is of great importance to optimize

light absorption in the thin film active layer. The analysis is strongly dependent on the electromagnetic modelling which typically involves the approximate computation of Maxwell's equations with certain boundary conditions. Techniques including discrete dipole approximation (DDA), Method of moments (MoM), boundary element method (BEM) or finite discrete time domain (FDTD), etc. are frequently used for EM modelling.

FDTD method directly solves a discrete difference form of Maxwell's equations for closely spaced points on an orthogonal mesh. Discretization in both space and time are made, and the EM fields are described on a discrete mesh made up of so-called Yee cells. The electric field is solved at a certain time, and then the magnetic field is solved at the next instant in time, in such way the solving process is repeated cyclically.

Figure 2.11 A typical layout of Lumerical FDTD simulation

A commercially available FDTD solver (Lumerical) was applied to perform EM wave calculations. Both 2D and 3D simulations can be performed. The simulation is carried out in a certain region with adequate boundary conditions. Electric and magnetic fields are detected using frequency profile monitors. **Figure 2.11** is a typical display of a 3D EM simulation of a nanoparticle on a substrate. The pink arrow indicates the light propagation direction and the blue arrow shows the light

polarization.

2.8 Conclusion

In this chapter we gave a brief introduction of the experimental techniques and simulation packages used in the thesis. The main experimental techniques used to investigate plasmonic organic photovoltaic systems were discussed, which includes steady-state and transient absorption spectroscopies, time-integrated and time-resolved spectroscopies, *I-V* and IPCE measurements. In addition to that, the FDTD simulation package which is frequently used for electromagnetic modelling is also introduced.

CHAPTER 3. Plasmonic Nanoparticles in the Hole transporting layer

3.1 Introduction

The incorporation of metallic nanostructures into OPV is often a challenging issue. A simple and widely used approach is to place them into the PEDOT:PSS hole transporting layer. Numerous reports have demonstrated successful embedding of plasmonic nanostructures in the PEDOT:PSS layer to level up the performance of the BHJ OSCs.^{65-69,71,76-78,80,93} Metallic nanostructures with hydrophilic ligands can be simply mixed in water-based PEDOT:PSS solution and spincoated on ITO.⁸⁶ For those with hydrophobic ligands or bare metal, they can be first deposited on the ITO and then covered with the PEDOT:PSS thin layer.^{65,94} The PEDOT:PSS serves not only for hole extraction, but also for the smoothing the ITO/metallic nanostructure rough surface, and as a spacer layer that prohibit direct contact between the metallic nanostructure and organic active layer. Using plasmonics to improve the performance of OPV is flourishing; yet the understanding of how surface plasmon interacts with photoexcitation species and affects the performance is still unclear. It might rely on much more complicated mechanisms rather than the plasmonic effects (strong near-field coupling and far-field scattering). For example, the bulk resistance may be reduced as the metal nanoparticles have good conductivity;⁸² the interfacial area has been enlarged by metal nanostructures in PEDOT:PSS layer to facilitate hole

collection,⁹³ *etc.* A deep investigation based on techniques such as ultrafast spectroscopy and electromagnetic modeling can reveal the photo-physical process and light manipulation by the metallic particles. Such knowledge will be a great boost for this field.

In this chapter, we present several studies of embedding plasmonic nanostructures into the PEDOT: PSS layer and study the interaction between surface plasmons and the excitons, polarons in the organic active layer. The first part is about large area, hexagonal arrays of silver nano-triangles (Ag-NTs) on ITO substrates that were fabricated and integrated into functional plasmonic OPV devices with PCDTBT:PCBM as the photoactive layer. Optical and photophysical properties of PCDTBT and PCDTBT: PCBM blend near the Ag-NTs with steady-state and transient optical spectroscopies were monitored. It is confirmed that the enhancement of absorption is ascribed to the plasmonic effects of the Ag-NTs. Additionally; improved performance of devices with the integration of the Ag-NT arrays was successfully demonstrated. Efficiency improvement from ~4.2% to up to 4.5% was demonstrated. The increase in PCE can be mainly attributed to the increase in short circuit current density by 12%. Due to the strong local E-field and scattering from LSPR of the hexagonal NT arrays, higher exciton generation rate can be expected in the photo-active layer, resulting in the increased J_{sc} . Through these experiments, the feasibility of integrating the simple, cheap, large-scale nanofabrication technique with existing OSC fabrication processes was demonstrated.

In the second part, we investigate a two dimensional wet-chemistry based plasmonic nanostructure: gold nanowire network that was deposited on ITO and then incorporated into P3HT: PCBM based OPV devices. The short circuit current density of the AuNWs device is enhanced by 14.6% and 23.2% with active layer thicknesses

of 80nm and 60nm. The nature of the enhancement in AuNWs incorporated P3HT system were studied by UV-VIS absorption, steady-state and time-resolved photoluminescence spectroscopies. These results demonstrate that the inclusion of ultrafine AuNWs in the immediate vicinity of P3HT layer increases photoluminescence (PL) intensity that is facilitated by a faster radiative recombination rate of the excited P3HT molecules. The spacer layer plays a crucial role in determining the relaxation dynamics of the emitting molecules. In this spacer-based AuNWs/P3HT system, the PL enhancement is originated from plasmon excitation field enhancement.

To get a clearer and more direct picture of such improvements in performance, the enhancement in a single silver nanowire (AgNW) effect on P3HT: PCBM device was scrutinized using spatially-resolved spectroscopy. Microscopic photoluminescence (μ -PL) spectroscopy found that the PL intensity is dependent on the polarization of the incident light, which is consistent with the polarization dependence of the organic solar cell performance with a single AgNW. Device EQE results indicate the performance improvement is wavelength dependent and reaches maximum near the tranverse mode of LSPR of the AgNW. The performance improvement is therefore concluded to mainly originate from the increased exciton density by the transverse modes of the surface plasmon in the AgNW. Besides, an improved FF is found for plasmonic devices. Through FDTD simulation, we speculate it may originate from a better distribution of exciton/polaron generation in device with AgNWs due to the light redistribution by the surface plasmon resonance.

In summary, through comprehensive spectroscopy study, we find that the interaction of plasmonic nanostructure in PEDOT:PSS and organic active layer is complicated. Direct contact of gold or silver nanostructure with organic polymers will

speed up their emissive exciton decay and also increase their photoluminescence intensity. This process often involves the Purcell effect and results in an increased scattering/local field effects. Non-radiative channels should also be present (Föster energy transfer and/or Dexter charge transfer); however they are difficult to separate from the increase of the radiative decay rate. The coverage of the nanostructures with the PEDOT:PSS spacer layer may quench the Purcell effect depending on the thickness of spacer layer and its coverage. The interaction of surface plasmon and exciton in polymer:PCBM however is negligible since the polymer exciton is very quickly quenched by PCBM through charge transfer. Besides, we did not find any evidence showing obvious interaction between surface plasmon of metallic nanostructure in PEDOT:PSS layer and polarons in polymer:PCBM. It indicates that surface plasmon and polaron do not interact with each other over a long range (>several nm). Through local field enhancement and scattering, light absorption can be enhanced in the active layer, while the photoexcitation dynamics are often less affected by metallic nanostructures incorporated in the PEDOT:PSS layer. Hence, embedding plasmonic nanostructure into PEDOT:PSS layer is a feasible approach to improve the performance of OPV.

3.2 Silver nano-triangle arrays in PEDOT:PSS

Previous calculation based on discrete dipole approximation (DDA) found out that under the same volume, the peak EM intensity at the local field for a sphere is of the order of 10^2 , for cubes is $\sim 10^3$, while for tetrahedron is 10^4 .⁹⁵ Nanostructures with sharp points (cubes, prisms, pyramids) can usually generate stronger local EM fields. On the other hand, using plasmonic nanostructures with sharp points are far and few.

Kulkarni, A. P. *et al.* demonstrated through photo-induced absorption (PIA) spectroscopy that silver nano-prisms can give rise to up to 3 times increase of polaron generation in 30nm thick P3HT:PCBM films.⁶¹ However, there is still a lack of demonstration on device performance improvement using metallic nano-prisms (triangles). It is possible that the ligand used for capping the nanostructure is unfavorable for charge collection in OSCs. Besides, in terms of computer simulation, periodic nanostructures are the best choice for modeling and device optimization. The boundary of simulation scenario can be set to periodic boundary condition in which only one unit cell of nanostructures is need for modeling. However, to the best of our knowledge, there were few experimental reports on enhancing OSC performance using periodic metallic nanostructures, partially due to the high cost of most lithography techniques needed to fabricate large scale of nano-sized periodic structures. For example, to fabricate a nanodisk array with periodicity 300nm would require $\sim 10^{18}$ nanodisks, which is impractical for masked techniques such as extreme UV lithography or electron beam lithography.

Nanosphere lithography (NSL) provides an alternative way to easily fabricate large-scale nano-triangle arrays. Importantly, the nano-triangles are ligand-free, which can eliminate the possibility of reducing charge collection efficiency due to some insulating ligands. To fabricated such large scale metallic NT arrays and incorporate them into OPV device is a challenging yet non-trivial task.

3.2.1 Nanosphere Lithography (NSL)

Through the extension of Deckman's 'natural lithography',⁹⁶ Van Duyne and other groups developed the nanosphere lithography to a mature technique fabricating large-scale 2D nanostructure arrays.⁹⁷⁻¹⁰² Basic steps of NSL are as follows:

(1) NSL mask preparation. The mask for lithography is usually formed by self-assembly of polystyrene (PS) or silica spheres on a highly hydrophobic substrate. PS spheres can readily self-assemble into a hexagonal array on the substrate after spin-coating,⁹⁷ or lifting off from the water surface,¹⁰³ As displayed schematically in **Figure 3.1 (a)**. Double or multilayer of self-assembled spheres could also be used as masks.^{104,105}

(2) Metal deposition and mask removal. After the formation of NSL masks, the metal is evaporated onto the mask. Metal deposited in the three-fold interstices will be left on the substrate when the mask is removed, forming an array of triangularly shaped nanoparticles as displayed in **Figure 3.1 (b)**. By geometric calculation, the bisector of the nano-triangles is:

$$a = \frac{3}{2}(\sqrt{3} - 1 - \frac{1}{\sqrt{3}})D \quad (\text{Eq. 3.1})$$

and the inter-particle spacing is:

$$d = \frac{1}{\sqrt{3}}D \quad (\text{Eq. 3.2})$$

where D is the diameter of the spheres for mask.¹⁰⁴

Figure 3.1 (a) Schematic of self-assembly evaporation mask. (b) AFM image of metallic triangles formed after removal of the masks.¹⁰⁶

3.2.2 Sample Preparation & Characterization

AgNT fabrication. Mono-dispersed polystyrene spheres (200 nm) in water suspension (10%, PolySciences Inc.), was diluted with an equal volume of ethanol.¹⁰⁷ A silicon substrate (3 cm × 3 cm) was cleaned by sonication sequentially in acetone, IPA, and deionized (DI)-water each for 5 mins followed by the immersion of the substrate in a 10% sodium dodecyl sulfate (SDS) solution for 24 hours. About 6 μL of the PS suspension was first dropped by pipette onto the silicon substrate, which was then slowly slid into a tilted tray containing DI-water. A monolayer of PS spheres was formed on the water surface and the silicon substrate was then slowly removed. A few drops of 2% SDS solution were added to the water to promote the monolayer formation. The monolayer of self-assembled PS spheres on the water surface was then lifted up with a clean piece of substrate (ITO, Si, glass, *etc.*) and dried in air. Next, a 20 nm thick Ag layer was deposited on the sample by thermal evaporation. Following which, the PS sphere template was removed by immersing the sample in THF for 30

mins, followed by sonication for 1 min; leaving behind hexagonal arrays of Ag-NTs on the substrate.

Device fabrication. Devices were fabricated using ITO substrates with Ag-NTs and without Ag-NTs following the configuration in **Figure 3.2 (a)**. And as shown in **Figure 3.2 (b)**, Ag has similar energy level with that of ITO, therefore the introduction of Ag-NT is expected not to adversely disrupt the energy level alignment in the OPV device. For ITO with Ag-NTs, only the effective cell region is covered with Ag-NTs, so as to make other parameters all the same compared to the control cells. Reference cells without Ag-NTs were also fabricated for a comparative study. For all the samples, the Ag-NTs were covered with a 30 nm thick PEDOT:PSS layer. The PEDOT:PSS coated substrate was subsequently annealed at 140 °C for 10 mins. The samples were then transferred into a nitrogen glove box to spincoat the photoactive BHJ layers. The BHJ solution of PCDTBT (1-Materials): PC₆₁BM (Nano-C) (1:4) prepared in chloroform with a concentration of 4 mg/ml was then spincoated over the PEDOT:PSS layer. The thickness of photoactive films is ~60 nm as measured by surface profiler (Alpha Step IQ). The devices were completed with the deposition of a 100 nm thick Al cathode by thermal evaporation. The effective cell area defined by the geometrical overlap between ITO and Al is ~0.071 cm².

Figure 3.2 (a) Schematic of the Ag-NT:PCDTBT:PCBM OSC configuration.(b) Electronic band levels of constituents of the OPV device.

Morphology Characterization. Thickness of films was measured using Alpha Step IQ surface profiler. The surface topography of the Ag-NTs array was imaged using an Asylum Research MFP-3D AFM operating in tapping mode. Morphology of PS mask was done with a SEM (JSM-6700F, 10.0 kV).

3.2.3 Results and Discussion

Morphology. **Figure 3.3** shows the SEM image of the PS mask before removal. Self-assembled PS spheres form a very ordered hexagonal array over a large area. As the AFM image shows in **Figure 3.4**, the AgNT arrays have a height of around 20-25 nm, which is an ideal value for later integration in an OPV device. Each side of the triangle is ~40 nm as estimated from scanning electron microscopy micrographs. The thickness of photoactive films is ~60 nm as measured by surface profiler.

Figure 3.3 SEM image of the PS mask before removal

The AgNTs however, are not perfectly triangular in shape. The corners are not very sharp; instead, they are very smooth and round. We ascribe this to the thermal evaporation used where the thermal diffusion of the Ag atoms gas may lead to the rounding of the corners. Another reason may be due to that the PS templates are not very tightly packed. Defects exist in the AgNT arrays, as shown in **Figure 3.4 (a)**, which is inevitable for this technique. These defects may also have a benign influence over the device function which we will discuss later.

Figure 3.4 (a) AFM image of the Ag-NTs arrays viewed in large scale. Defects can also be seen in region where AgNTs are conjoined to one another. (b) Detail shape of a representative Ag-NT hexagon. (c) Vertical profile of the Ag-NTs showing their heights.

Steady-state Absorption. As displayed in **Figure 3.5**, Ag-NT arrays on glass show a broad extinction peak centered at around 460 nm. This broad peak can be attributed to the LSPR of Ag-NTs. Although broadening of LSPR will weaken the oscillator strength and lessen the plasmonic effects at resonance; the extensive spectrum region from the plasmonic effects can enhance the total absorption of the active layer. The SPR peak of metallic nanostructures depends strongly on their dielectric environment based on the following relation: $\omega_{SP} = \omega_p / \sqrt{1 + 2\epsilon_m}$ where ω_{SP} is the plasma frequency and ϵ_m is the permittivity of the surrounding medium.¹⁰⁸⁻¹¹⁰ When covered by a 30 nm thick PEDOT:PSS layer, the LSPR peak shifts to around 500 nm; indicating now that the Ag-NTs are embedded in a higher dielectric environment than air (PEDOT:PSS refractive index $n \sim 1.3-1.5$). Besides, the LSPR becomes even broader, implying there is a damping force exerted on the LSPR. It may

originate from the energy/charge transfer between Ag-NT and PEDOT:PSS, since there is no insulating ligand covering the bare metallic nanostructure and mitigating these damping mechanisms.

Figure 3.5 Extinction spectra of AgNTs in air and covered with 30nm PEDOT:PSS layer.

Figure 3.6 exhibits the extinction enhancement of PCDTBT:PCBM active layer with AgNTs. The enhancement happens from 350 nm to 700 nm covering the major spectral region of the active layer that harvests light. As depicted in **Figure 3.6 (b)**, the relative extinction enhancement has a peak at around 468 nm, which is very near to the LSPR peak of AgNTs. Hence, we can confirm the larger extinction of the film with AgNTs comes from the LSPR of the silver nanostructures. **However, since AgNTs are expected to have strong absorption near LSPR, we cannot conclude here that the enhancement of extinction with AgNTs leads to an enhancement of PCDTBT:PCBM active layer. Further evidence is needed and will be given in next paragraphs.**

Figure 3.6 (a) Extinction spectra of PCDTBT:PCBM film and PCDTBT:PCBM with Ag-NTs. (b) Extinction enhancement of PCDTBT:PCBM film when incorporating Ag-NT array shows a peak at 468 nm.

Time-resolved Photoluminescence. Steady state PL spectra of PCDTBT films as shown in **Figure 3.7** exhibit broad and featureless emission over the spectral region of 620nm-760nm following pumping at 400 nm and 500 nm. The PL spectra are centered at around 680nm, corresponding well with other reports.¹¹¹ Both spectra exhibit a prominent PL enhancement with the Ag-NT array. An enhancement of 27% and 75% integrated over 620 nm to 750 nm was found for the 400 nm and 500 nm excitations, respectively.

Figure 3.7 PL comparison of PCDTBT and Ag-NT: PCDTBT films excited at (a) 500 nm and (b) 400 nm.

Three interactions between fluorophores and metallic surfaces may be possible:

- (1) Exciton quenching: exciton quenching can take place through nonradiative energy transfer between fluorescent molecules and metal such as Forster-like or Dexter-like energy transfer.¹¹²
- (2) Enhanced local field strength: the enhanced local field will lead to a higher exciton generation and therefore more intense PL.
- (3) An increase in radiative rate of fluorophore: Increased radiative rate will reduce the emissive exciton lifetime and increase the PL intensity.¹¹³

Figure 3.8 shows the PL dynamic for PCDTBT/PEDOT:PSS films with and without the Ag-NT arrays following 400 nm excitation ($1.5 \mu\text{J}/\text{cm}^2$). The decay shown in **Figure 3.8** can be fitted using a multi-exponential function⁸⁶:

$$I_{PL} = \sum_{i=1}^n A_i \exp\left(-\frac{t}{\tau_i}\right) \quad (3.3)$$

where A_i is the amplitude of the i^{th} decay, τ_i is the i^{th} exponential constant. For PCDTBT only sample, two lifetimes are obtained: $\tau_1 = 130 \pm 50$ ps and $\tau_2 = 620 \pm 50$ ps, with the former being attributed to the recombination of unrelaxed excitons and

the latter to the fully relaxed ones.²⁷ This results in an averaged lifetime of 300 ± 50 ps. With Ag-NT arrays, the corresponding lifetimes are: $\tau_1 = 110 \pm 50$ ps and $\tau_2 = 590 \pm 50$ ps, which leads to an averaged lifetime of 270 ± 50 ps. Consider that the experimental uncertainty of the streak camera is around ~ 50 ps, the lifetimes for both are comparable.

We suspect that when the Ag-NT arrays are covered with 5-10 nm PEDOT:PSS buffer layer to separate them from PCDTBT molecules, exciton quenching due to Dexter energy transfer is not expected to play a significant role. Forster energy transfer is also not significant considering that the absorption of AgNTs and emission of PCDTBT molecules do not overlap well with each other. Similar conclusions were acquired in other reports that P3HT polymer's excitons are also negligibly affected by the presence of Ag nanoprisms or Ag nanoparticles.¹¹⁴

Hence, the PL intensity increase can be mainly ascribed to originate from the enhanced exciton/photon density in the vicinity of Ag-NT array. The strong scattering and near-field coupling around the LSPR lead to higher exciton generation rate and therefore more intense emission.

Figure 3.8 PL comparison of PCDTBT and Ag-NT: PCDTBT films excited at (a) 500nm and (b) 400nm.

Nanosecond Transient Absorption. TAS spectra of PCDTBT:PC₆₁BM with/without Ag-NTs pumping at 500 nm ($35 \mu\text{J}/\text{cm}^2$) are shown in **Figure 3.9**. The measured spectra range is from 530 nm to 650 nm, where there is negative ΔOD signal (i.e., a decreased absorption and increased transmission of light). It originates from the ground state bleaching (GSB) of the PCDTBT:PCBM blend following photoexcitation with above bandgap excitation.^{115,116} GSB can be seen as the state-filling of excitonic and polaronic states resulting in a decrease of ground-state's absorbing light to excited states. Over this ns to μs timescale, this signal is attributed to the charge carriers (i.e. hole polarons) because in the blend, the singlet excitons are rapidly quenched by electron transfer from the PCDTBT to the PCBM and also the triplet exciton population is expected to be negligible.¹¹⁶ Hence, the recovery (or decay) of the ΔOD signal to the equilibrium can therefore be attributed to the recombination of the hole polaron population and the magnitude of the ΔOD signal is an indication of the population of photogenerated carriers in the sample.

Figure 3.9 TAS spectra in the GSB region of (a) PCDTBT:PCBM with Ag-NT arrays and (b) without Ag-NT arrays.

The GSB at different delay times all exhibit a higher magnitude for samples with Ag-NTs compared to the controlled samples without Ag-NTs. An estimated increase of 40% in magnitude is found, indicating that the polaron population in samples with Ag-NTs using 500 nm pumping light is increased by 40% compared to the control.

Meanwhile, the near invariance of the transient decay of the GSB (monitored at 580nm) for the AgNT sample and the control as depicted in **Figure 3.10** clearly demonstrates that the hole polaron recombination dynamics are not significantly altered by the presence of the Ag-NT arrays. We can thus conclude that when covered with a thin PEDOT:PSS buffer layer (5-10 nm), the effect of Ag-NTs on polarons is merely the increase of the population; they neither prolong their lifetime nor speed up their recombination rate.

Figure 3.10 Transient dynamic monitored at 580nm for PCDTBT:PCBM films with and without Ag-NTs.

Photovoltaic Performance. **Figure 3.11** shows the current-voltage (J - V) characteristics of devices with/without Ag-NTs. As depicted in

Table 3.1, device performance of the control cells is consistent with those in the literature¹¹⁶⁻¹¹⁸. With Ag-NTs, device performance can increase from 4.2% up to 4.5%. This can be attributed to an enhancement of the short circuit current (J_{sc}) from -8.55 to -9.57 mA/cm². Open-circuit voltage (V_{oc}) and the fill factor (FF) are comparable to the control, indicating it is possible to enhance the absorption of the active layer without degrading other important parameters.

Figure 3.11 *J-V curves for PCDTBT:PCBM OSC with and without Ag-NT arrays.*

Table 3.1 *A comparison of the PCE, J_{SC} , V_{OC} , FF of the OPV devices with/without Ag-NTs*

	PCE (%)	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF
With Ag-NTs	4.5	-9.57	0.89	0.53
Reference	4.2	-8.55	0.90	0.55

To monitor the spectral dependence of the Ag-NTs on the J_{SC} enhancement, the incident photon-to-electron conversion efficiency (IPCE) of the devices with and without Ag-NTs were measured (**Figure 3.12**). Enhancement of the external quantum efficiency (EQE) was calculated by $(EQE_{Ag-NTs} - EQE_{control}) / EQE_{control} \times 100\%$. A maximum enhancement of EQE (20%) is found to be at around 510 nm, near the LSPR of Ag-NTs embedded in PEDOT:PSS. Hence, we can conclude the increase of the J_{SC} comes from the LSPR induced absorption enhancement of the OPV device.

Figure 3.12 (a) EQE for PCDTBT:PCBM OSC with and without Ag-NT arrays. (b) Relative EQE enhancement of the OSC with Ag-NT arrays shows a maximum at around 510nm.

Reports using different plasmonic nanostructures embedded in PEDOT:PSS buffer layer gained a short-circuit current density improvement by 5-20% as summarized in

Table 3.2 from selected publications.^{68,69,86,93,119-121} It is found the J_{sc} enhancement using Ag-NT array is comparable to that of previous reports. In previous arguments of Ag-NT advantages, large absorption enhancement is claimed to be expected since Ag-NTs can generate very strong local fields compared to other nanostructures. Nonetheless, the J_{sc} enhancement is limited (~12%). To probe the possible mechanisms, Finite-different Time Domain (FDTD) simulation was used to model the plasmonic devices. The triangles used have round corners that the simulated LSPR resonance mimics the structure made experimentally. PCDTBT:PCBM dielectric constants are acquired from literature¹²², and the extinction coefficients are extracted from steady-state absorption data. The refractive indices of PEDOT:PSS, ITO are from references^{123,124} and Ag, Al are obtained from the software. The electromagnetic (EM) fields from two perpendicular directions are shown in **Figure 3.13** Near the LSPR (~520 nm) peak, the EM field can be hundred times of the incident field at the edge part. However, we notice that the EM field enhancement is mainly located in the plane of the Ag-NT and at the bottom nearer to the substrate. Hence, light is not efficiently coupled into the PCDTBT: PCBM active layer.¹²⁵ To fully exploit the advantage of triangle shaped plasmonic nanostructure, the best way is to embed it into the active layer so that the strong near-field can be well utilized. However, other problems may occur, like exciton quenching that occurs when the active layer is in direct contact with metals. Passivation of the bare metal with ligands is necessary.

Table 3.2 J_{sc} enhancement by plasmonic nanostructures embedded in PEDOT:PSS
selected from various publications.

Publication	Type of Plasmonic OPV devices	Reference PCE (%)	Reference J_{sc} (mA/cm ²)	Plasmonic PCE (%)	Plasmonic J_{sc} (%)	J_{sc} Enhancement (%)
Wu, <i>et al.</i> ⁸⁶	AuNPs(45 nm) in P3HT:PCBM	3.6	9.2	4.2	10.2	11.6
Lu, <i>et al.</i> ⁶⁸	AgNPs (40-50 nm)+AuNPs (40-50 nm) in PTB7:PCBM	8.0	15.0	8.7	17.7	18.0
Baek, <i>et</i>	AgNPs (10-100nm) in	6.4	11.2	7.6	12.7	13.0

<i>al.</i> ¹¹⁹	PCDTBT: PC70BM					
Baek, <i>et al.</i> ¹¹⁹	AgNPs (10- 100nm) in PTB7: PC70BM	7.9	14.9	8.6	16.3	9.4
Kim, <i>et al.</i> ⁹³	AgNPs (13 nm) in P3HT:PCBM	3.0	9.0	3.6	10.8	20.0
Fung, <i>et al.</i> ⁹³	AuNPs (10 nm- 100 nm) in P3HT:PCBM	3.1	8.5	3.5	8.9	5.2
Li, <i>et al.</i> ¹²¹	AgNPs (20NM)+Ag prisms (60 nm) in P3HT:PCBM	3.6	9.0	4.3	10.6	18.0
Wang, <i>et al.</i> ¹²⁰	octahedral AuNPs (70 nm) in P3HT:PC70BM	3.5	10.7	4.4	11.2	5.0
Kalfagiannis <i>et al.</i> ⁶⁹	AgNP (12-23nm) in P3HT: PCBM	2.4	7.9	2.8	9.3	18.2

Figure 3.13 *Simulated EM field distribution around Ag-NT with incident light (520nm) polarized at (a) TM and (b) TE directions. TM is the polarization along the cross section and TE is vertical to the cross section. Inset shows the top view of the Ag-NT and the field monitor. Intensity is in log scale.*

3.3 Gold nanowire network in PEDOT:PSS

Harnessing localized plasmon excitation allows the realization of optically thick but physically thin photovoltaic devices.¹²⁶ Through the experimental demonstration of using Ag NTs to improve OPV performance, we acquire basic knowledge on how surface plasmon affects the electric and optic behaviour of OPV devices. However, the factors governing the enhancement including the effects of the spacer layer as well as the thickness of the photovoltaic layer have not yet been thoroughly exploited.

In this part, a simple and novel ultrathin AuNWs fabrication technique based on solution-phase synthesis were developed which were then integrated in OPV devices comprising P3HT:PCBM photoactive layer for SP enhanced device performance. We will focus our discussion on the effects of the spacer on the relaxation dynamics of excited P3HT molecules near AuNWs. In addition, we will also examine the optimum thickness of the photoactive layer where the maximum surface plasmon enhancement was demonstrated.

3.3.1 Experiment methods

AuNWs synthesis. AuNWs synthesis is simple and has relatively high output. A simple one-step wet chemistry approach¹²⁷ was used to acquire AuNWs at room temperature. Basic steps of the synthesis are shown in **Figure 3.14**. 100 μL

Oleylamine (OA), 3 mg $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and 150 μL triisopropylsilane (TIPS) were added into 2.5 ml hexane to form a yellow solution. Here OA was used as the stabilizer for one-dimensional growth. TIPS was used as a reducing agent. The solution was kept shaking at room temperature for around 8 hours until the solution color became dark, indicating the formation of ultrathin AuNWs. After that, the solution was added into 7.5 mL ethanol, centrifuged at 2500 rpm for 10 min, and then the precipitate was redispersed in 2.5 mL hexane. A 2-D network of AuNWs were self assembled on substrates after immersing them in the diluted AuNW solution for 15min.

Devices & Film fabrication. The AuNW network coated ITO substrate was then used for device fabrication. The PEDOT:PSS layer was spincoated and measured to have a thickness of around 15 nm. Prior to the deposition of PEDOT:PSS, surface treatment with a diluted PEDOT:PSS in an iso-propanol solution (1:20) was employed in order to improve the wettability of aqueous PEDOT:PSS towards the hydrophobic AuNWs. P3HT:PCBM active layer was prepared by spincoating a blend solution of P3HT:PCBM (10:8) with a final concentration of 18 mg/cm^3 in 1,2 dichlorobenzene (DCB). The thickness of the P3HT:PCBM photoactive layers was measured to be 60 nm and 80 nm depending on different spincoating speed. The devices were completed by evaporation of cathode Al (100 nm) and then followed by a low temperature annealing at 60°C for 2.5 hours. For spectroscopic characterizations, quartz instead of ITO substrates was used for AuNW and organic layers deposition.

Figure 3.14 Schematic representation of AuNW synthesis

Morphology Characterization. Pico LE scanning probe microscope (SPM) system in tapping mode and a TEM JEOL JEM-2010 were used to acquire the AFM and TEM images of AuNW network respectively.

3.3.2 Results and Discussion

Morphology. **Figure 3.15 (a)** shows the AFM image of a self-assembled AuNW network on Si substrate where the average diameter of AuNWs is 7-9 nm as measured by its cross-sectional line profile. The high resolution TEM image described in **Figure 3.15 (b)** clearly indicates that ultrathin AuNWs are parallel and closely packed to form a two-dimensional network structure.

Figure 3.15 (a) AFM image of AuNW network on Si substrate (b) High resolution TEM image of AuNWs

Figure 3.16 displays the surface morphology of PEDOT:PSS on ITO with and without AuNWs. The RMS roughness increases slightly from 2.4 nm to 2.7 nm (RMS roughness of ITO used: 4.8 nm). **Figure 3.17** shows the surface morphology of P3HT:PCBM films (80 nm and 60 nm) with and without AuNWs. RMS roughness for 80 nm thick film increases from 0.59 nm to 0.61 nm and for 60 nm thick film from 0.61 nm to 0.62 nm with AuNWs. Clearly, it indicates the morphology of layers in device is not adversely affected.

Figure 3.16 Surface morphology of thin PEDOT:PSS layer on ITO (a) without and (b) with AuNWs.

Figure 3.17 Surface morphology of P3HT:PCBM film with thickness 80nm in (a) control device, (b) with AuNWs, with thickness 60nm in (c) control and (d) Au-NWs.

Linear Absorption. As displayed in **Figure 3.18 (a)**, the absorption peak of AuNWs on quartz substrate at 516 nm is assigned to their transverse LSPR. Depending on the aspect ratio of nanorods/nanowires, the longitudinal resonance typically occurs at higher wavelengths. However, here the NW length is much longer than the wavelength of light; therefore such localized modes of surface plasmon will not exist. Depositing AuNWs on ITO and coated with PEDOT:PSS layer redshifted the LSPR to around 625 nm as higher dielectric environment will decrease the SPR frequency.

In order to simulate the conditions within a solar cell created by reflection from the cathode, an Al blanket layer (100 nm) was deposited on the photoactive P3HT layer. **Figure 3.18 (b)** illustrates the absorption (%) in P3HT photoactive layer with and without AuNWs measured in reflection geometry. The interaction between

localized surface plasmons in metal nanostructures and incident photons creates a high density of photons at the near-field distance and a strong local electromagnetic field builds up.^{109,128,129} Absorption of P3HT molecules is effectively enhanced when the resonant frequency matches with it and this is essential for increased photogeneration of charge carriers. Furthermore, consider the geometry of the AuNW bundles is ideal for plasmonic subwavelength light scattering; we expected it would also help light absorption through lengthening the optical path in the active layer. The self-assembled AuNW network on substrates comprised of thin AuNWs (as shown in TEM) that bundled together forming a band of wires having a height of about 7-9 nm and a width of around 100-150 nm. Simulations were done with FDTD software comparing the optical behaviors of a single AuNW and the AuNWs bundle in device. For a single AuNW, the LSPR position seems to be little affected by the high dielectric environment. The scattering is negligible since the diameter is too small to efficiently scatter light. On the other hand, for AuNW bundle, LSPR strongly redshift to ~620 nm as observed in experiment. The subwavelength scattering now becomes obvious near the resonance and thus is expected to affect the light absorption in the active layer.

Figure 3.18 (a) Absorbance of AuNW network in different dielectric environment. (b) Relative absorption enhancement (%) upon integrating AuNWs in the proximity of P3HT:PCBM blend film on the PEDOT:PSS coated ITO substrate. The inset shows the absorption spectra of pristine P3HT on the PEDOT:PSS coated quartz substrate with and without AuNWs.

Figure 3.19 Simulated Absorption, scattering and extinction cross-sections of (a) a single Au-NW of diameter 9 nm and (b) a bundle of Au-NWs having a height 9 nm and width 130 nm.

PL and TRPL. The interaction of P3HT molecules and surface plasmon of AuNWs were characterized by PL and TRPL spectroscopies. Four types of samples were prepared: P3HT film (40 nm thick) on quartz substrate, on quartz substrate coated with 15 nm PEDOT:PSS, on quartz substrate deposited with AuNWs and on quartz deposited with AuNWs and then coated with PEDOT:PSS. **Figure 3.20 (a)** shows the PL intensity comparison between the four samples. Strongest PL intensity comes from P3HT with bare AuNWs; a 2.5 fold enhancement can be found compared to P3HT only sample. The PL intensity of sample with both PEDOT:PSS and AuNWs ranks in the second position, and that with PEDOT:PSS only shows the weakest PL intensity.

From examining the PL dynamics of the four samples, more information can be inferred. As displayed in **Figure 3.20 (b)**, pristine P3HT molecules show a typical lifetime of 550 ± 50 ps which reduces to 410 ± 50 ps when directly in contact with AuNWs. It indicates that a faster radiative decay rate may also play a role in enhancing the PL. The effect of PEDOT:PSS spacer layer was also investigated. With PEDOT:PSS spacer layer, the decay rate is faster (490 ± 50 ps) and the PL intensity is slightly quenched, which can be attributed to exciton quenching by charge transfer at P3HT/PEDOT:PSS interface. With both AuNWs and PEDOT:PSS, PL enhancement due to AuNWs is still present although a little weaker; the decay rate is almost invariant for AuNW/PEDOT:PSS/P3HT (490 ± 50 ps) and PEDOT:PSS/P3HT (500 ± 50 ps) samples, implying the PEDOT:PSS spacer layer were successfully used to eliminate the effect of AuNWs on P3HT exciton dynamics. Since P3HT exciton dynamics is not affected now by AuNWs due to the spacer layer, the residual PL enhancement can be safely ascribed to electromagnetic field manipulation by surface plasmon.

Figure 3.20 Steady-state photoluminescence (a) and time-resolved PL lifetime profile (b) of P3HT with and without AuNWs. Excitation wavelength is 500 nm. TRPL decay profiles are monitored at 650 nm.

Device Performance. J - V behavior was characterized on 60 nm and 80 nm thick P3HT:PCBM devices with and without AuNWs as displayed in **Figure 3.21**. The electric parameters are listed in

Table 3.3. Upon integrating AuNWs, the J_{sc} increased from 7.87 to 9.02 mA/cm² in the 80 nm devices and from 6.38 to 7.86 mA/cm² in the 60 nm devices. The photocurrent was thus enhanced by 14.6% and 23.2% in the 80 nm and 60 nm devices respectively. In all devices, the V_{oc} remained constant at 0.65 V. The FF slightly dropped for 80nm devices from 0.48 to 0.46 and more significantly for 60 nm devices from 0.56 to 0.48, which may be ascribed to some slight modification of work function of the hole transporting layer by AuNWs. Eventually, the performance increased from 2.4 to 2.7% for 80 nm devices and from 2.3 to 2.5% for 60 nm devices.

Figure 3.21 J - V curves of devices with and without AuNWs for (a) 80 nm and (b) 60 nm thick devices.

Table 3.3 Device parameters with and without AuNWs

P3HT:AgNPs	PCE (%)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	R_s (Ω cm ²)
Control (80nm)	2.4±0.1	-7.87±0.37	0.65±0.00	0.48±0.00	19.75
With AuNWs (80nm)	2.7±0.1	-9.02±0.39	0.65±0.01	0.46±0.01	20.73
Control (60nm)	2.3±0.2	-6.38±0.25	0.65±0.01	0.56±0.03	19.45
With AuNWs (60nm)	2.5±0.1	-7.86±0.24	0.65±0.01	0.48±0.01	23.65

In order to examine the wavelength dependent photocurrent, we recorded the IPCE spectra for the 80 nm and 60 nm thick devices which follow the same trend as J_{sc} from J-V measurement. It is found that the IPCE of both devices were enhanced in the spectral region from 400 nm to 650 nm. **Figure 3.23** displays the calculated enhancement (%) against wavelength. It is significantly enhanced around 620 nm coinciding with the SPR band of AuNWs in the ITO-PEDOT:PSS environment (**Figure 3.18**). In both J-V and IPCE measurements, the current enhancement is more pronounced in thinner PV cells. The increased absorption in photoactive layer can be attributed to plasmon near-field enhancement or the effect from the enhanced scattering (far-field effect).

Figure 3.22 IPCE enhancement (%) in 400-700nm spectral range for the AuNWs integrated device with thickness 80nm. The inset plot is IPCE spectra of the control and AuNWs incorporated devices.

The maximum exciton generation rate ($G_{\max}$) was calculated based on the analysis reported by Mihailetschi et al.^{110,130,131} To confirm the nanostructure induced absorption enhancement in AuNW incorporated device, the experimental photocurrent J_{ph} is plotted as a function of effective voltage ($V_o - V$) for the 80nm-thick device and 60nm-thick device (**Figure 3.23**). J_{ph} is obtained by subtracting dark current (J_D) from the current under illumination (J_L). V_o is the compensation voltage defined under the condition that J_L equals J_D . In the low effective voltage region, J_{ph} increases linearly with voltage and at higher effective voltage, all free charge carriers are extracted at zero recombination and J_{ph} saturates to qGL where G is the maximum exciton generation rate and L is the thickness of photoactive layer. The occurrence of the saturated photocurrent allows us to calculate the possible maximum exciton generation rate $G_{\max}$. For the devices with active layer thickness of 80nm and 60nm, the maximum exciton generation rate is increased from 8.31×10^{27} to $9.04 \times 10^{27} \text{ m}^{-3} \text{ s}^{-1}$ and from 7.32×10^{27} to $9.22 \times 10^{27} \text{ m}^{-3} \text{ s}^{-1}$ respectively after incorporating AuNWs. A

higher increment was found for the 60nm device which correlates well with the increased absorption in the Au-NWs integrated devices. In addition, the exciton dissociation efficiency at the short circuit condition ($V_{\text{eff}} = V_o$) was calculated from the normalized photocurrent density $J_{\text{ph}}/J_{\text{sat}}$. The value only increased from 73.6% to 77.0% for 80 nm and 77.4% to 80.6% for 60 nm AuNW incorporated devices, indicating the primary enhancement mechanism is the increased absorption of the active layer.

Figure 3.23 Photocurrent (J_{ph}) versus effective applied voltage (V_{eff}) for control and Au-NWs incorporated P3HT:PCBM devices with (a) thickness ~80 nm and (b) thickness ~60 nm.

3.4 Single Silver nanowire in PEDOT:PSS

Chemically synthesized silver nanowires (Ag NWs) have been widely studied in various applications such as surface plasmon waveguides,^{132,133} surface enhanced Raman spectroscopy,¹³⁴ surface plasmon coupled emission (SPCE),^{135,136} single photon detection,¹³⁷ etc., due to their single crystal structure, well-defined geometry.¹³⁸ They have also been incorporated into the photoactive layer of organic solar cells to improve their performance.⁷⁷ The quasi-one-dimensional NWs present an intriguing model system to study the optic and electric effects of metallic nanostructures on the OPV systems. The advantages of using single silver nanowire are obvious: they have a typical dimension with a length several μm and diameter tens to hundred nm that can be easily found in microscope; the quasi-one-dimensional physic property also makes the polarization-dependent study of characteristics possible; they can be easily fabricated through wet-chemistry processing. Until now, based on our best knowledge, there are no reports on the investigation of single metallic nanostructure plasmonic effects on OPV systems. It compels us to make a comprehensive study in this field with a single AgNW through microscopic techniques. Furthermore, any ensemble effects that obscure the photoexcitation dynamics will be absent here.

3.4.1 Experimental Details

Ag NW synthesis. Ag NWs were synthesized through a slow titration method reported previously in the literature.^{139,140} Typical synthesis begins with a mixture of 0.668 g of Polyvinylpyrrolidone (PVP) and 0.022 g of KBr in 20 mL of ethylene glycol being heated to 170 °C for 20-30 min. The silver seeds are then introduced to the solution by adding 0.050 g of silver chloride (AgCl) into the solution. Then followed by a slow

titration of the growth solution, 0.220 g silver nitrate (AgNO_3) in 10 mL of ethylene glycol, for 12-15 min. The titration of the AgNO_3 progressively stacks Ag^+ ions onto the silver seeds, while the PVP restricts this stacking to anisotropic growth of one dimensional NW, and the KBr salt precursor moderates the wire diameter to ensure long thin NWs. The solution remains at 170 °C for 30 additional minutes to complete the NW growth. The dispersion is then centrifuged three times with methanol at 6000 rpm for 30 minutes each time to extract the NWs from the dispersion. The final dry precipitates was dispersed in 20 ml methanol for further use.

Device Fabrication.. Silver nanowires (0.5% in concentration) suspension¹⁴¹ in ethanol was then dispersed onto ITO substrate by spincoating at a rpm of 1000. 30 nm PEDOT:PSS was then spin-coated as hole transporting layer. The substrates were transferred to an inert environment and baked at 120 °C for 5 min. After that, P3HT:PCBM (weight ratio 1:0.8) was spin-coated to get a 100 nm thick film. A 100 nm aluminium metal cathode was evaporated above the BHJ layer and the devices were then baked at 150 °C for 20 min before measurement. For macroscopic characterization, control cells without AgNWs were also fabricated.

Micro I-V characterization. Micro I-V measurements were done on single AgNW using a 532 nm continuous wave laser with fluence $\sim 7.4 \times 10^4 \text{ mW cm}^{-2}$ and a Keithley 2420. Reference measurement was done with light irradiation on the non-AgNW region in the vicinity of the single AgNW.

Morphology characterization. The surface topography of the AgNWs was imaged using a SEM (JSM-6700F, 10.0 kV) or an Asylum Research MFP-3D AFM in tapping mode. The diameter of Ag NWs was determined by a scanning electron microscope (SEM, JEOL 7001F).

FDTD simulation. Given the quasi-one dimension characteristics of Ag NW, two-dimensional simulation scenario was used as the NW direction can be treated to be infinite long. Anti-symmetric boundary condition was set along the polarization of electromagnetic waves; perfectly matched layers were used for the propagation of electromagnetic waves along the y axis. Electric and magnetic fields are detected using frequency profile monitors. Dielectric constants of P3HT:PCBM, ITO, PEDOT:PSS and Ag are extracted from other reports^{122,124,142,143}.

3.4.2 Results and Discussion

Morphology. **Figure 3.24** shows AgNWs images taken by SEM and optic microscope. As **Figure 3.24 (a)** shows, AgNWs had a diameter of around 60-100 nm and a length of around 10 μm . **Figure 3.24 (b)** provides the image of the same AgNW taken by (up) bright field, (middle) dark field of optic microscope and (down) SEM.

Figure 3.24 (a) SEM image of several AgNWs. (b) The same single AgNW in (up) bright (b) dark field of microscope and in (lower) SEM.

AgNWs embedded in device was also characterized using AFM to check if morphology of the device was affected. As indicated in **Figure 3.25 (a)**, after

covering the single AgNW with a 30 nm PEDOT: PSS hole transporting layer, there was a residual height of around 30 nm that could not be fully flattened by PEDOT: PSS. This is as we expect since the AgNW had a diameter of around 60 nm while the PEDOT: PSS thickness was only 30 nm. The spincoating of the 100 nm thick P3HT: PCBM active layer then flattened the region as shown in **Figure 3.25 (b)** that there was no protruding part from the AgNW.

Figure 3.25 A single AgNW covered with (a) 30 nm thick PEDOT:PSS and (b) PEDOT:PSS and 100 nm thick P3HT:PCBM layers.

Linear Absorption. Scattering and extinction spectra of the AgNW are sensitive to the incident light polarization. As indicated in **Figure 3.25 (a)**, the absorption of the incident light with polarization perpendicular to the main axis of AgNW (90 deg) has a peak at around 420 nm corresponding to the LSPR in the cross section. When the incident light polarization is along the long axis direction (0 deg), the absorption peak becomes broaden and red-shifts to around 500 nm. Multiple longitudinal modes of surface plasmon are expected to be excited. P3HT: PCBM with a single AgNW was measured to have higher extinction than the controlled

P3HT: PCBM film under light spot region ($\sim 1.85 \mu\text{m}$ in diameter) using optic microscope (**Figure 3.26 (b)**).

Figure 3.26 (a) Scattering and extinction spectra of a single AgNW for light polarization parallel (0 deg) and perpendicular (90 deg) to the main axis. (b) Extinction spectra of P3HT:PCBM film with and without the single AgNW (incident light non-polarized).

Exciton Generation. To examine the effects of AgNW on the generation and recombination of P3HT excitons, P3HT photoluminescence intensity was investigated for region with and without single AgNW. In the PL measurement, P3HT only film was chosen rather than P3HT: PCBM blends as excitons will be highly quenched in the latter case that makes the PL hard to be detected.

Tuning the incident polarization from 0 to 90 degree with respect to the NW axis, PL intensity of P3HT gradually increases, as shown in **Figure 3.27**. For the angles from 0 to 20 degree, the PL intensity is weaker than the controlled P3HT PL intensity; upon further increase of the angle above 20 degree, the PL intensity increases and is stronger than that of the control. It clearly demonstrates the effect of AgNW on P3HT light absorption and exciton generation. When light is incident with polarization along the AgNW axis (0 deg), due to the dimension ($\sim$ several μm) which is much larger

than the wavelength, it mainly acts as light blocker so that light absorption in P3HT would be decreased due to the shadowing effect. Perpendicular to the NW (90 deg), the dimension is several tens of nm, which is much smaller compared to the wavelength, the excitation of transverse modes of LSPR leads to an enhanced absorption of P3HT (increased exciton density), and which in turn results in a higher PL intensity. Note that the AgNW can also give out emission in this frequency region,¹³⁵ however, the reported fluence for such emission is several orders higher than that we used for PL measurement here, thus any PL signal from AgNW is negligible compared with that from P3HT.

Figure 3.27 (a) PL of the P3HT film with a single AgNW following excitation with different polarization of light. (b) Polarization dependence of PL intensity for P3HT film with a single AgNW.

Exciton Recombination. **Figure 3.28** displays the PL dynamics after excitation by 500nm fs-laser pulse. All the lifetimes can be fitted in the spectrum region 650nm to 720nm by using a single exponential decay, indicating only one emissive photoexcitation species exists, i.e., the singlet exciton of P3HT. The lifetime for the

control P3HT film was 563 ± 50 ps; for P3HT with AgNW, lifetime was fitted to be 470 ± 50 ps when exciting along the NW; and significantly decreased to 310 ± 50 ps when exciting perpendicular to the NW. The lifetimes have a variance of around 50 ps due to the streak camera resolution. The dramatic change of exciton lifetime may indicate the strong interaction of the P3HT excitons and the transverse modes of LSPR in the NW. The interaction can include radiative or non-radiative surface plasmon and exciton coupling. Similar results were found in previous reports.^{67,144} In Section 3.3, the polarization dependent effects are averaged in the ensemble measurements of AuNWs.

Figure 3.28 (a) The dynamics of P3HT excitons with and without AgNW under different polarized excitation. (b) Typical TRPL image captured by streak camera for P3HT film with a single AgNW excited by two different polarization of light.

The strong interaction between surface plasmon and excitons in P3HT was speculated to participate in the charge transfer process and facilitate the exciton dissociation in P3HT:PCBM. Some reports explained that the coupling mechanism leads to a higher ratio of hot exciton population and these excited excitons are beneficial for charge transfer.^{65,67} However, in an actual P3HT: PCBM blend, the case

may be different since exciton lifetime is now shortened considerably. To probe the exciton dynamics in the P3HT:PCBM blends, microscopic transient absorption (μ -TA) was done to investigate the effect by single AgNW. The transient dynamics of the singlet excitons was monitored at 1150 nm which lies in the photoinduced absorption (PIA) region of the P3HT singlet exciton as reported previously.^{145,146} Detail explanation and experimental proof can also be seen in Chapter 6.

The addition of PCBM to P3HT significantly shorten the lifetime of P3HT excitons as most of them diffuse to the interface and undergo charge transfer to PCBM molecules. The exciton dynamics in the P3HT:PCBM system is complicated, which includes processes such as self-trapping, structural relaxation, high-order recombination, charge transfer of excitons generated close to the interface, exciton diffusion to interface and undergo charge transfer, radiative recombination, *etc.*^{145,147} Some of these processes can happen at similar time region (several ps) and compete with one another. For simplicity, only two lifetimes were chosen to fit the P3HT exciton dynamics in P3HT:PCBM and an averaged lifetime was then calculated. Lifetimes of excitons in P3HT:PCBM OPV devices with and without single AgNW is listed in **Table 3.4**. Unlike the strong interaction between surface plasmon and P3HT exciton in the P3HT only film, it is found in P3HT:PCBM the exciton dynamics is only slightly affected in the presence of the transverse mode of LSPR in AgNW (**Figure 3.29**). This indicates the exciton quenching by PCBM is much faster compared to the surface plasmon and exciton interaction. The strong interaction between surface plasmon and exciton in P3HT film is much weakened in P3HT:PCBM blend. Whether the interaction between surface plasmon and exciton can promote the exciton dissociation efficiency need to be further investigated by

electric characterization.

Figure 3.29 PIA decay of singlet exciton monitored at 1150nm for P3HT:PCBM film with and without a single AgNW.

Table 3.4 Fitted Parameters for the PIA of singlet exciton decay.

	A_1	τ_1 (ps)	A_2	τ_2 (ps)	τ_{avg} (ps)
Ref	0.29 ± 0.01	1.8 ± 0.1	0.19 ± 0.01	19 ± 1	8.5 ± 0.6
0 deg	0.29 ± 0.01	1.6 ± 0.1	0.20 ± 0.01	19 ± 1	8.5 ± 0.5
90 deg	0.33 ± 0.01	1.9 ± 0.1	0.15 ± 0.01	20 ± 1	7.4 ± 0.6

Micro I-V characterization. The device performed best when the incident polarization was perpendicular to the NW direction. An enhancement in short circuit current by 37.5% can be found compared to the reference. With the incident polarization parallel to the NW direction, device performance slight drops, with the short circuit current decrease by ~6% (**Figure 3.30**). Note that the fill factor is relatively poor for all devices compared to widely-accepted numbers. It is due to the

illumination intensity is several order higher than the solar radiation intensity, which causes much higher bimolecular loss and thus a reduction in FF. The V_{oc} under the high fluence light is also relatively low. The reason is not clear intuitively; V_{oc} should increase with illumination intensity as the difference between quasi-Fermi levels of electrons and holes increases with higher carrier concentration. We suspect that the higher fluence irradiation may have induced some disorder in the density of states. Degradation in the electrode or PEDOT:PSS layer may also contribute to such loss in V_{oc} .

Figure 3.30 (a) Micro I-V characterized curves (b) Polarization dependence of the short-circuit current for the reference and plasmonic devices with a single AgNW. (c) Performance profile when perpendicular-polarized light scanned across the single AgNW.

Figure 3.30 (b) presents the polarization dependent short circuit current results, which is very similar to that shows in polarization dependent PL intensity measurement (**Figure 3.27 (b)**). It implies that the two may share the same mechanism: exciton and polaron generation is boosted by the transverse modes of localized surface plasmon resonance in the NW. This can be further proved by scanning the device performance in the vicinity of the AgNW with light source polarization and scanning direction perpendicular to the NW. As shown in **Figure 3.30 (c)**, a Gaussian profile of the performance can be found as the light changes its

position. The peak happens when the light has the best overlapping with the AgNW. A full width at half maximum (FWHM) of $1.85\ \mu\text{m}$ can be fitted for the Gaussian profile, that is, the effective diameter of the light source.

The polarization-dependent exciton generation with the single AgNW can be validated by examining the light field distribution. From the FDTD simulation, it was found that the AgNW can focus and redistribute the incident light to the active layer when the incident polarization is perpendicular to the NW direction (90 deg, TM) (**Figure 3.31 (a)**). Light would be blocked from penetrating the active layer and mainly focused in the ITO layer if the incident polarization is along the NW direction (TE) (**Figure 3.31 (b)**). For comparison, the E field distribution for the control is shown in **Figure 3.31 (c)**.

Figure 3.31 *E field distribution in the plasmonic device when incident light (532nm) is polarized (a) perpendicular and (b) parallel to the main axis of the AgNW. (c) E field distribution in the reference device.*

Macro I-V characterization. Electrical characterization is necessary for validation that the incorporation of AgNWs can truly improve the performance under solar illumination. To do so, devices with and without AgNWs were fabricated and characterized. **Figure 3.32** shows the *I-V* characteristics of the control and hybrid plasmonic devices. The device performance improved from 3.1% to 3.4% by AgNWs

incorporation- an average of 10 cells as shown in **Table 3.4**. Best hybrid plasmonic device had a performance of 3.6%. The major contribution is ascribed to the J_{sc} increasing from 8.36 mA cm^{-2} to 8.74 mA cm^{-2} . Meanwhile, FF also had been ameliorated slightly from 0.62 to 0.64. For the best performing hybrid plasmonic device with AgNWs, J_{sc} and FF could reach 9.01 mA cm^{-2} and 0.66, respectively. Shunt (R_{sh}) and series (R_s) resistances were comparable for the control and hybrid devices. The plasmonic device performance may be further optimized by increasing the loading of AgNWs; however, incorporating more AgNWs can also bring about greater morphological issues for the solar cell which may result in high variance of the performance. Nevertheless, investigating the loading effects of the AgNWs on the device performance was not pursued in this academic exercise.

Figure 3.32 Macroscopic characterized I - V curves for cells with and without AgNWs under (a) illumination and (b) dark condition.

Table 3.5 Device performance of the reference and plasmonic devices.

	PCE (%)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	R_s (Ω cm ²)	R_{sh} (k Ω cm ²)
Control	3.1 ± 0.2	-8.4 ± 0.4	0.59 ± 0.01	0.62 ± 0.01	3.72	26.4
Plasmonic Devices	3.4 ± 0.1	-8.7 ± 0.2	0.60 ± 0.01	0.64 ± 0.01	3.60	23.1
Best Plasmonic Device	3.6	-9.0	0.61	0.66	3.75	58.0

EQE of the plasmonic and the reference devices show differences in the 500 nm to 600nm region where the EQE enhancement reach a maximum at ~550 nm (**Figure 3.33 (a)**). The spectrum-dependent EQE enhancement and the peak position of the enhancement clearly point to the LSPR origin (**Figure 3.33 (b)**). The peak has around 100 nm redshift compared to the scattering peak of AgNW (~450 nm as shown in **Figure 3.26 (a)**, 90 deg). It is reasonable since the scattering measurement was done on quartz substrate and the AgNW was surrounded with air. In plasmonic device, the dielectric environment was much higher (P3HT:PCBM refractive index $n \sim 2.1$ in the visible range) which can lead to a significant redshift of LSPR according to the Mie theory.¹⁴⁸

Figure 3.33 (a) EQE and (b) relative enhancement of EQE for the reference and plasmonic devices.

The increase in FF may be attributed to the introduction of AgNW which improve conductivity and thus facilitate charge transport and collection. However, the invariance of the averaged series and shunt resistances excludes these factors. Similar to what observed for AuNWs' effect on P3HT:PCBM system, exciton dissociation efficiency was not significantly improved by the AgNW. As shown in **Figure 3.34**, the exciton dissociation efficiency at short circuit condition can reach 90% for both devices. Hence, it can also not be used to explain the improvement of averaged FF. Since FF is determined by the competition between charge extraction and recombination, it is important to check whether other factors that may affect the charge recombination. As far as we know, the hole mobility in polymer domain is usually one order lower than that of electrons in the fullerene domain.^{149,150} The imbalance in mobility can result in a lower FF since holes cannot be extracted as efficiently as electrons. With the LSPR of AgNW, light near the resonance can be efficiently redistributed and focused near the AgNW, i.e., at the PEDOT:PSS side (as seen from the light distribution in **Figure 3.31**). In other words, more excitons and charges are generated near the PEDOT:PSS. It can facilitate the hole collection when they are generated near the anode side and improve the FF by balancing the hole and

electron transport. For micro I - V measurement, light intensity was several orders higher than that of solar irradiation, bimolecular recombination will be more severe for plasmonic devices and it is a plausible reason why we did not observe an increased in FF. This conclusion is consistent with previous report⁸³ and can successfully explain why there is a better I - V profile (high FF) in the plasmonic device.

Figure 3.34 Photocurrent (J_{ph}) versus effective applied voltage (V_{eff}) for control and Ag-NWs incorporated P3HT:PCBM devices.

3.4 Conclusion

In summary, in this chapter, we have demonstrated the feasibility of integrating different types of plasmonic nanostructures into the hole transporting layer PEDOT:PSS of bulk heterojunction organic solar cell. We found that these plasmonic nanostructures generally can increase the short circuit current of the OPV devices by 5%- 23% and thus yield a better performance. This is confirmed to originate from the LSPR of the embedded nanostructures. The strong local field generated by LSPR can be utilized to enhance light absorption and improve light distribution. The strong

forward light scattering due to LSPR can also favor light absorption in the active layer. However, the ratio of forward scattered light highly depends on the shape and size of nanostructures and should be designed carefully. Besides, we also have correlated with optical spectroscopy analysis to examine the effect of surface plasmon on excitonic and polaronic properties. It is found that direct contact with the plasmonic nanostructures will accelerate the exciton decay in the polymer. With a proper spacer layer inserted between them, exciton quenching by metallic nanostructures will be decreased. The interaction between polaron and surface plasmon seems negligible. Therefore this can lead to an increase in the short circuit current while ensuring a good V_{oc} and FF.

CHAPTER 4. Plasmonic Nanoparticles

Blended in the Active Layer

4.1 Introduction

As discussed in the last chapter, metallic nanostructures are typically embedded in the hole transporting layer PEDOT: PSS or distributed on ITO covered by PEDOT: PSS layer in an attempt to improve the performance of OSCs. Using this approach, advantages include reduced possibilities of exciton quenching, charge localization and disruption of the active layer morphology. Nevertheless, since the plasmonic field decays exponentially as a function of distance, light cannot be effectively coupled into the active layer when the nanostructures are far away from it. This is especially for small nanoparticles (<20 nm), as their scattering is not efficient and therefore could only be used as subwavelength antennas that their enhanced near-field is coupled to the active layer.¹⁵¹ When they are located external to the active layer, they will have a minimum effect in enhancing the absorption of the active layer. Besides, the backscattering and reflection of the incident light by large nanostructures (>40 nm) can prevent a fraction of light from reaching the active layer, which will eventually decrease the average photon density in the active layer.

To exploit the LSPR near field and strong scattering, metallic nanostructures should be incorporated into the active layer. The strong near field induced by LSPR can be well coupled into the absorbing materials; the incident light can be scattered and reflected multiple times in the active layer, thereby increasing their optical path

length.⁷⁸ In addition, it is also easier to disperse nanostructures into the active layer than in the former.¹⁵¹ As to the issues concerned such as exciton quenching effect, proponents argue that the organic ligands used as surfactants for the nanostructures could also minimize the excitonic quenching problem.

Despite these predicted advantages, the experimental results are highly controversial. Both enhancement^{76,78,81,82,120,121} and detracting^{84,152} in performance of the OPV devices when incorporating such nanoparticles (NPs) into the BHJ active layer have been reported in the recent years. There may be some negative effects such as exciton/charge quenching, morphological disruption that compete with and compromise positive effects such as higher exciton generation rate, etc, which leads to incongruous experimental results. In addition there also exists the possibility of non-plasmonic enhancement. An investigation of the fundamental photophysics and charge dynamics in these hybrid plasmonic OSCs would be critical. However, reports focusing on these aspects are far and few between.⁸⁷

In this chapter, a series of representative hybrid plasmonic OPV devices comprising of oleylamine-capped silver NPs (AgNPs) blended in P3HT:PCBM film were fabricated. Transient optical spectroscopy as well as electrical characterization was utilized to study the charge carrier dynamics and transport in these films/devices. fs-TAS reveals that there is a high rate of polaron quenching in the AgNPs-P3HT:PCBM blends compared to the P3HT:PCBM control blends due to the fast trapping of polarons by AgNPs which compromises the increased exciton generation density. Additionally, there is fast trap-assisted recombination that is ascribed to increased subgap trapping states at the interfacial region of P3HT:PCBM originating

from the AgNPs -- as confirmed by nanosecond transient absorption spectroscopy (ns-TAS) as well as intensity dependent V_{oc} and dark current measurements.

The findings provide new insights into the fundamental photophysics and charge dynamics in plasmonic OSCs. Suggestions and guidelines for further development of high performance hybrid plasmonic OSC devices are discussed at the end of this chapter.

4.2 Experiments

AgNPs Synthesis. The AgNPs were synthesized through the reduction of AgNO_3 by oleylamine in refluxing 1,2-dichlorobenzene (boiling point: 181 °C). Briefly, 12mg AgNO_3 (Sigma-Aldrich) was dissolved in 500 μL oleylamine (70%, Sigma-Aldrich) and then rapidly injected into 10mL refluxing 1,2-dichlorobenzene. The solution turned from light-yellow color to dark brown within several minutes. After 8 hours, the reaction was completed. To remove the excessive oleylamine and byproducts, the production solution was added with 30 mL methanol, following by 20 min centrifugation at 4000 rpm and then redispersed in 10 mL 1,2-dichlorobenzene. The above process was repeated for 3 times and the final dry precipitate was dispersed in 10mL 1,2-dichlorobenzene for further use.

Device Fabrication. **Figure 4.1** shows the schematic of the hybrid plasmonic OPV device. AgNPs are dispersed into the P3HT:PCBM active layer. Clean patterned ITO glass was sequentially sonicated in DI-water, acetone and IPA for 15 min each and then cleaned with oxygen plasma. After that, 30 nm PEDOT: PSS was spin-coated above the ITO and then baked at 140 °C in nitrogen atmosphere for 10 min. A

100 nm thick BHJ layer was subsequently spin-coated on top of the PEDOT:PSS layer. The concentration of the P3HT:PCBM used is 10 mg/mL:8 mg/mL. For the hybrid blends, different ratio of AgNPs in 1,2-dichlorobenzene were mixed with the P3HT:PCBM and were spun at 700 rpm for 2 min. The maximum weight ratio of AgNPs:P3HT used is $< \sim 3.8\%$. For better annotation, we had use volume ratio of P3HT: AgNPs 1:1, 1:1/2, 1:1/4, 1:1/8, 1:1/16, 1:0 to represent AgNPs concentration from high to low in our report hereafter. A 100nm Al metal cathode was evaporated above the BHJ layer and the devices were then baked at 150 °C for 20 min before measurement.

Figure 4.1 Schematic of the AgNPs-P3HT:PCBM hybrid plasmonic OPV device.

Characterization. AgNPs were characterized by transmission electron microscopy (TEM) (JEM-2010FEF, 200 kV). Steady-state absorption spectra were collected using a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. Other experimental details can be found in Chapter 2.

4.3 Results and Discussion

4.3.1 Morphology characterization

TEM characterization of AgNPs as shown in **Figure 4.2** indicates the size of most AgNPs is around ~20-25 nm. The size of AgNPs is suitable to be dispersed in the active layer of P3HT:PCBM with a thickness of 100 nm. Besides, the oleylamine ligand is compatible to P3HT:PCBM solution in DCB which is of vital importance for hybrid plasmonic OSCs. **Figure 4.4** presents the morphology of P3HT:PCBM films with and without AgNPs. The RMS roughness for P3HT:PCBM over $5 \times 5 \mu\text{m}$ region is 0.9 nm while for that with highest AgNPs load is 1.0 nm, indicating the film morphology is not much disturbed by AgNPs. Other hydrophilic ligands capped nanoparticles may strongly aggregate in the film and significantly degrade the film morphology.⁸⁴

Figure 4.2 A representative TEM image of the AgNPs.

Figure 4.3 AFM images of the morphology of P3HT:PCBM films (a) without and (b) with AgNPs. RMS roughness for (a) is 0.9 nm and (b) is 1.0 nm.

4.3.2 Linear absorption spectroscopy

Steady-state absorption of AgNPs was measured in 1, 2-Dichlorobenzene (DCB), showing a sharp extinction peak at 417 nm with full width at half maximum ~49 nm. The extinction peak is ascribed to the LSPR of the AgNPs in DCB solvent. We simulated the LSPR of AgNPs using a diameter of 24 nm in DCB and found a very good correspondence between simulation and experiment (**Figure 4.4 (a)**).

Figure 4.4 (a) The experimental measured and simulated LSPR of AgNPs (b) Absorbance of AgNPs and P3HT:PCBM films with/without AgNPs.

When embedded in P3HT:PCBM film, the absorption property are presented in **Figure 4.4 (b)**. It is expected AgNPs LSPR would be redshift and broadened due to higher permittivity and the more lossy local environment of P3HT: PCBM film. However, it is impossible to tell apart the LSPR of AgNPs from the hybrid films. The extinction of hybrid films are higher than that of the controlled film (pure P3HT:PCBM fabricated under the same condition). The parasite absorption of AgNPs is minimal compared to the highly absorptive organic blends, therefore we can conclude that the absorption enhancement does really come from P3HT:PCBM film. Besides, the incorporation of AgNPs does not change much of the film thickness (~100nm, measured using Alpha step-profile, films are almost of the same thickness within the machine's resolution). Furthermore, the three vibronic peaks of P3HT (at ~510 nm, ~560 nm and ~600 nm, corresponding to the 0-2, 0-1 and 0-0 vibronic transitions of P3HT) do not show any obvious shift in the hybrid films, indicating the crystalline order of P3HT is not significantly compromised.¹¹⁵ In brief, the above facts imply that the enhancement of P3HT:PCBM absorption originates from an increased density of photons in the film. We can conclude that the plasmonic effects do play a role in the increased absorption, by near-field coupling and scattering.

4.3.3 Device Performance

As shown in **Figure 4.5 (a)** and **Table 4.1**, the control P3HT: PCBM devices (without AgNPs) exhibit an average PCE of ~3.1%, with an V_{OC} of 0.60 V, J_{SC} of -8.98 mA/cm², and a FF of 0.57 – typical of the values reported for the P3HT: PCBM system. The incorporation of AgNPs brings about a detrimental effect on the performance of the OSCs. The PCEs, FFs and V_{OC} s all decrease with increasing AgNPs concentration. The J_{SC} on the other hand fluctuates, but is typically less than

that of the control. From **Figure 4.5 (b)**, IPCE of the devices shows that the external quantum efficiencies of the hybrid cells are typically less than that of the control over the broad region.

Figure 4.5 (a) *J-V* curves of AgNPs-P3HT:PCBM and P3HT:PCBM OSCs. (b) *EQE* curves of AgNPs-P3HT:PCBM and P3HT:PCBM OSCs.

Table 4.1 Device Performance of AgNPs-P3HT:PCBM and P3HT:PCBM OSCs.

P3HT:AgNPs	PCE (%)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF
1:0	3.10 ± 0.19	-8.98 ± 0.34	0.60 ± 0.01	0.57 ± 0.02
1:1/16	2.60 ± 0.42	-7.88 ± 0.65	0.58 ± 0.02	0.57 ± 0.03
1:1/8	2.60 ± 0.18	-8.48 ± 0.46	0.55 ± 0.01	0.56 ± 0.01
1:1/4	1.72 ± 0.27	-6.71 ± 0.43	0.52 ± 0.01	0.49 ± 0.05
1:1/2	1.65 ± 0.21	-6.99 ± 0.33	0.53 ± 0.02	0.45 ± 0.04
1:1	1.00 ± 0.35	-5.98 ± 1.13	0.46 ± 0.03	0.36 ± 0.03

4.3.4 Intensity-dependent V_{oc} measurements

Intensity-dependent V_{oc} measurements were done under illumination from ~0.3 sun power to 1 sun power. As depicted in **Figure 4.6**, that V_{oc} versus $\ln(I)$ (I is the illumination intensity) shows an increased slope (S) when increasing the load of AgNPs. For control cell, the fitted S is $1.41 \text{ kT}/q$, while it increases to $2.09 \text{ kT}/q$ for the hybrid plasmonic cell with the highest AgNPs concentration (**Table 4.2**).

Figure 4.6 Intensity-dependent open-circuit voltage measurement of the AgNPs-P3HT:PCBM and P3HT:PCBM OSCs.

Table 4.2 Fitting results of the intensity dependent V_{oc} measurements.

P3HT:AgNPs	1:0	1:1/16	1:1/8	1:1/4	1:1/2	1:1
Slope ($S = kT/q$)	0.035	0.044	0.043	0.049	0.052	0.052
y-intercept	0.44	0.38	0.35	0.30	0.29	0.21
n	1.41	1.75	1.73	1.95	2.09	2.09

The slope S is highly dependent on the charge recombination processes in the OPV system. In brief, the charge recombination processes in OPV can be broadly classified into two categories according to their kinetics³⁴: (a) geminate recombination; and (b) non-geminate recombination. Geminate recombination is a monomolecular process that occurs when two opposite charges originating from the same exciton (following dissociation) recombine. It is also often referred to as recombination through a charge-transfer complex at the interface of the donor (D) and acceptor (A) with the hole located at the HOMO of the donor and the electron at LUMO of the acceptor. This process occurs at the same rate independent of the light intensity and dominates the recombination at early times (i.e., hundreds of ps to few ns). Typically, it contributes a relatively small loss in the optimized P3HT:PCBM system (~7% – 15%^{26,34}). In contrast, non-geminate recombination occurs when two free opposite charges (originating from different excitons) recombine. Its rate depends on the intensity of the light excitation and dominates over the ns-μs timescale. For a 3-D Langevin recombination (involving free charges), the theoretical recombination order is two (bimolecular). On the other hand, trapped-assisted recombination occurs when one free charge recombines with another charge immobilized in a trap state^{153,154} or interface state¹⁵⁵, which is usually a monomolecular process described by the Shockley-Read-Hall (SRH) trapped-assisted recombination mechanism.¹⁵⁶

Intensity-dependent open-circuit voltage measurements are widely used to probe the recombination mechanisms in OSCs.^{154,157-159} It has been shown that the V_{OC} of OSCs can be expressed¹⁵⁹ as:

$$V_{OC} = \frac{1}{q} (E_{LUMO}^{Fullerene} - E_{HOMO}^{Polymer} - \Delta) - \frac{kT}{q} \ln\left(\frac{np}{N_c^2}\right) \quad (\text{Eq. 4.1})$$

where the energy shift Δ originates from the disorder in the BHJ film, n and p are the electron and hole densities in the fullerene and polymer domains at open circuit, N_c is the density of states in the conduction band, q is the elementary charge, E is the energy level, k is the Boltzmann constant and T is the temperature. Under open circuit conditions, $\nabla J_{n,p} = \pm q(G - R) = 0$, where $J_{n,p}$ is the electron (hole) current density, G is the carrier generation rate (proportional to light intensity I) and R is the carrier recombination rate. In the limit where Langevin recombination dominates,

$$R = \gamma(np - n_i^2), \text{ we have } np \cong \frac{G}{\gamma} \text{ where } \gamma \text{ is the Langevin recombination prefactor, } n_i$$

is the intrinsic carrier concentration which is negligible compared to the photogenerated carrier concentration. A plot of V_{OC} versus the natural logarithm of the light intensity I yields a straight line equation with a slope $S (= kT/q)$. On the other hand, if the loss mechanism is dominated by the SRH (monomolecular) process,

$$R = \frac{C_n C_p N_t (np - n_i^2)}{C_n (n + n_1) + C_p (p + p_1)}, \text{ where } C_n \text{ and } C_p \text{ are the capture coefficients of the}$$

electrons and holes by the traps, N_t is the trap density, p_1 and n_1 are the number of holes/electrons in the valence/conduction band for the case in which the Fermi level

falls at the trap energy level. $n_1 = N_c \exp(\frac{E_t - E_c}{kT})$ and $p_1 = N_v \exp(\frac{E_v - E_t}{kT})$ where E_t

is the trap energy level, E_c , E_v is the conduction band and valence band level respectively. Neglecting the intrinsic carrier densities and approximating $n \cong p$, we

$$\text{have } n \cong p \cong \frac{(C_n + C_p)}{C_n C_p N_t} G, \text{ the slope will then be } S = 2(kT/q). \text{ In general, } S = nkT/q,$$

where n is the ideality factor (under illumination) that is dependent on the transport and recombination processes in OSCs.¹⁶⁰ Typically, in most organic systems where the trap-assisted SRH recombination is present and competes with the Langevin

recombination kinetics, intensity-dependent V_{OC} measurements would yield an ideality factor (under illumination) in the range of $1 \leq n \leq 2$.

The increase in the slope S is a clear evidence of increased trap states and increased SRH (monomolecular) recombination with increasing AgNPs concentration. In the P3HT:PCBM only reference cells, traps originating from the defect sites during fabrication¹⁵⁴ and the intrinsic tail states below the transporting level¹⁶¹ may contribute to the SRH processes. At relatively higher concentrations of AgNPs (i.e. P3HT:AgNPs ratio $> 1:1/4$), the trap-assisted recombination dominates the kinetics and therefore n approaches 2. For trap-assisted recombination to occur, the probability for the traps to capture a free charge must be higher than that for the reemission of charges from the traps. We therefore propose that these traps arise from the AgNPs which are located between P3HT and PCBM domains – where both the holes in the P3HT domain and the electrons in the PCBM domain could be easily captured by these traps. This could account for the increased trapped-assisted recombination with increasing AgNPs concentration. These traps may originate from the metal core of the AgNPs with ineffective OA-ligand coverage. This is highly likely since Ag has a Fermi level of 4.2 – 4.7 eV; which lies in between that of the LUMO of PCBM and the HOMO of P3HT and could therefore be a midgap state for carrier trapping and recombination. The ligands may also have an influence on the charge trapping as the charge hopping rate is dependent on ligand length; and some functional groups of the ligand may also provide localized states. Topp *et al* had previously shown that AuNPs encapsulated with different ligands (e.g. with P3HT itself, dodecylamine and pyridine) all had undesirable effects on the PCE of P3HT:PCBM OSCs.¹⁶² The presence of such detrimental effects even for nearly ligand-free Au NPs strongly

suggests that the metallic core plays a significant role in degrading the OSC performance¹⁶², though the ligands may also play some part in worsening it. Further study is necessary to reveal how these traps form once metallic nanoparticles are inside the film.

4.3.5 Dark-Current Characteristics

The dark forward bias characteristics of an OSC are highly dependent on the transport and recombination processes. The common diode equation with the presence of a series resistance R_S and a parallel shunt resistance R_{SH} is expressed as:

$$J_{dark} = J_0 \left[\exp\left(\frac{V - JR_S}{n_{dark} kT / q}\right) - 1 \right] + \frac{V - JR_S}{R_{SH}} \quad (\text{Eq. 4.2})$$

where n_{dark} is the dark ideality factor, J_0 is reverse saturation current density while k , T and q are the Boltzmann constant, temperature and elementary charge, respectively. An estimate of R_{SH} could be determined from the inverse of the gradient under low bias; while the parameters J_0 , R_S and n_{dark} could be obtained by fitting the exponential region under forward bias.

Table 4.3 lists the fitted dark current parameters under forward bias (see **Figure 4.7**). J_0 increases drastically by ~ 3 orders – from 3.32×10^{-6} to 4.22×10^{-4} mA/cm². Furthermore, n_{dark} increases gradually from 1.66 in the control cells to 2.34 in the cells with the highest Ag concentration – consistent with n (under illumination) in the intensity-dependent V_{OC} measurements. The non-ideality of the dark characteristics has been shown to depend on the deeply trapped carriers in the dominant charge transport component of the donor-acceptor blend.^{160,163} The presence of a high degree of energetic disorder in the DOS (i.e., broad trap distribution, deep traps, etc.) of the dominant charge transport phase can lead to large ideality factors. Hence, the increase in n_{dark} can be interpreted as implication of an increased energetic disorder originating from AgNPs induced subgap traps, which lower the charge injection efficiency.¹⁶⁴

Figure 4.7 Dark current forward bias curve of the AgNPs-P3HT:PCBM and P3HT:PCBM OSCs. Solid lines are the fitted curves. The intercept of the dashed lines with the dark current axis yield the reverse saturation current in these OSCs.

Table 4.3 Fitted Dark current parameters of AgNPs-P3HT:PCBM and P3HT:PCBM OSCs.

P3HT:AgNPs	J_0 (mA cm ⁻²)	n_{dark}	R_s (Ω cm ²)	R_{SH} (kΩ cm ²)	R^2 (coefficient of determination)
1:0	3.32×10^{-6}	1.66	9.23	6.36	0.9596
1:1/16	2.42×10^{-4}	2.33	7.22	2.50	0.9993
1:1/8	1.63×10^{-4}	2.15	7.65	4.40	0.9997
1:1/4	3.23×10^{-4}	2.28	9.72	2.72	0.9987
1:1/2	3.61×10^{-4}	2.29	17.91	9.20	0.9977
1:1	4.22×10^{-4}	2.34	23.35	16.59	0.9837

4.3.6 Charge Dynamics in the fs-ns Temporal Regime

fs-TAS was performed on 100 nm thick P3HT-PCBM only control films and those blended with the AgNPs. The DT signal obtained from these samples with equivalent thickness (of ~100 nm) would allow us to compare the relative populations of the

residual excited species at different times following photoexcitation under the same conditions (e.g. same pump fluence, same detection setup/geometry etc.). **Figure 4.8** (a) shows the representative differential transmission (DT) spectra spanning 520 nm to 1200 nm for the control samples at different delay times following photoexcitation.

Figure 4.8 The effect of AgNPs on the exciton and polaron generation observed via fs-TAS. (a) fs-TAS of P3HT:PCBM film ranged from 520nm to 1200nm. Selected times are 1ps, 10ps, 100ps, 1ns, and 2ns after excitation with 500nm laser beam. A comparison of the fs-TAS

The peaks at ~600 nm and ~560 nm shown in **Figure 4.8** (a) corresponds to the 0-0 and 0-1 vibronic transitions from ground state to first excited states. Another peak (0-2 at 510nm) is not shown in this figure. These vibronic peaks indicates that the excitons in P3HT interact with different phonon replica. It is not difficult to ascribe the positive signal (i.e. $\Delta T/T > 0$ – increased transmittance of the probe beam)

region spanning from 520 nm-620 nm to ground state bleaching signatures.¹¹⁵ This photobleaching (PB) signal arises due to the state-filling of the excitonic and polaronic states, which is proportional to the population of the excitons and polarons in the photoexcited films.¹⁶⁵ The negative $\Delta T/T$ signal at ~700 nm is due to the PIA of delocalized polarons in the crystalline P3HT domains. The early time spectra at 1 ps that show a weak positive peak around 740 nm within the broad negative PIA valley arises from the stimulated emission (SE) of P3HT singlet excitons.^{25,115} This peak disappears within 10 ps, indicating the fast quenching of P3HT excitons by the PCBM acceptor. In the NIR region, there is a broad PIA peak centered at around 1150nm at early times of 1 ps, which subsequently decays within 50 ps. Following which, a long-lived PIA peak centered around 1000 nm remains up to the ns timescale.

The PIA signal at 1150 nm can be ascribed to singlet exciton since its decay time corresponds well with the typical active time of excitons in P3HT:PCBM (diffusion in P3HT domain and dissociation at the heterojunction). To prove it, we monitored the PIA signal at 1150 nm in pristine P3HT as shown in **Figure 4.9 (a)**. It can be fitted by two lifetimes: 5 ± 1 ps and 200 ± 10 ps. The shorter lifetime can be attributed to exciton self-trapping, torsional relaxation and excitation energy transfer between segments,¹⁴⁷ while the longer lifetime is due to the recombination of excitons. A lifetime of several hundred ps is typical for singlet excitons in polymer semiconductors. In P3HT, the quantum efficiency of PL is very low (~1%), and the PL may not be a good representative for exciton dynamics. TRPL of P3HT as shown in **Figure 4.9 (b)** can be fitted by a lifetime of $\sim 560 \pm 50$ ps. The TRPL lifetime is comparable to that of TA at 1150 nm- the slight differences may be ascribed to the

fact that TRPL is sensitive to the emissive processes which are in turn convolved with the nonradiative processes while TA is sensitive to all processes in the polymer.¹⁴⁶

Figure 4.9 (a) PIA signal monitored at 1150 nm in P3HT film (b) Normalized TRPL monitored from 650 nm to 720 nm in P3HT film.

In P3HT:PCBM blends, a similar conclusion can be gained. The 1150 nm feature can be found by comparing the GSB signal at 560 nm with the PIA signal at 1150nm in P3HT:PCBM blends. As shown in **Figure 4.10**, after exciting the ground state electrons to an excited state, the decreased electron population in the ground state gives rise to a GSB signature as sensed by the probe. The system recovers back to the equilibrium state only after the excited species relax back to ground state. At a time scale < 5 ps, both the PIA signal and the GSB signal exhibit the same decay rate – indicating that they both originate from a common species – i.e. the singlet exciton. After 5 ps, the ground state recovery becomes slower due to increased contributions from the long-lived polaron and CT state formation after exciton dissociation.¹⁴⁵ At this timescale, the GSB signal cannot be fully assigned to singlet excitons. The PIA at 1150 nm decreases continually to almost zero within ~ 50 ps as the excitons diffuse to the interface and are quenched. Hence, we can conclude the TAS signal at 1150 nm to be from the PIA of singlet excitons. Our measurements are consistent with previous reports.^{26,145} Long-lived PIA signals centred at 1000 nm that do not recover back to

the equilibrium over the entire time window of the fs-TAS setup has been confirmed to originate from P3HT polarons in the disordered domains using various techniques.

21,145,146,166

Figure 4.10 Transient dynamics of at 560nm (GSB) and at 1150nm.

It would be wise to use the two PIA magnitude and decay to monitor exciton/polaron generation and recombination. For example, at 1ps delay, the PIA peak at 1150 nm originates from the mainly singlet exciton population present in the films; while at 1 ns delay, the PIA peak at 1000 nm originates from the mainly polaron population (or free charges) present (since all the excitons would have undergone dissociation/recombination by then).

Monitoring and comparing the relative magnitudes of these DT signals at 1150nm and 1000nm in the control and the AgNPs blended BHJ thin films of equivalent thickness would make clear the effects of AgNPs on the charge generation and recombination.

Figure 4.11 (a) shows the DT signals at 1 ps delay for the control and two AgNPs-P3HT:PCBM samples (i.e., with low AgNPs concentration (1:1/16 P3HT to AgNPs) and high AgNPs concentration (1:1 ratio) – for clarity, only these three spectra will be plotted. It is clear that the absolute magnitudes at 1150nm are more pronounced in the AgNPs-P3HT:PCBM blends compared to the control with an estimated increase of ~27% and 31% (over the 0-1 ps timescale) for the low and high concentration respectively. This is clear evidence that the singlet exciton generation rate is indeed enhanced by the presence of the AgNPs, consistent with the results from the steady-state absorption. Nevertheless, at 1 ns, the magnitude of the DT signals is almost not changing in all the samples, indicating that a comparable polaron population is present in all the samples. It indicates, although there is an increase singlet exciton generation rate brought by LSPR, it does not translate to a corresponding increase in the free charge generation.

Figure 4.11 *Transient decays of AgNPs-P3HT:PCBM and P3HT:PCBM BHJ films.*

(a) *The singlet exciton decay monitored at 1150 nm. (b) The signal at 1000 nm is a superposition of exciton and polaron decay. (c) GSB decay monitored at 560 nm.*

Let us list several possible reasons pertaining to this asymmetric behavior: (1) Exciton recombination rate become faster due to Foster resonant energy transfer (FRET) and/or Dexter energy transfer (DET) in the presence of AgNPs; (2) Higher order recombination (e.g., bimolecular recombination) happens in the vicinity of AgNPs caused by the strong near-field. (3) The traps induced by AgNPs capture charges and/or excitons, resulting in a decreased free polaron amount at 1ns.

The decay transients at 1150 nm (i.e., the singlet exciton) for the control and the two AgNPs-P3HT:PCBM samples (i.e. 1:1/16 and 1:1 ratio) as displayed in **Figure 4.12**, shows an non-varying trend, indicating the recombination dynamics of singlet exciton is not affected by AgNPs in the blend. Further validation was also done in pristine P3HT. No PCBM was added to these samples as the presence of any acceptor materials will quench the PL signals. These P3HT only films were also subjected to the same thermal annealing conditions as those BHJ films. **Figure 4.13** shows their PL decay transients which are invariant in all the samples – possessing a typical lifetime of $\sim 560 \pm 50$ ps. Furthermore, an essential criterion for efficient FRET to occur is the strong spectra overlap between the emission spectrum of donor and the absorption spectrum of the acceptor.¹⁶⁷ Given that the emission of the P3HT excitons at $\sim 650 - 710$ nm has little overlap with the LSPR peak of the AgNPs, any resonance energy transfer between P3HT excitons and the surface plasmons of the AgNPs is expected to be negligible. Similarly, DET between the P3HT excitons and

the surface plasmons of the AgNPs is also expected to very small due to the presence of >2 nm long oleylamine ligands overcoating the AgNPs; which is beyond the effective electronic coupling distance ($<20 \text{ \AA}$) for DET to occur.¹⁶⁸ The TRPL results appear to contradict the findings in Chapter 4 where we observed a strong interaction between single AgNW surface plasmon and P3HT exciton. One possible explanation is, with a large dimension (e.g., AgNW with diameter ~60-100 nm, length: ~ μm), the interaction between surface plasmon and exciton may be stronger due to a much stronger scattering field, which can play a role in affecting the exciton dynamics; besides, the number of AgNPs per volume in the macroscopic TRPL measurement is far from comparable to that measured on a single AgNW with micro-TRPL technique. The overall interaction, even if they have, would be on the average negligible in the macroscopic measurement, i.e., obscured by the ensemble effects. Hence, it can still be concluded that AgNPs here would not significantly affect the dynamics of excitons in these organic materials, thereby excluding the possibility of (1).

Figure 4.12 Excitation intensity-dependent (a) polaron and (b) exciton generation.

For (2), the possibility of exciton-exciton, exciton-polaron annihilation and exciton trapping in the presence of AgNPs could be discounted based on the non-changing PL transients in all the samples. Next, to test the hypothesis of (2) on the polarons, pump intensity dependent studies monitoring the DT dynamics over the

spectra range of 900 nm to 1050 nm up to 1 ns delay were also performed. From the non-changing DT transients for all the samples (**Figure 4.12**), the possibilities of an increased rate of bimolecular recombination through exciton-polaron or polaron-polaron annihilation in the presence of the AgNPs could also be ruled out.

Figure 4.13 Normalized time-resolved photoluminescence of AgNPs-P3HT and P3HT films.

As displayed in **Figure 4.11 (b)**, DT transients at 1000 nm showed some difference within 100 ps between the control and the hybrid samples. The time is within the realm of exciton active time, i.e., exciton recombination and dissociation. Since exciton dynamics are invariant, only the polaron dynamics have changed. Excluding factors discussed above, the only possible reason of the asymmetry behaviour could arise from (3) – a fast trapping of the polarons by the AgNPs.

A fraction of these trapped charges could also undergo fast recombination at the P3HT:PCBM interface as the GSB decay transients at 560 nm shows a slight decrease in magnitude of the long-lived component that is ascribed to the free and trapped polarons (see **Figure 4.11 (c)**). While these oleylamine coated AgNPs can

bring about an increase in exciton generation (in the vicinity of the AgNPs) in the BHJ films that could lead to more free charges following exciton dissociation, these AgNPs could also function as traps for the polarons in its locality. Hence, these two competing effects result in a null increase in the polaron population, correlated with electrical characteristics in revealing the existence of traps brought by AgNPs.

4.3.7 Charge Dynamics in the ns- μ s Temporal Regime

To monitor the polaron dynamics, the transients at the GSB peak of 560 nm from ns to μ s was measured. The GSB signals arise from a superposition of the signals from the photoexcited species (e.g. excitons and polarons *etc*). In ns to μ s time regime, there are no singlet excitons; besides, other excited species, such as CT excitons, triplet excitons would also either disappear or be absent in the annealed P3HT:PCBM. The only species form existing at this time scale would be polarons. Hence, it is reasonable to conclude that the GSB from ns to μ s can be purely due to polarons. Here we use the transient at 560 nm to trace the evolution of polarons in control and hybrid films.

Polaron dynamics in annealed P3HT:PCBM as a function of pump intensity was firstly measured, as depicted in **Figure 4.14**. The typical characteristics of the polaron dynamics in annealed P3HT:PCBM films is a fast decay within several hundred ns, following by a long-lived component extending beyond our TAS measuring time window. Similar dynamical evolution has been found in transient photocurrent measurements.^{149,169} To model transient absorption dynamics of polarons, Howard Ian A. *et al* modelled the TAS decay from 750 nm to 900 nm using

a combination of monomolecular germinate recombination and Langevin bimolecular recombination.³⁴ The spectrum region is attributed to the photo-induced absorption of both CT and polarons. Through the fitting, the ratios of photoexcitations that undergo germinate or nongerminate recombination can be calculated and interpreted. Nevertheless, CT states are thought to decay in a few ns (germinate recombination), which is beyond the temporal resolution of the ns-TAS setup (~6 ns). Besides, monitoring GSB decay may be a more suitable approach in measuring the polaron dynamics since the polarons are generated in both the disordered region (more localized) and crystalline region (more delocalized) are expected to have different dynamics. On the other hand, the very broad PIA signal spanning 750 nm-1100 nm from polarons makes it difficult to monitor all their contributions. Hence we used the GSB signal instead. Another model commonly used in the literature by considering a single averaged recombination rate $R = k\bar{N}^\alpha$, where α is the recombination order and k is the recombination prefactor independent on the averaged carrier density $\bar{N}$.^{45,46} However this model was tested to poorly fit our dataset and it also lack a deep physical understanding of the recombination mechanism. As for understanding the polaron recombination mechanisms, there are always dispute on whether the polaron recombination at this time region is due to the Langevin process or due to the Shockely-Read-Hall like trap-assisted recombination.^{48,51,52} Based on the above points, it is of significance to build a new model that can well interpret the TAS polaron recombination in annealed P3HT:PCBM films under different excitation intensities and can account for the contribution from both the Langevin and SRH recombination. The two mechanisms may co-exist but only either one of them dominates when experimentalists observe them under different conditions, e.g., the illumination intensities.

Driven by these considerations, we build our model of polaron recombination consisting of both SRH (first-order) and Langevin (second-order) processes. As an approximation, we assume that the two processes occur independently. A fraction (f) of the initially generated charges undergo Langevin recombination while the rest ($1 - f$) undergo SRH recombination.^{34,170} In addition, under high fluence, a carrier concentration dependent mobility $\mu \propto N^\alpha$ arising from the energetic disorder in the DOS is usually necessary for modeling.^{161,171-174} where α is the concentration dependent exponent.¹⁷⁰ The expression of the model is as below:

$$\begin{aligned}
 \frac{dN_{\text{mon}}}{dt} &= -\gamma_1 N_{\text{mon}}^\alpha N_{\text{mon}} \\
 \frac{dN_{\text{bim}}}{dt} &= -\gamma_2 N_{\text{bim}}^\alpha N_{\text{bim}}^2 \\
 \frac{N}{N_0} &= ((1-f)^{-\alpha} + \alpha\gamma_1 N_0^\alpha t)^{-1/\alpha} + (f^{-(\alpha+1)} + (\alpha+1)\gamma_2 N_0^{(\alpha+1)} t)^{-1/(\alpha+1)} \\
 &= ((1-f)^{-\alpha} + k_1 t)^{-1/\alpha} + (f^{-(\alpha+1)} + k_2 t)^{-1/(\alpha+1)}
 \end{aligned} \tag{Eq. 4.3}$$

where N_{mon} and N_{bim} refers to the charges undergoing SRH (monomolecular) and Langevin (bimolecular) recombination, respectively; γ_1 and γ_2 are the recombination prefactors; and $k_1 = \alpha\gamma_1 N_0^\alpha$, $k_2 = (\alpha+1)\gamma_2 N_0^{(\alpha+1)}$. k_1 and k_2 are dependent on the recombination rates of SRH and Langevin processes, respectively.

Figure 4.14 Intensity-dependent ns-TAS dynamic of GSB at 560nm. Solid lines are the fitted curves.

Table 4.4 Parameters extracted from a global fit of the intensity dependent ns-TAS dynamics.

P3HT:AgNPs	γ_1 (cm ³ s ⁻¹)	γ_2 (cm ³ s ⁻¹)	α	f
Without AgNPs	$1.36 \pm 0.01 \times 10^{-19}$	$1.98 \pm 0.09 \times 10^{-41}$	0.42 ± 0.03	0.128 ± 0.001 (low)
				0.375 ± 0.001 (med)
				0.561 ± 0.002 (high)

Global fitting was done on the intensity dependent series of the dynamics. Three intensities were applied: $\sim 60 \mu\text{J}/\text{cm}^2$, $\sim 80 \mu\text{J}/\text{cm}^2$, $\sim 130 \mu\text{J}/\text{cm}^2$. The data is well fitted as seen in **Figure 4.14**. The extracted parameters are listed in **Table 4.4**. The concentration dependent exponent α for P3HT:PCBM is very close to the reported values.³⁴ From the fits, it is clear that the ratio of charges undergo Langevin process gradually become prominent under higher fluence in P3HT:PCBM system (as

indicated by the increase of f from 12.8% to 56.1%). This intensity dependent recombination may account for the conclusion of earlier reports' on either a negligible,^{27,149,175} or a dominant Langevin process in P3HT:PCBM.^{33, 34}

Next, the comparison of polaron dynamics between the control P3HT:PCBM and the hybrid films is made via the TAS dynamics results as shown in **Figure 4.15**.

Table 4.5 listed the fitting parameters for films with different AgNPs loading. The primary difference among the AgNP embedded cells and control cells is k_1 , which is determined by the trap density and capture coefficients. k_1 increases by 3 times with increased AgNP concentration while k_2 remains relatively insensitive. It is a clear indication of the increase of subgap trap density with the incorporation of AgNPs functioning as recombination centers for charge carriers.

Figure 4.15 *The ns-TAS dynamics of GSB at 560 nm of the P3HT:PCBM and AgNPs-P3HT:PCBM films. Solid lines are the fitted curves. The pump wavelength is 500 nm and the fluence $60 \mu\text{J cm}^{-2}$.*

Table 4.5 *Fitting parameters for the ns-TAS GSB decay monitored at 560nm using the model developed in this chapter.*

P3HT:AgNPs	$k_1 (1 \times 10^{-2} \text{ ns}^{-1})$	$k_2 (1 \times 10^{-3} \text{ ns}^{-1})$	α	f
1:0	0.65 ± 0.05	2.50 ± 0.13	0.43 ± 0.03	0.167 ± 0.003
1:1/16	0.51 ± 0.04	1.78 ± 0.09	0.36 ± 0.02	0.164 ± 0.003
1:1/8	0.96 ± 0.07	2.12 ± 0.11	0.43 ± 0.02	0.169 ± 0.002
1:1/4	1.59 ± 0.13	1.99 ± 0.12	0.55 ± 0.03	0.166 ± 0.003
1:1/2	1.42 ± 0.13	2.07 ± 0.13	0.49 ± 0.03	0.162 ± 0.002
1:1	1.95 ± 0.16	2.17 ± 0.14	0.57 ± 0.03	0.155 ± 0.002

The origin of these traps remains unclear. They may originate from the metal core of the AgNPs due to partial oleylamine-ligand coverage. As mentioned earlier,

traps may also exist in the functional groups of the ligand which capture the charges nearby. Topp *et. al.* had previously shown that gold nanoparticles (AuNPs) encapsulated with different ligands (*i.e.*, with dodecylamine, pyridine *etc*) all had undesirable effects on the PCE of P3HT:PCBM OSCs,¹⁵² however little fundamental conclusion can be got for the understanding of the trap origins. But it is not the focus of this study to unravel these dependencies. Future research should be done to clarify how these traps form.

4.4 Implication for design of hybrid plasmonic OPV

Embedding metallic nanostructures into the active layer of OPV devices provides a simple and efficient approach for boosting the OPV performance, where effects like strong EM field confinement and far field scattering can be exploited. Nevertheless, the effectiveness of the approach on improving the performance of OPV is usually convolved by a complex interplay of competing effects. A careful choice of the constituents and optimization of device is necessary in designing such hybrid plasmonic OPV devices. From the analysis of our experimental results, together with previous literature reports,^{78,80,87,152,176,177} several key factors can be summarized for the design of hybrid plasmonic OPVs:

(a) *Location of plasmonic NPs.* Due to the strong distance-dependence, the best way is to embed the plasmonic NPs inside the active layer.^{78,178,179} However, as concluded from charge dynamics measurements, charge carrier traps may be introduced through the ligands or the NPs. Although optical enhancement is achieved, these NPs may detrimentally affect the exciton,^{85,86 152} and polaron lifetimes.⁸⁷ Hence,

a practical way is to embed the NPs in the charge transport layers (e.g., PEDOT:PSS, ZnO *etc*) and as close as possible to the active layer.

(b) *NP size*. NP size plays an important role in the optical absorption of the active layer. It is admitted that an intermediate NP size (i.e., 30nm-60nm) is the optimized size for light harvesting in OPV.⁷⁸ Though smaller NPs (<20nm) can function as subwavelength antennas to couple light into the near field,¹⁷⁹ these smaller NPs have weak light scattering and possess a higher surface-to-volume ratio that may yield more charge trapping sites. Larger NP (>60nm) on the other hand may bring about excessive metallic absorption, disruption of the BHJ morphology and shunting problems.

(c) *Capping ligands/outer shells*. Capping ligands/shells should enable uniform dispersion of NPs in the active layer, otherwise unnecessary aggregation will disrupt the OPV morphology.^{87,152,180} The thickness of the capping ligand/shell is also of great significance. Too thin an outer layer will result in losses of photoexcitations via charge/energy transfer between organic materials and the metallic nanostructure.¹⁵² Too thick an outer shell on the other hand may impede charge transport and increase the resistance of the device. Given ligands are poorly decorated on NPs, NPs could still act as charge trapping sites.

4.5 Conclusion

In conclusion, a combination of electrical and optical characterization techniques was utilized to unveil the carrier dynamics and loss mechanisms in organic-ligand encapsulated AgNPs hybrid plasmonic OSCs. Although there is an increase of exciton

generation in these hybrid plasmonic OSCs (with exciton dynamics comparable to that of the control samples), it was found that the high trapping rate of the generated polarons limits the amount of free carriers in the hybrid systems. The carrier dynamics were investigated over the temporal regimes spanning that of generation, recombination, transport and extraction (i.e. over 7 orders of magnitude from 100 fs to 5 μ s) and they provide essential validation of the findings from the electrical characterization techniques. It was found that the traps introduced by AgNPs promote trap-assisted recombination and eventually degrade the performance of the hybrid plasmonic OSCs. These new insights into the hybrid plasmonic organic solar cells provide clear guidelines for the design of hybrid plasmonic OSCs.

CHAPTER 5. Plasmonic Nanocavity for Broadband Light Trapping

5.1 Introduction

As shown in the previous two chapters, embedding metallic nanoparticles into the active layer can fully exploit plasmonic effects to enhance light absorption. However, other problems such as increased trap densities may compromise such benefits. On the other hand, embedding them into the PEDOT:PSS spacer layer is a conservative way to improve the performance, where the enhancement is often limited. Experimentally, most of the reported enhancement is around 10-20%.^{65-67,73,74,77,78} Others reported an abnormal increase which may be attributed to improvement of other factors such as charge mobilities, contact, etc. For example, Kyungkon Kim and David L. Carroll shows small Ag nanoparticles can improve the performance of poly (3-octylthiophene) P3OT/C₆₀ by 50%-70% due to a better electric conductivity;⁸² Anthony J. Morfa *et al* demonstrated the P3HT:PCBM device could be boosted by 70% with incorporation of silver nanoparticles (Ag NPs),⁶⁶ nevertheless, we noticed the control efficiency is only 1.3%, which is much lower than commonly accepted control efficiency (>3%) in optimized cells. Other factors' such as amelioration may contribute to such anomalous increase.

Theoretically, Ricky B. Dunbar *et al* investigated the absorption of plasmonic solar cells in three configurations: (1) nanoparticles in the active layer; (2) nanostructured metallic electrode; and (3) in-scattering nanoparticles (e.g., in PEDOT:PSS layer). They used a 60nm PCPDTBT:PC₆₀BM active layer and

rectangular shaped Ag nanostructure as the standard modeling system. They found that only about 19% enhancement of absorption can be expected using dispersed silver nanoparticles, and the value drops to 13% using nanostructured electrode. In devices, the in-scattering configuration strongly limits the absorption of the active layer due to severe back-reflection.¹⁸¹ Zhuo Ye *et al* reported ~23% increase in absorption for a 160 nm thick P3HT:PCBM cell using periodic Ag nanowall gratings.¹⁸² Using interstitial lattice rather than square lattice patterned plasmonic nanostructures; Luzhou Chen *et al* demonstrated a further improvement in light absorption due to the stronger coupling of the LSPR among adjacent nanostructures and the coupling of plasmonic modes to guide modes.¹⁸³ In brief, experimental and theoretical results are in agreement with each other that the total light absorption enhancement over the broad absorption region of the active layer is limited to around 20% for an active layer larger than 60 nm. Further improvement becomes difficult by using above-mentioned mechanisms.

In this chapter, a mechanism known as plasmonic cavity resonance (PCR) is proposed to boost the OPV absorption with aluminium nanostructures. While the PCR concept is frequently used in applications such as plasmonic lasing,¹⁸⁴ sensing,¹⁸⁵ etc., rarely it has been used or mentioned in light harvesting for OPV devices.^{182,186} It has been shown that the plasmonic nano-patch cavities^{187,188} formed between the Al nanodisks and the Al cathode possess superior light scattering properties, resulting in enhanced light trapping in the ultrathin active layer. With respect to the control device with a 60 nm thick PCPDTBT:PC₆₀BM (Poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl) - 4H - cyclopenta [2,1-b:3,4-b']dithiophene-2,6-diyl]]:[6,6]-Phenyl-C61-butyric acid methyl ester) layer, integrated light absorption enhancements up to 40% can be expected in the plasmonic OPV device with an array of Al nanodisks.

The basic mechanism of the light trapping by using PCR in an OPV device is investigated using FDTD simulations. It is found PCR can leverage on the unique ability of surface plasmons to focus or confine broadband light in a nanocavity that support plasmon modes. The selection of materials, metallic structures is discussed and a viable strategy to develop low-cost, high efficient, ultra-thin plasmonic OPV devices is suggested. Furthermore, a combination of both optic and electric simulation is employed to predict the performance of the hybrid plasmonic OPV device. An improvement in device performance by 30% through the PCR light trapping strategy can be achieved.

5.2 The Physics of Plasmonic Cavity Resonance

5.2.1 Nano-patch cavity

Nanopatch cavities have been used in creating ultrasmall mode volume lasers operating at near infrared frequencies.^{189,190} Schematic of typical nanopatch cavities is displayed in **Figure 5.1**, which comprises of a circular or rectangular metal patch, a gain medium and a metal reflector. Surface plasmon is used to squeeze light in the cavity under diffraction limit. Besides, it has also been used for output beam shaping to realize single-lobe far-field output radiations with narrow beam waists.¹⁸⁹

The cavity can both sustain TM and TE modes. However, due to the characteristics of surface plasmon (TM mode wave), TE modes do not couple well with the surface plasmons. For circular nanopatch cavity, TM modes (TM_{mnp}) can be expressed as:¹⁹¹

$$\begin{aligned}
E_z(r, \phi, z) &= E_0 J_m(k_r r) \cos\left(\frac{p\pi}{h} z\right) \exp(\pm im\phi) \\
E_r(r, \phi, z) &= -\frac{p\pi/h}{k_r} E_0 J'_m(k_r r) \sin\left(\frac{p\pi}{h} z\right) \exp(\pm im\phi) \\
E_\phi(r, \phi, z) &= \mp im \frac{p\pi/h}{k_r} E_0 \frac{J_m(k_r r)}{k_r r} \sin\left(\frac{p\pi}{h} z\right) \exp(\pm im\phi)
\end{aligned} \tag{Eq. 5.1}$$

where h is the height of the cavity, $k_r^2 = (\omega_{mnp}/c)^2 \varepsilon - (p\pi/h)^2$, ω_{mnp} is the cavity resonance frequency and ε is the dielectric constant of the medium inside the cavity. J_m is the Bessel function of the first kind. m, n, p refer to the mode number in radial, polar and azimuthal directions, respectively.

Figure 5.1 A schematic of (a) circular and (b) nanopatch cavity Blue region is the gain medium sandwiched between two metal pieces.¹⁹⁰

The formula is derived for micropatch cavities in which effects like fringe effects can be neglected. For ultra-small nanoscale cavity, pure analytical formula may be hard to get for the cavity mode frequencies. There may be only one single fundamental mode existing in the cavity when the volume shrinks to certain size. Martin Kuttge *et al* argued that such lowest-order single mode are actually identical in nature to the plasmonic hot-spot geometries that are observed in particle dimmers, i.e., its localized, static mode.¹⁹²

5.2.2 PCR Simulation

In our effort to elucidate the physical principles of light trapping with the PCR, a simple simulation scenario was presented. As displayed in **Figure 5.2**, a single plasmonic nanodisk and an infinite plasmonic plane is sandwiched by an ultrathin dielectric layer. The configuration is rather like a metal-insulator-metal (MIM) type structure with one metal plane being replaced by a small nanodisk. The dielectric layer corresponds to the active layer in OPV. In order to create similar scenario with plasmonic OPV, we chose Al nanodisk, Al plane, and a dielectric layer with refractive index $n=2$, which is comparable to that of the BHJ layer in OPV. Al nanodisk is chosen to have a diameter (D) of 60nm and height (H) of 30 nm.

Figure 5.2 Schematic of the simulated structure with a single Al nanodisk in a nano-patch cavity configuration in (a) isometric view and (b) planar cross-sectional view.

To monitor the scattering property of the system, Q_{scat} is defined as the ratio of the scattered power to the product of the incident intensity with the geometrical cross section (i.e., the area of the particle projected on the substrate).¹⁹³ The scattered power is calculated by integrating the Poynting vector of the scattered field over a box enclosing the nanostructure. The scattering of the system is highly dependent on the

thickness of the dielectric layer. As shown in **Figure 5.3**, when the dielectric thickness (T) is smaller than or comparable to the diameter (D) of Al nanodisk (i.e. $T/D \leq 1$), the scattering spectrum exhibits two distinct peaks; with one relatively narrower peak at the bluer side (~ 400 nm- 420 nm) and the other broader one at the redder wavelengths. The blue peak is relatively invariant in position when the thickness of the dielectric layer changes. On the other hand, the red peak blue-shifts significantly when the active layer thickness increases. Once the thickness of the dielectric layer is larger than the diameter of the nanodisk ($T > D$), the two peaks merge to a single peak.

Figure 5.3 Normalized scattering cross-section of PCR with different active layer thickness.

To make it clear the origin of the two peaks, the electric field intensity distribution in the x - z plane was drawn for the configuration with a 30nm thick dielectric layer. As displayed in **Figure 5.4 (a)**, the blue peak (~ 410 nm) shows EM field lobes at both the top and bottom edges of the nanodisk, which is a typical quadruple plasmon resonance.¹⁹⁴ It can be regarded as a dipole-like resonance since this resonance originates from two dipoles that oscillate in phase with one dipole near

the top interface and the other at the bottom interface of the Al nanodisk (**Figure 5.4 (b)**). At this resonance, the E field concentrated mainly at the cladding side of the nanodisk. In OPV, there will be huge loss of light incident on the active layer since much light is focused on the cladding side (i.e., the PEDOT: PSS and ITO side).

Figure 5.4 Electric field intensity distribution (in log scale) and surface charge distribution (schematic) in the $x - z$ plane of (a,b) the blue peak and (c,d) the red peak.

The red peak's EM field distribution on the other hand, is mainly concentrated at the top edge of the nanodisk and extends over the dielectric layer (**Figure 5.4 (c)**). The x-y plane EM field distribution (**Figure 5.5**) is examined and found to be similar with a TM₁₁₀ mode of a circular nano-patch cavity.^{187,188}

Figure 5.5 *Electric field intensity distribution of the red peak in the x-y plane.*

To verify our conclusion on the physical origin of these two resonances, further simulations were performed. In the simulations, Al plane was removed to clarify the origin of the resonances. With the same Al nanodisk immersed in a uniform dielectric medium ($n=2$), the LSPR appears at ~ 440 nm, which is close to the position of the blue peak (~ 410 nm). It is evident that these two resonances are from a similar mechanism-, i.e., the blue peak is in fact a dipole-like resonance. The slightly difference in position between the LSPR of a single Al nanodisk and the one in the MIM configuration above should be attributed to the interaction between Al nanodisk and Al plane. As shown in **Figure 5.3**, when $T/D \geq 1$, the blue peak shifts to a position close to 440nm. It is reasonable to conclude that for much thicker active layer, the interaction between the nanodisk and the plane is negligible and the blue/red peaks merge to yield the LSPR of a single nanodisk.

The red resonance in MIM configuration above does not have any counterpart in the single nanodisk case, thus as it is claimed above it originates from a cavity resonance- resulting from the strong interaction between the two metal ends. An effective refractive index approximation (ERIA) following the report by Kuttge *et. al.*¹⁹⁵ is applied to the active layer to clarify its plasmonic cavity origin. This approach is intended for cavities formed by microdisk. For the large microdisks, one can expect more than one resonating mode confined in the cavity. As the disk diameter shrinks to dimensions much smaller than the wavelength of the incident light, only a single mode can be sustained.¹⁹⁵ From the dispersion relations of a typical planar metal-insulator-metal (MIM) structure, an effective refractive index, n_{eff} , can be derived:

$$\tanh(k_d d / 2) = \begin{cases} -\frac{\varepsilon_d k_m}{\varepsilon_m k_d} & , \text{ for the anti-symmetric mode} \\ -\frac{\varepsilon_m k_d}{\varepsilon_d k_m} & , \text{ for the symmetric mode} \end{cases} \quad (\text{Eq. 5.2})$$

where $k_d = \sqrt{k_{sp}^2 - \varepsilon_d \frac{\omega^2}{c^2}} = \sqrt{n_{eff}^2 - \varepsilon_d} \frac{\omega}{c}$, $k_m = \sqrt{k_{sp}^2 - \varepsilon_m \frac{\omega^2}{c^2}} = \sqrt{n_{eff}^2 - \varepsilon_m} \frac{\omega}{c}$, d is the thickness of active layer, ε_d and ε_m are the real parts of dielectric constants of the active layer and the metal (i.e. Al plane), respectively; k_d and k_m being the wavevectors of the propagating waves in the active layer and metal and k_{sp} being the wavevector of the surface plasmons; ω being the frequency; and c being the speed of light.

The dielectric layer and Al plane are then substituted by a slab with $n_{eff}(\omega)$ in a cylindrical region central to the Al nanodisk as shown in **Figure 5.6**. To minimize the number of variables in these simulations, the slab's effective radius is chosen to be 42

nm as an average number of the interactions occurring between the Al nanodisk and Al plane when the thickness of the active layer changes.

Figure 5.6 Simulated peak positions of the blue and red resonance using the original structure shown in Fig. 5.2 and that of the ERIA structure shown in the inset for various active layer thicknesses.

For each thickness of the active layer, an effective index is computed from the SPP dispersion relations before applying to the FDTD simulation. The scattering peak is found to corresponds well with the red resonance of the MIM structure in position as plotted in **Figure 5.6**. Hence, it is plausible to conclude the red resonance in MIM structure does originate from the fundamental cavity mode, likely to be that of the TM₁₁₀ mode. Similar conclusions were acquired with a simulation of Ag nanodisk on top a Si substrate with air as the cladding.^{196,197} – they claimed a short wavelength resonance as dipole-like space modes at the Ag-air interface and long wavelengths modes to be geometric resonance of the SPPs at the Ag-substrate interface.

As discussed above, light trapping is affected by the plasmonic cavity resonance and it is highly beneficial for light harvesting in the active layer. On the other hand,

the near field of the dipole-like mode does not overlap significantly with the active layer, and consequently light concentration in the active layer is reduced. The destructive interference of the incident and scattered light (i.e. Fano interference)^{198,199} at the blue side of the LSPR resonance will result in optical losses. For a Ag nanodisk, its LSPR appears at around 500-600 nm, which overlaps with the absorbing region of most active layer. Loss will occur for light below the LSPR ($\lambda < \lambda_{LSPR}$) and results in a reduction of the broadband absorption enhancement. For the case of Au nanodisk, since its LSPR is located in the red spectral region, the PCR peak is likely to be located deeper in the red. Hence, the advantage of PCR is not possible to contribute much to light absorption for most active layer with a bandgap of 1.6-2.0 eV.

Al is a suitable metal for the PCR approach to light harvesting. The optical losses due to the dipole-like plasmon resonance mode is minimal since the resonance is located at ~400nm where the solar irradiation is relatively weak and the active layer exhibits weak absorbance. Al PCR on the other hand provide good spectral match with the active layer absorption band, especially for low bandgap OPVs. Although Al SPR is limited to high damping and thus the PCR formed is not strong in confining light compared to Ag, it is still a nice choice in terms of spectral matching and fabrication cost. The choice of nanodisk-shape is also important in terms of confining more light into the cavity. The thin, circular metallic nanostructure provides stronger forward scattering compared to structures of other shapes such as triangles, spheres, hemispheres, *etc.*²⁰⁰

5.3 Plasmonic Cavity Resonance Applied in an Organic Photovoltaic Device

Following the above analysis and insight, the PCR is applied to a real device scenario. As depicted in **Figure 5.7 inset**, the configuration of the plasmonic OPV comprises a 100 nm Al cathode, a 60 nm active layer, an array of Al nanodisks embedded in the 20nm PEDOT: PSS layer, a 100nm thick ITO anode and the glass substrate from top to bottom. Light is incident from the glass side using a plane wave source from 400 nm to 900 nm. Outside the region, the absorption or solar irradiation is negligible and is not considered. The standard AM1.5 solar spectrum is used as the simulation source. The refractive indices of ITO, PEDOT:PSS and polymer-PCBM blends used are obtained from references²⁰¹⁻²⁰³. The light absorption enhancement is defined by:

$$Enh = \frac{\int_0^\infty [\alpha(\lambda) - \alpha_0(\lambda)] \Phi(\lambda) d\lambda}{\int_0^\infty \alpha_0(\lambda) \Phi(\lambda) d\lambda} \quad (\text{Eq. 5.3})$$

where $\alpha(\lambda)$ and $\alpha_0(\lambda)$ are the absorption coefficients of the active layer in the control device and the plasmonic device, respectively; $\Phi(\lambda)$ is the photon flux per wavelength of the AM1.5 spectrum.

5.3.1 Thickness Dependence

The absorption enhancement versus active layer thickness is displayed in **Figure 5.7**. The periodicity P is fixed to 250 nm. It is shown that the absorption enhancement drops rapidly when the active layer thickness increases from 20 nm to 60 nm. For $T > 60$ nm, losses may replace enhancement as the PCR is so weak that light

confinement via this approach can no longer compensate the metallic absorption and back reflection losses from Al nanodisk.

Figure 5.7 The absorption enhancement versus different active layer thicknesses for various active layer materials. Inset shows a schematic of a representative section of the hybrid OPV device with one Al nanodisk.

PCR is thereby limited to its highly thickness dependence. To create PCR, the diameter of nanodisk should be comparable or larger than that of the active layer thickness. On the other hand, too large a diameter of the nanodisk would incur high loss via metallic absorption and back reflection. Hence, PCR is suitable for ultrathin active layers ($< \sim 60\text{nm}$).

It is also found that the PCPDTBT:PC₆₀BM active layer exhibits the highest absorption enhancement over the range 45 – 70 nm active layer thickness which can be attributed to its lower absorption coefficient resulting in a less lossy plasmonic cavity resonance. Light can travel in the cavity multiple times and absorption enhancement is the best.

5.3.2 Periodicity Dependence

The periodicity dependence is examined based on the 60 nm thick PCPDTBT:PC₆₀BM active layer. With the periodicity varying from 100 to 500 nm, the absorption enhancement reaches a maximum at around 250 nm as displayed in **Figure 5.8**. Due to the strong scattering property, the effective cross section of plasmonic nanostructures is much larger than their geometrical cross section.¹⁹⁴ When the nanodisk density is high ($P < 250$ nm), the optical loss due to metallic absorption, back scattering is strong enough to be compensated the benefit by forward scattering and PCR light trapping. On the other hand, when $P > 250$ nm, the density of scattered center and cavity decreases and it results in a decrease of the enhancement.

Figure 5.8 The absorption enhancement of PCPDTBT:PC₆₀BM active layer as a function of the Al nanodisk periodicity. The Al nanodisk's parameters used are: $D = 60$ nm, $H = 20$ nm.

5.3.3 Diameter Dependence

To seek the diameter effect on the light absorption enhancement, several diameters were used in the simulation. As D is increased from 60 nm to 80 nm and 100 nm, the light harvesting of the active layer becomes more efficient (**Figure 5.9 (a)**). Absorption enhancement compared to the control cell is 9.48%, 27.01%, and 40.85% respectively. If the Al cathode is removed, intuitively, the PCR will not form, and the light trapping by PCR will not be present. As seen in **Figure 5.9 (b)**, the absorption enhancement from 600 nm-900 nm disappears. The interaction between nanodisks and metal plane (i.e., the formation of PCR) is sensitive to the thickness of the active layer (T) and the diameter of the nanodisk (D) as illustrated above. When D is larger or comparable to T , the interaction is strong enough to form a plasmonic cavity resonance. The larger the D , the stronger the plasmonic cavity resonance would be. This can be visualized by the E field distribution as displayed in **Figure 5.10**. With the increase in diameter, the light is more strongly confined in the active layer. For even larger diameters (e.g., 120 nm), the light absorption starts to drop. (-18.7%) This can be ascribed to several reasons: (1) a stronger back-reflection by large nanodisk and (2) a mismatch of the plasmonic cavity resonance position with the absorption bands of the active layer. This latter effect can be seen from **Figure 5.3** where both the dipole-like (blue) peak and the PCR (red) peak redshifts as the ratio of T/D is reduced (i.e. here T is fixed at 60 nm).

Figure 5.9 (a) Absorption in the PCPDTBT: PC60BM active layer with different Al nanodisk diameters. (b) Absorption in the PCPDTBT: PC60BM active layer with different Al nanodisk diameters, but without the Al cathode

Figure 5.10 E field distribution (in log scale) in the x-z plane of the PCR formed by nanodisks with diameter (a) 60 nm (b) 80 nm and (c) 100 nm.

5.3.4 Shape Dependence

Several other shapes of Al nanostructures were compared to that of nanodisks (**Figure 5.11**). When the optimized nanodisks are replaced by oblate spheroids and cuboids with similar dimensions (spheroid: major axis radius: 50 nm, minor axis radius: 10 nm, periodicity: 300 nm; cuboid: $a=b=100$ nm, $c=20$ nm). A weaker enhancement of 17.44% was acquired for spheroids. The decrease in absorption enhancement can be mainly ascribed to the curved surface of the spheroid, which mitigates the formation of strong plasmonic cavity resonance with the Al cathode unlike the nanodisks. As for cuboids, the light absorption enhancement is comparable to that of nanodisks, indicating rectangle plasmonic cavity is also strongly formed that benefit the light harvesting.

Figure 5.11 Absorption of AM 1.5 solar photons in the PCPDTBT: PC60BM active layer with different shapes of Al nanostructures (cuboid, disk, spheroid).

5.3.5 Plasmonic Metal Dependence

Figure 5.12 examines several commonly used metals for light harvesting in OPV. Silver still yields the best performance, with an increase of 47.0% enhancement in

light absorption. Due to less damping of the SPR, silver can provide the strongest plasmonic effects compared to other metals. It is thus even a less match of the spectrum compared to aluminum; silver can still provide a promising light absorption enhancement. Aluminum is the second best metal, with a light absorption enhancement almost comparable with silver. It prevails over silver in the visible range for light harvesting as shown in **Figure 5.12** due to reasons analyzed above. Nevertheless, in the NIR region, the stronger scattering due to strong SPR makes silver exceeds aluminum in light harvesting. Gold ranks after aluminum, with an increase of 28.0% with a promising light enhancement only in NIR region as discussed above. Copper degrades the light absorption by 46.1%. The strong parasite metallic absorption in the visible region makes it improper for light harvesting.

Figure 5.12 Absorption of AM 1.5 solar photons in the PCPDTBT: PC60BM active layer with different metallic nanodisks.

5.4 Device Simulation

A combination of optical and electrical simulation is used to evaluate the performance of hybrid plasmonic OPV device. Basic process is depicted in **Figure 5.13**. A hybrid plasmonic OPV device can be discretized into many sub-cells; every sub-cell has a thickness same with the whole devices, and an area with the size depending on the mesh size. Every cell works independent of each other while the whole OPV device performance is an integration of the current-voltage characteristics of all the sub-cells. Firstly, the FDTD simulation is carried out, from which the optical distribution along the z axis for a certain sub cell is acquired. Then, the optical distribution along the z axis is input into the electric model and the current-voltage characteristics of the sub cell can be extracted. Finally, all the current density of the sub cells are integrated along the x and y axis and the performance of the whole device is acquired.

Figure 5.13 Diagram of the optic-electric simulation process.

5.4.1 Model

Modelling a BHJ OPV device where the donor and acceptor are interpenetrate with each other forming a bi-continuous network is challenging. Koster *et al.* adopted a metal-insulator-metal (MIM) picture to successfully depict the I-V behavior of the OC1C10-PPV / PCBM devices.²⁰⁴ Later, the model has been widely developed and used in other OPV systems.²⁰⁵⁻²⁰⁹ In the picture, the BHJ active layer is treated as a single phase semiconductor with the LUMO of the acceptor and the HOMO of the donor as valence and conduction band, respectively. (Figure 5.14) The semiconductor itself is sandwiched between two electrode which has ohmic contact with the semiconductor. The bandgap E_g is the energy difference between the LUMO of the acceptor and the HOMO of the donor.

Figure 5.14 Schematic of the energy level in a BHJ OPV in the MIM picture under a bias V_a .

Charge carriers' motion is considered to be affected by both drift and diffusion. Drift and diffusion of the charge carrier is driven by the internal electric field and carrier concentration, respectively. Meanwhile, charge carriers are undergoing

recombination which decreases the extracted current density. For simplicity, only Langevin process is involved in the recombination, i.e., free carrier-carrier bimolecular recombination. The generation of the free charge carriers is considered to be totally mediated by the charge transfer state at the donor-acceptor interface, i.e., the exciton dissociates across the interface forming a bound e-h pair and subsequently dissociate into free charges. The dissociation probability is determined by the Onsager-Braun model. The CT state (bound electron-hole pair) may recombine to the ground state with a decay rate k_f or dissociate into free charges. The probability for the CT state to dissociate into free charges is given by:

$$p(x, T, F) = \frac{k_{\text{diss}}(x, T, F)}{k_{\text{diss}}(x, T, F) + k_f(T)} \quad (\text{Eq. 5.4})$$

where k_{diss} is the dissociation rate that competes with the recombination rate k_f of the bound e-h pair. k_{diss} is dependent on the e-h distance (x) temperate (T) and electric field (F) and is derived as follow:

$$\begin{aligned} k_{\text{diss}}(x, T, F) &= \frac{3R}{4\pi a^3} e^{-E_B/k_B T} J_1(2\sqrt{-2b}) / \sqrt{-2b} \\ &= \frac{3R}{4\pi a^3} e^{-E_B/k_B T} (1 + b + b^2 / 3 + \dots) \end{aligned} \quad (\text{Eq. 5.5})$$

where E_B is the binding energy of electron-hole pair; $b = q^3 F / (8\pi\epsilon k_B^2 T^2)$, F is the field strength and J_1 is the 1st order Bessel function. In disordered polymer-fullerene system, electron-hole pair separating distance is not constant. Normalized distribution can be used to depict the e-h distance:

$$\begin{aligned} P(a, T, F) &= \int_0^\infty p(x, T, F) f(a, x) \\ f(a, x) &= \frac{4}{\sqrt{\pi} a^3} x^2 e^{-x^2/a^2} \end{aligned} \quad (\text{Eq. 5.6})$$

Langevin recombination is expressed as:

$$R = \frac{q}{\langle \varepsilon \rangle} \langle \mu \rangle (np - n_{\text{int}}^2) \quad (\text{Eq. 5.7})$$

where $n_{\text{int}} = N_c \exp(-E_{\text{gap}} / 2V_t)$, is the intrinsic carrier density of electrons and holes. $\langle \mu \rangle$ and $\langle \varepsilon \rangle$ are the spatially averaged sum of hole and electron mobilities, and the dielectric constant, respectively.

The basic equation set used in the simulation is a combination of Poisson equation, current continuity equations, and drift-diffusion equations:

$$\begin{aligned} \frac{\partial^2}{\partial x^2} \psi(x) &= \frac{q}{\varepsilon} [n(x) - p(x)], \\ \frac{\partial}{\partial x} J_n(x) &= qU(x), \\ \frac{\partial}{\partial x} J_p(x) &= -qU(x), \\ J_n(x) &= -qn\mu_n \frac{\partial}{\partial x} \psi + qD_n \frac{\partial}{\partial x} n, \\ J_p(x) &= -qp\mu_p \frac{\partial}{\partial x} \psi - qD_p \frac{\partial}{\partial x} p \end{aligned} \quad (\text{Eq. 5.8})$$

where $\psi(x)$ is the electric potential related to the carrier density $n(x)$ and $p(x)$, the current density $J_n(x)$ and $J_p(x)$ is determined by the net generation rate of the charge carriers. $D_{n,p} = \mu_{n,p} V_t$ are the carrier diffusion coefficients following the Einstein relation.²¹⁰

Solving for the equation set follows an iteration scheme developed by Gummel.²¹¹ As shown in **Figure 5.15**, in Gummel's iteration, an initial guess of the parameters is made and a correction $\delta\psi$ is calculated to the guessed potential. The new potential is then input to the equations and new carrier densities are acquired. The process is repeated until convergence reaches.

Figure 5.15 Flow diagram of the simulation process.²⁰⁴

5.4.2 Simulation Results & Discussion

Most reports focused on the performance of PCPDTBT:PC₇₀BM while the PCPDTBT:PC₆₀BM is rarely reported. For simplicity, we adapted the electric parameters reported for standard PCPDTBT:PC₇₀BM to that of PCPDTBT:PC₆₀BM. Parameters are listed in **Table 5.1**.

Table 5.1 Parameters of PCPDTBT:PC₆₀BM used in the simulation

E_g (eV)	ε (ε_0)	N_{eff} (cm ⁻³)	a (nm)	k_f (s ⁻¹)	μ_e (cm ² /Vs)	μ_h (cm ² /Vs)
1.0	3.4	2.5×10^{19}	1.47	1×10^5	6×10^{-3}	1×10^{-4}

Figure 5.16 presents the simulated J - V curves of plasmonic OPV devices. Incorporation of Al nanodisks leads to an improvement in performance from 2.06% to

2.69% in 60 nm-thick PCPDTBT:PC₆₀BM device. The major improvement can be ascribed to the increase in short circuit current density (J_{sc}) from 5.62 to 7.46 mAcm⁻². Fill factor (FF) slightly drops for the plasmonic cell, which is attributed to stronger Langevin recombination when confining light in the active layer. The open-circuit voltage (V_{oc}) remains almost unchanged.

Figure 5.16 Simulated J - V characteristics of the PCPDTBT:PC60BM reference and hybrid plasmonic OPV cells.

Table 5.2 Simulated performance of the control and hybrid plasmonic PCPDTBT:PC60BM OPV devices.

	PCE (%)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF
Reference	2.1	-5.62	0.56	0.66
With Al nanodisk	2.7	7.46	0.57	0.63

5.5 Conclusions

In summary, a low-cost and high efficiency broadband light trapping strategy has been proposed in thin film a heterojunction OPV device which is achieved by embedding an array of Al nanodisks between ITO anode and the ultra-thin organic active layer. Plasmonic nanocavities formed between Al nanodisks and the underlying Al cathode exhibit superior light trapping properties, leading to enhanced absorption in the ultrathin active layer in the gap. Numerical simulations were presented to understand the basic mechanism of light trapping and the physics of PCR in the MIM structure of an OPV device. The structure-performance relationships for the hybrid plasmonic OPV devices have been established that will enable the tuning of light harvesting properties by appropriate selection of materials and optimal structure design. A coupling of optic and electric simulation is also used to evaluate the performance of the hybrid plasmonic OPV device based on the PCR design which found a similar increase of performance with that of light absorption.

CHAPTER 6. Conclusions and Future Work

6.1 Conclusions

The concept of hybrid plasmonic OPV, has gained substantial interests in the research field since it was proposed. The commercialization of organic solar cells may be realized soon with the aid of plasmonic nanostructures.

In this thesis, a comprehensive study on hybrid plasmonic OPV systems is presented. Metallic nanostructures were incorporated into PEDOT:PSS hole transporting layer or the active layer of OPV; Optical properties were examined using ultrafast spectroscopy and correlated with device electric properties. Further design of plasmonic OPV was also investigated to optimize light absorption of the active layer.

When the plasmonic nanostructures are embedded in PEDOT:PSS layer, it is found that they can generally boost light absorption in the active layer; thereby increasing the short circuit current density by 5%- 23%. The localized surface plasmon resonance is attributed to such enhancement. Strong local field can be generated when the light frequency is near the resonance of the localized surface plasmon, and this can benefit light absorption for polymer molecules in the vicinity. Besides, the strong forward light scattering by these metallic nanostructures also favors light absorption in the active layer through high-angle and multi-scattering. The percentage of forward scattered light highly depends on the shape and size of nanostructures and should be designed carefully. Furthermore, the effect of surface

plasmon or the plasmonic nanostructures on the excitonic and polaronic properties were also investigated. Direct contact of plasmonic nanostructure with organic polymer will speed up their exciton decay and also increase their photoluminescence intensity. This process often involves the Purcell effect and an increase scattering/local field. Non-radiative channels should also be present which includes the Foster energy transfer and/or Dexter charge transfer. However they are difficult to separate from radiative decay increase. Inserting PEDOT:PSS spacer layer between plasmonic nanostructures and organic active layer will quench the effect to some extent, depending on how thick the spacer layer is and how well it protects the nanostructures. The interaction of surface plasmon and exciton in polymer:PCBM blend however is negligible since the polymer exciton is very rapidly quenched by PCBM through charge transfer. There is no evidence showing any obvious interaction occurring between the surface plasmons in the metallic nanostructure encapsulated by PEDOT:PSS layer and polarons. This implies that the surface plasmon and polaron usually cannot interact with each other in a long range (>several nm) if they have. Since there is little modification of exciton and polaron properties in polymer:PCBM blend when plasmonic nanostructures are embedded in PEDOT:PSS layer, it means that this approach can increase the short circuit current while ensuring a good V_{oc} and FF.

When plasmonic nanostructures are directly incorporated into the active layer, the issue will become more complicated. For oleylamine-capped silver nanoparticles with size 25-30 nm blended with the standard annealed P3HT: PCBM films and devices, the device performance degraded resulting in drops in the short circuit current density, fill factor and open circuit voltage. Exciton generation is found to be boosted with the aid of the silver nanoparticles in P3HT:PCBM. Exciton dynamics is

negligibly affected in polymer or polymer:PCBM blend. However, excitons cannot be equivalently translated into free polarons. It is suspected that there may be some traps brought in due to silver nanoparticles and can rapidly trap the polarons once they are generated near the traps. The presence of the traps is uncovered by examining the polaron dynamics over time from ns to μ s, when polarons in the hybrid films undergo faster recombination. The faster recombination was modeled and attributed to faster trap-assisted recombination due to more traps present. The spectroscopic results are congruent with the electrical characterizations.

To further increase the light absorption of OPV using plasmonic nanostructures while not affecting the exciton/polaron dynamics, a novel light-trapping concept was also developed for plasmonic nanostructures in PEDOT:PSS layer. In this approach, plasmonic cavity resonance was proposed to trap light in the active layer. Such attractive light trapping strategy can be acquired by simply placing carefully designed aluminum nanodisks in the PEDOT:PSS layer which interact with the aluminum cathode and form strong plasmonic cavity between them. The ultrathin active layer between the two aluminum pieces can then be under the influence of strong EM field and absorb light as much as possible. A study based on 60nm thick PCPDTBT: PCBM active layer found solar light absorption can be increased by 40%. Electrical modeling was also integrated with optical modeling of the hybrid plasmonic OPV system for the first time. The light absorption enhancement was found to correspond to a performance enhancement by 30%. Further improvement of the device performance may be also achieved with silver nanostructure formed cavity.

6.2 Future work

Through the studies using a variety of techniques, a better understanding on the mechanisms of performance improvement or losses has been provided. Yet, several issues still need be solved in plasmonic OPV and should be considered in the future of study.

(a) *Periodic metallic nanostructure fabrication technique.* Nanosphere lithography provides us an easy and cheap way to fabricate large scale periodic nanostructures. However, a lot of defects exist in the periodic array fabricated using this technique. In addition, the shape of the nanostructures is limited. For example, nanodisk array is proven to better in light trapping, nevertheless, the fabrication of it is difficult. A more versatile, easier and more promising nanostructure fabrication technique is needed to further develop the hybrid plasmonic organic solar cells. For example, using anodic aluminum oxide (AAO) as template, plasmonic nanoparticles array with disk-like shape can be achieved.⁶⁸ Other techniques such as sparse colloidal lithography (SCL)²¹², hole-mask colloidal lithography (HCL)²¹², reactive ion etching (RIE)⁹³ will also be useful in providing us versatile nanostructure arrays.

(b) *Ligands effects.* Currently, we are still not clear about how ligands covering the metallic nanoparticles affect the device performance. Further investigation is necessary to clarify this issue so that embedding plasmonic nanostructures into the active layer will become more convenient and promising. Possible candidates of the ligands include: polyvinylpyrrolidone (PVP), long chain

thiols (e.g., dodecanethiol), oleic acid, other amines (e.g., dodecylamine) and so on.

Figure 6.1 Chemical structures of several proposed ligands: PVP, dodecylamine, dodecanethiol and oleic acid.

(c) *Interaction between CT states and surface plasmon.* The organic systems covered in this thesis have very high charge transfer efficiencies, i.e., most of the excitons generated can dissociate into charges. For annealed P3HT:PCBM, reported charge transfer efficiency is around 90%^{34,111}; for PCDTBT:PCBM, an internal quantum efficiency of 100% was reported.²¹³ In other systems, such as PCPDTBT:PCBM, MEH-PPV:PCBM, APFO-3:PCBM systems, strong geminate recombinations limits the charge transfer efficiencies.^{214,215}
^{216,217} An interesting question would be if the surface plasmon can assist exciton dissociation in these systems. Two-photon photoemission (2PPE) and time-resolved two-photon photoemission (TR-2PPE) spectroscopies would allow us to probe the CT states of the donor acceptor species and their interaction with surface plasmons.⁷² These techniques are under development in our group and we expect that new physical insights can be uncovered using them.

Figure 6.2 Chemical structures of several proposed polymers: PCPDTBT, MEH-PPV, APO3.

Figure 6.3 Schematic of 2PPE setup and working mechanism.

(d) Further design optimization of broadband light-trapping plasmonic nanostructures. In a bid to further improve the light absorption in organic solar cell, the design of nanostructures using simulation would be very necessary. Different nanoantennae will be designed to best focus light, such as bowtie type nanoantennae, trapezoid array, etc.²¹⁷

Bowtie

Trapzoid

Figure 6.4 *Proposed plasmonic nanostructures for light harvesting in organic solar cells: (a) bowtie nanoantennae and (b) trapezoid array.*

References

- (1) Ghosh, A. K.; Feng, T. *J. Appl. Phys.* **1973**, *44*, 2781.
- (2) Chamberlain, G. A. *Solar Cells* **1983**, *8*, 47.
- (3) Nunzi, J. M. *C. R. Phys.* **2002**, *3*, 523.
- (4) Hoppe, H.; Sariciftci, N. S. *J. Mater. Res.* **2004**, *19*, 1924.
- (5) Chidichimo, G.; Filippelli, L. *International Journal of Photoenergy* **2010**.
- (6) Service, R. F. *Science* **2011**, *332*, 293.
- (7) You, J. B.; Dou, L. T.; Yoshimura, K.; Kato, T.; Ohya, K.; Moriarty, T.; Emery, K.; Chen, C. C.; Gao, J.; Li, G.; Yang, Y. *Nature Communications* **2013**, *4*.
- (8) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.
- (9) Ko, C. J.; Lin, Y. K.; Chen, F. C.; Chu, C. W. *Appl. Phys. Lett.* **2007**, *90*.
- (10) Zhu, Z.; Waller, D.; Gaudiana, R.; Morana, M.; Muhlbacher, D.; Scharber, M.; Brabec, C. *Macromolecules* **2007**, *40*, 1981.
- (11) Park, S. H.; Roy, A.; Beaupre, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photonics* **2009**, *3*, 297.
- (12) Liang, Y. Y.; Xu, Z.; Xia, J. B.; Tsai, S. T.; Wu, Y.; Li, G.; Ray, C.; Yu, L. P. *Advanced Materials* **2010**, *22*, E135.
- (13) Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E. D. *Progress in Photovoltaics* **2012**, *20*, 12.
- (14) Wang, D. H.; Kim, J. K.; Seo, J. H.; Park, O. O.; Park, J. H. *Sol. Energy Mater. Sol. Cells* **2012**, *101*, 249.
- (15) Peters, C. H.; Sachs-Quintana, I. T.; Kastrop, J. P.; Beaupre, S.; Leclerc, M.; McGehee, M. D. *Adv. Energy Mater.* **2011**, *1*, 491.
- (16) Sun, Y. M.; Takacs, C. J.; Cowan, S. R.; Seo, J. H.; Gong, X.; Roy, A.; Heeger, A. J. *Advanced Materials* **2011**, *23*, 2226.
- (17) Yun, J. M.; Yeo, J. S.; Kim, J.; Jeong, H. G.; Kim, D. Y.; Noh, Y. J.; Kim, S. S.; Ku, B. C.; Na, S. I. *Advanced Materials* **2011**, *23*, 4923.
- (18) Moujoud, A.; Oh, S. H.; Hye, J. J.; Kim, H. J. *Sol. Energy Mater. Sol. Cells* **2013**, *111*, 216.
- (19) Hau, S. K.; Yip, H. L.; Baek, N. S.; Zou, J. Y.; O'Malley, K.; Jen, A. K. Y. *Appl. Phys. Lett.* **2008**, *92*.
- (20) Sondergaard, R. R.; Makris, T.; Lianos, P.; Manor, A.; Katz, E. A.; Gong, W.; Tuladhar, S. M.; Nelson, J.; Toumi, R.; Sommeling, P.; Veenstra, S. C.; Rivaton, A.; Dupuis, A.; Teran-Escobar, G.; Lira-Cantu, M.; Sapkota, S. B.; Zimmermann, B.; Wurfel, U.; Matzarakis, A.; Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2012**, *99*, 292.
- (21) Osterbacka, R.; An, C. P.; Jiang, X. M.; Vardeny, Z. V. *Science* **2000**, *287*, 839.
- (22) Brown, P. J.; Thomas, D. S.; Kohler, A.; Wilson, J. S.; Kim, J. S.; Ramsdale, C. M.; Sirringhaus, H.; Friend, R. H. *Physical Review B* **2003**, *67*.
- (23) Piris, J.; Dykstra, T. E.; Bakulin, A. A.; Loosdrecht, P. H. M. v.; Knulst, W.; Trinh, M. T.; Schins, J. M.; Siebbeles, L. D. A. *The Journal of Physical Chemistry C* **2009**, *113*, 14500.
- (24) Sheng, C. X.; Tong, M.; Singh, S.; Vardeny, Z. V. *Physical Review B* **2007**, *75*, 085206.
- (25) Hwang, I.-W.; Moses, D.; Heeger, A. J. *J. Phys. Chem. C* **2008**, *112*, 4350.
- (26) Guo, J.; Ohkita, H.; Benten, H.; Ito, S. *Journal of the American Chemical Society* **2010**, *132*, 6154.
- (27) Banerji, N.; Cowan, S.; Leclerc, M.; Vauthey, E.; Heeger, A. J. *Journal of the American Chemical Society* **2010**, *132*, 17459.

-
- (28) Hallermann, M.; Kriegel, I.; Da Como, E.; Berger, J. M.; von Hauff, E.; Feldmann, J. *Adv. Funct. Mater.* **2009**, *19*, 3662.
- (29) Clarke, T. M.; Durrant, J. R. *Chemical Reviews* **2010**, *110*, 6736.
- (30) Loi, M. A.; Toffanin, S.; Muccini, M.; Forster, M.; Scherf, U.; Scharber, M. *Adv. Funct. Mater.* **2007**, *17*, 2111.
- (31) Gould, I. R.; Young, R. H.; Mueller, L. J.; Albrecht, A. C.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8188.
- (32) Tvingstedt, K.; Vandewal, K.; Gadisa, A.; Zhang, F.; Manca, J.; Inganäs, O. *J. Am. Chem. Soc.* **2009**, *131*, 11819.
- (33) Faist, M. A.; Kirchartz, T.; Gong, W.; Ashraf, R. S.; McCulloch, I.; de Mello, J. C.; Ekins-Daukes, N. J.; Bradley, D. D. C.; Nelson, J. *J. Am. Chem. Soc.* **2011**, *134*, 685.
- (34) Howard, I. A.; Mauer, R.; Meister, M.; Laquai, F. d. r. *Journal of the American Chemical Society* **2010**, *132*, 14866.
- (35) Jamieson, F. C.; Agostinelli, T.; Azimi, H.; Nelson, J.; Durrant, J. R. *Journal of Physical Chemistry Letters* **2010**, *1*, 3306.
- (36) Grzegorzczak, W. J.; Savenije, T. J.; Dykstra, T. E.; Piris, J.; Schins, J. M.; Siebbeles, L. D. A. *J. Phys. Chem. C* **2010**, *114*, 5182.
- (37) Blom, P. W. M.; Mihailetschi, V. D.; Koster, L. J. A.; Markov, D. E. *Advanced Materials* **2007**, *19*, 1551.
- (38) Hwang, I. W.; Moses, D.; Heeger, A. J. *J. Phys. Chem. C* **2008**, *112*, 4350.
- (39) Ohkita, H.; Cook, S.; Astuti, Y.; Duffy, W.; Tierney, S.; Zhang, W.; Heeney, M.; McCulloch, I.; Nelson, J.; Bradley, D. D. C.; Durrant, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 3030.
- (40) Shoaee, S.; Clarke, T. M.; Huang, C.; Barlow, S.; Marder, S. R.; Heeney, M.; McCulloch, I.; Durrant, J. R. *J. Am. Chem. Soc.* **2010**, *132*, 12919.
- (41) Bakulin, A. A.; Rao, A.; Pavelyev, V. G.; van Loosdrecht, P. H.; Pshenichnikov, M. S.; Niedzialek, D.; Cornil, J.; Beljonne, D.; Friend, R. H. *Science* **2012**, *335*, 1340.
- (42) Grancini, G.; Maiuri, M.; Fazzi, D.; Petrozza, A.; Egelhaaf, H. J.; Brida, D.; Cerullo, G.; Lanzani, G. *Nat. Mater.* **2013**, *12*, 29.
- (43) Deibel, C.; Wagenpfahl, A.; Dyakonov, V. *Phys. Rev. B* **2009**, *80*.
- (44) Juska, G.; Genevicius, K.; Nekrasas, N.; Sliuzys, G.; Dennler, G. *Appl. Phys. Lett.* **2008**, *93*.
- (45) Shuttle, C. G.; O'Regan, B.; Ballantyne, A. M.; Nelson, J.; Bradley, D. D. C.; Durrant, J. R. *Phys. Rev. B* **2008**, *78*.
- (46) Rauh, D.; Deibel, C.; Dyakonov, V. *Adv. Funct. Mater.* **2012**, *22*, 3371.
- (47) Kirchartz, T.; Pieters, B. E.; Kirkpatrick, J.; Rau, U.; Nelson, J. *Phys. Rev. B* **2011**, *83*.
- (48) Street, R. A.; Schoendorf, M. *Phys. Rev. B* **2010**, *81*.
- (49) Kuik, M.; Koster, L. J. A.; Wetzelaer, G. A. H.; Blom, P. W. M. *Phys. Rev. Lett.* **2011**, *107*.
- (50) Shockley, W.; Read, W. T., Jr. *Physical Review* **1952**, *87*, 835.
- (51) Deibel, C.; Wagenpfahl, A. *Phys. Rev. B* **2010**, *82*.
- (52) Street, R. A. *Phys. Rev. B* **2010**, *82*.
- (53) Tzabari, L.; Tessler, N. J. *Appl. Phys.* **2011**, *109*.
- (54) Cowan, S. R.; Roy, A.; Heeger, A. J. *Phys. Rev. B* **2010**, *82*.
- (55) Tumbleston, J. R.; Ko, D. H.; Samulski, E. T.; Lopez, R. *Appl. Phys. Lett.* **2009**, *94*.
- (56) Tumbleston, J. R.; Ko, D. H.; Samulski, E. T.; Lopez, R. *Optics Express* **2009**, *17*, 7670.
- (57) Ko, D. H.; Tumbleston, J. R.; Zhang, L.; Williams, S.; DeSimone, J. M.; Lopez, R.; Samulski, E. T. *Nano Lett.* **2009**, *9*, 2742.
- (58) Chen, L. Z.; Sha, W. E. I.; Choy, W. C. H. *Optics Express* **2012**, *20*, 8175.

-
- (59) Tvingstedt, K.; Dal Zilio, S.; Inganas, O.; Tormen, M. *Optics Express* **2008**, *16*, 21608.
- (60) Gjessing, J.; Marstein, E. S.; Sudbo, A. *Optics Express* **2010**, *18*, 5481.
- (61) Kulkarni, A. P.; Noone, K. M.; Munechika, K.; Guyer, S. R.; Ginger, D. S. *Nano Lett.* **2010**, *10*, 1501.
- (62) Diukman, I.; Tzabari, L.; Berkovitch, N.; Tessler, N.; Orenstein, M. *Optics Express* **2011**, *19*, A64.
- (63) Atwater, H. A.; Polman, A. *Nat. Mater.* **2010**, *9*, 205.
- (64) Tsai, S. J.; Ballarotto, M.; Romero, D. B.; Herman, W. N.; Kan, H. C.; Phaneuf, R. J. *Optics Express* **2010**, *18*, A528.
- (65) Lee, J. H.; Park, J. H.; Kim, J. S.; Lee, D. Y.; Cho, K. *Organic Electronics* **2009**, *10*, 416.
- (66) Morfa, A. J.; Rowlen, K. L.; Reilly, T. H.; Romero, M. J.; van de Lagemaat, J. *Appl. Phys. Lett.* **2008**, *92*.
- (67) Wu, J. L.; Chen, F. C.; Hsiao, Y. S.; Chien, F. C.; Chen, P. L.; Kuo, C. H.; Huang, M. H.; Hsu, C. S. *ACS Nano* **2011**, *5*, 959.
- (68) Lu, L. Y.; Luo, Z. Q.; Xu, T.; Yu, L. P. *Nano Lett.* **2013**, *13*, 59.
- (69) Kalfagiannis, N.; Karagiannidis, P. G.; Pitsalidis, C.; Panagiotopoulos, N. T.; Gravalidis, C.; Kassavetis, S.; Patsalas, P.; Logothetidis, S. *Sol. Energy Mater. Sol. Cells* **2012**, *104*, 165.
- (70) Yang, L. Q.; Zhang, T.; Zhou, H. X.; Price, S. C.; Wiley, B. J.; You, W. *Acs Applied Materials & Interfaces* **2011**, *3*, 4075.
- (71) Kang, M. G.; Xu, T.; Park, H. J.; Luo, X. G.; Guo, L. J. *Advanced Materials* **2010**, *22*, 4378.
- (72) Jailaubekov, A. E.; Willard, A. P.; Tritsch, J. R.; Chan, W. L.; Sai, N.; Gearba, R.; Kaake, L. G.; Williams, K. J.; Leung, K.; Rossy, P. J.; Zhu, X. Y. *Nat. Mater.* **2013**, *12*, 66.
- (73) Niesen, B.; Rand, B. P.; Van Dorpe, P.; Cheyng, D.; Tong, L. M.; Dmitriev, A.; Heremans, P. *Adv. Energy Mater.* **2013**, *3*, 145.
- (74) You, J. B.; Li, X. H.; Xie, F. X.; Sha, W. E. I.; Kwong, J. H. W.; Li, G.; Choy, W. C. H.; Yang, Y. *Adv. Energy Mater.* **2012**, *2*, 1203.
- (75) Muller-Meskamp, L.; Kim, Y. H.; Roch, T.; Hofmann, S.; Scholz, R.; Eckardt, S.; Leo, K.; Lasagni, A. F. *Advanced Materials* **2012**, *24*, 906.
- (76) Chen, H. C.; Chou, S. W.; Tseng, W. H.; Chen, I. W. P.; Liu, C. C.; Liu, C.; Liu, C. L.; Chen, C. H.; Wu, C. I.; Chou, P. T. *Adv. Funct. Mater.* **2012**, *22*, 3975.
- (77) Kim, C. H.; Cha, S. H.; Kim, S. C.; Song, M.; Lee, J.; Shin, W. S.; Moon, S. J.; Bahng, J. H.; Kotov, N. A.; Jin, S. H. *ACS Nano* **2011**, *5*, 3319.
- (78) Wang, D. H.; Park, K. H.; Seo, J. H.; Seifter, J.; Jeon, J. H.; Kim, J. K.; Park, J. H.; Park, O. O.; Heeger, A. J. *Adv. Energy Mater.* **2011**, *1*, 766.
- (79) Wang, D. H.; Kim, J. K.; Lim, G. H.; Park, K. H.; Park, O. O.; Lim, B.; Park, J. H. *Rsc Advances* **2012**, *2*, 7268.
- (80) Paci, B.; Spyropoulos, G. D.; Generosi, A.; Bailo, D.; Albertini, V. R.; Stratakis, E.; Kymakis, E. *Advanced Functional Materials* **2011**, *21*, 3573.
- (81) Spyropoulos, G. D.; Stylianakis, M. M.; Stratakis, E.; Kymakis, E. *Appl. Phys. Lett.* **2012**, *100*.
- (82) Kim, K.; Carroll, D. L. *Appl. Phys. Lett.* **2005**, *87*.
- (83) Kim, R. S.; Zhu, J. F.; Park, J. H.; Li, L.; Yu, Z. B.; Shen, H. J.; Xue, M.; Wang, K. L.; Park, G.; Anderson, T. J.; Pei, Q. B. *Optics Express* **2012**, *20*, 12649.
- (84) Xue, M.; Li, L.; de Villers, B. J. T.; Shen, H. J.; Zhu, J. F.; Yu, Z. B.; Stieg, A. Z.; Pei, Q. B.; Schwartz, B. J.; Wang, K. L. *Appl. Phys. Lett.* **2011**, *98*.
- (85) Oo, T. Z.; Mathews, N.; Xing, G.; Wu, B.; Xing, B.; Wong, L. H.; Sum, T. C.; Mhaisalkar, S. G. *J. Phys. Chem. C* **2012**, *116*, 6453.

-
- (86) Wu, J.-L.; Chen, F.-C.; Hsiao, Y.-S.; Chien, F.-C.; Chen, P.; Kuo, C.-H.; Huang, M. H.; Hsu, C.-S. *ACS Nano* **2011**, *5*, 959.
- (87) Xue, M. *Appl. Phys. Lett.* **2011**, *98*, 253302.
- (88) Berera, R.; Grondelle, R.; Kennis, J. M. *Photosynthesis Research* **2009**, *101*, 105.
- (89) Berera, R.; van Grondelle, R.; Kennis, J. T. M. *Photosynth. Res.* **2009**, *101*, 105.
- (90) Lakowicz, J. R. *Principles of fluorescence spectroscopy*; 3rd ed.; Springer: New York, 2006.
- (91) Abramczyk, H. *Introduction to laser spectroscopy*; 1st ed.; Elsevier: Amsterdam ; Boston, 2005.
- (92) <http://www.mpg.de/495195/pressRelease200402241>.
- (93) Fung, D. D. S.; Qiao, L. F.; Choy, W. C. H.; Wang, C. D.; Sha, W. E. I.; Xie, F. X.; He, S. L. *J. Mater. Chem.* **2011**, *21*, 16349.
- (94) Kim, S. S.; Na, S. I.; Jo, J.; Kim, D. Y.; Nah, Y. C. *Applied Physics Letters* **2008**, *93*.
- (95) Yoon, W. J.; Jung, K. Y.; Liu, J. W.; Duraisamy, T.; Revur, R.; Teixeira, F. L.; Sengupta, S.; Berger, P. R. *Solar Energy Materials and Solar Cells* **2010**, *94*, 128.
- (96) Deckman, H. W.; Dunsmuir, J. H.; Garoff, S.; Mchenry, J. A.; Peiffer, D. G. *Journal of Vacuum Science & Technology B* **1988**, *6*, 333.
- (97) Hulteen, J. C.; Treichel, D. A.; Smith, M. T.; Duval, M. L.; Jensen, T. R.; Van Duyne, R. P. *J. Phys. Chem. B* **1999**, *103*, 3854.
- (98) Jensen, T. R.; Schatz, G. C.; Van Duyne, R. P. *J. Phys. Chem. B* **1999**, *103*, 2394.
- (99) Jensen, T. R.; Malinsky, M. D.; Haynes, C. L.; Van Duyne, R. P. *J. Phys. Chem. B* **2000**, *104*, 10549.
- (100) Malinsky, M. D.; Kelly, K. L.; Schatz, G. C.; Van Duyne, R. P. *J. Phys. Chem. B* **2001**, *105*, 2343.
- (101) Ormonde, A. D.; Hicks, E. C. M.; Castillo, J.; Van Duyne, R. P. *Langmuir* **2004**, *20*, 6927.
- (102) Zhang, X. Y.; Yonzon, C. R.; Van Duyne, R. P. *J. Mater. Res.* **2006**, *21*, 1083.
- (103) Huang, W. Y.; Qian, W.; El-Sayed, M. A. *J. Phys. Chem. B* **2005**, *109*, 18881.
- (104) Haynes, C. L.; Van Duyne, R. P. *J. Phys. Chem. B* **2001**, *105*, 5599.
- (105) Karuturi, S. K.; Luo, J.; Cheng, C.; Liu, L.; Su, L. T.; Tok, A. I. Y.; Fan, H. J. *Advanced Materials* **2012**, *24*, 4157.
- (106) Litorja, M.; Haynes, C. L.; Haes, A. J.; Jensen, T. R.; Van Duyne, R. P. *J. Phys. Chem. B* **2001**, *105*, 6907.
- (107) Cong, C.; Junus, W.; Shen, Z.; Yu, T. *Nanoscale Research Letters* **2009**, *4*, 1324
- (108) Xu, G.; Tazawa, M.; Jin, P.; Nakao, S.; Yoshimura, K. *Appl. Phys. Lett.* **2003**, *82*, 3811.
- (109) Park, H.-J.; Vak, D.; Noh, Y.-Y.; Lim, B.; Kim, D.-Y. *Appl. Phys. Lett* **2007**, *90*, 161107.
- (110) Chen, F.-C.; Wu, J.-L.; Lee, C.-L.; Hong, Y.; Kuo, C.-H.; Huang, M. H. *Appl. Phys. Lett* **2009**, *95*, 013305.
- (111) Di Nuzzo, D.; Wetzelaer, G.-J. A. H.; Bouwer, R. K. M.; Gevaerts, V. S.; Meskers, S. C. J.; Hummelen, J. C.; Blom, P. W. M.; Janssen, R. A. J. *Advanced Energy Materials* **2012**, n/a.
- (112) Campion, A.; Gallo, A. R.; Harris, C. B.; Robota, H. J.; Whitmore, P. M. *Chemical Physics Letters* **1980**, *73*, 447.
- (113) Lakowicz, J. R. *Anal. Biochem.* **2001**, *298*, 1.
- (114) Stavytska-Barba, M.; Salvador, M.; Kulkarni, A.; Ginger, D. S.; Kelley, A. M. *The Journal of Physical Chemistry C* **2011**, *115*, 20788.
- (115) Marsh, R. A.; Hodgkiss, J. M.; Albert-Seifried, S.; Friend, R. H. *Nano Letters* **2010**, *10*, 923.

-
- (116) Etzold, F.; Howard, I. A.; Mauer, R.; Meister, M.; Kim, T.-D.; Lee, K.-S.; Baek, N. S.; Laquai, F. d. r. *Journal of the American Chemical Society* **2011**, *133*, 9469.
- (117) Blouin, N.; Michaud, A.; Leclerc, M. *Advanced Materials* **2007**, *19*, 2295.
- (118) Chu, T.-Y.; Alem, S.; Verly, P. G.; Wakim, S.; Lu, J.; Tao, Y.; Beaupre, S.; Leclerc, M.; Belanger, F.; Desilets, D.; Rodman, S.; Waller, D.; Gaudiana, R. *Appl. Phys. Lett.* **2009**, *95*, 063304.
- (119) Baek, S. W.; Noh, J.; Lee, C. H.; Kim, B.; Seo, M. K.; Lee, J. Y. *Sci Rep-Uk* **2013**, *3*.
- (120) Wang, D. H.; Kim, D. Y.; Choi, K. W.; Seo, J. H.; Im, S. H.; Park, J. H.; Park, O. O.; Heeger, A. J. *Angew Chem Int Edit* **2011**, *50*, 5519.
- (121) Li, X. H.; Choy, W. C. H.; Lu, H. F.; Sha, W. E. I.; Ho, A. H. P. *Adv. Funct. Mater.* **2013**, *23*, 2728.
- (122) Dennler, G.; Forberich, K.; Ameri, T.; Waldauf, C.; Denk, P.; Brabec, C. J.; Hingerl, K.; Heeger, A. J. *Journal of Applied Physics* **2007**, *102*.
- (123) Hoppe, H.; Sariciftci, N. S.; Meissner, D. *Molecular Crystals and Liquid Crystals* **2002**, *385*, 233.
- (124) Monestier, F.; Simon, J. J.; Torchio, P.; Escoubas, L.; Florya, F.; Bailly, S.; de Bettignies, R.; Guillerez, S.; Defranoux, C. *Solar Energy Materials and Solar Cells* **2007**, *91*, 405.
- (125) Fung, D. D. S.; Qiao, L.; Choy, W. C. H.; Wang, C.; Sha, W. E. I.; Xie, F.; He, S. *Journal of Materials Chemistry* **2011**, *21*, 16349.
- (126) atwater, H. A.; Polman^{2*}, A. *Nature Materials* **2010**, *9*, 205.
- (127) Feng, H.; Yang, Y.; You, Y.; Li, G.; Guo, J.; Yu, T.; Shen, Z.; Wu, T.; Xing, B. *Chem. Commun.* **2009**, 1984.
- (128) Tvingstedt, K.; Persson, N.-K.; Inganäs, O.; Rahachou, A.; Zozoulenko, I. V. *Appl. Phys. Lett.* **2007**, *91*, 113514.
- (129) Duche, D.; Torchio, P.; Escoubas, L.; Monestier, F.; Simon, J.-J.; Flory, F.; Mathian, G. *Solar Energy Materials and Solar Cells* **2009**, *93*, 1377.
- (130) Mihailetschi, V. D.; Koster, L. J. A.; Hummelen, J. C.; Blom, P. W. M. *Physical Review Letters* **2004**, *93*, 216601.
- (131) Mihailetschi, V. D.; Xie, H.; Boe, B. d.; Koster, L. J. A.; Blom, P. W. M. *Adv. Funct. Mater.* **2006**, *16*, 699.
- (132) Pyayt, A. L.; Wiley, B.; Xia, Y. N.; Chen, A.; Dalton, L. *Nat. Nanotechnol.* **2008**, *3*, 660.
- (133) Wang, W. H.; Yang, Q.; Fan, F. R.; Xu, H. X.; Wang, Z. L. *Nano Lett.* **2011**, *11*, 1603.
- (134) Fang, Y. R.; Wei, H.; Hao, F.; Nordlander, P.; Xu, H. X. *Nano Lett.* **2009**, *9*, 2049.
- (135) Song, M.; Chen, G. X.; Liu, Y.; Wu, E.; Wu, B. T.; Zeng, H. P. *Optics Express* **2012**, *20*, 22290.
- (136) Zhou, Z. K.; Li, M.; Yang, Z. J.; Peng, X. N.; Su, X. R.; Zhang, Z. S.; Li, J. B.; Kim, N. C.; Yu, X. F.; Zhou, L.; Hao, Z. H.; Wang, Q. Q. *ACS Nano* **2010**, *4*, 5003.
- (137) Akimov, A. V.; Mukherjee, A.; Yu, C. L.; Chang, D. E.; Zibrov, A. S.; Hemmer, P. R.; Park, H.; Lukin, M. D. *Nature* **2007**, *450*, 402.
- (138) Liu, N.; Li, Z. P.; Xu, H. X. *Small* **2012**, *8*, 2641.
- (139) Lee, J.-Y.; Connor, S. T.; Cui, Y.; Peumans, P. *Nano Letters* **2008**, *8*, 689.
- (140) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Advanced Materials* **2003**, *15*, 353.
- (141) Staleva, H.; Skrabalak, S. E.; Carey, C. R.; Kosel, T.; Xia, Y. N.; Hartland, G. V. *Phys. Chem. Chem. Phys.* **2009**, *11*, 5889.
- (142) Schmidt-Mende, L.; Watson, M.; Mullen, K.; Friend, R. H. *Mol. Cryst. Liq. Cryst.* **2003**, *396*, 73.

-
- (143) Palik, E. D. *Handbook of optical constants of solids II*; Academic Press: Boston, 1991.
- (144) Oo, T. Z.; Mathews, N.; Xing, G. C.; Wu, B.; Xing, B. G.; Wong, L. H.; Sum, T. C.; Mhaisalkar, S. G. *Journal of Physical Chemistry C* **2012**, *116*, 6453.
- (145) Guo, J. M.; Ohkita, H.; Bente, H.; Ito, S. *J. Am. Chem. Soc.* **2009**, *131*, 16869.
- (146) Piris, J.; Dykstra, T. E.; Bakulin, A. A.; van Loosdrecht, P. H. M.; Knulst, W.; Trinh, M. T.; Schins, J. M.; Siebbeles, L. D. A. *J. Phys. Chem. C* **2009**, *113*, 14500.
- (147) Xie, Y.; Li, Y.; Xiao, L. X.; Qiao, Q. Q.; Dhakal, R.; Zhang, Z. L.; Gong, Q. H.; Galipeau, D.; Yan, X. Z. *J. Phys. Chem. C* **2010**, *114*, 14590.
- (148) Link, S.; El-Sayed, M. A. *Int. Rev. Phys. Chem.* **2000**, *19*, 409.
- (149) Christ, N.; Kettlitz, S. W.; Zuefle, S.; Valouch, S.; Lemmer, U. *Physical Review B* **2011**, *83*.
- (150) Mihailitchi, V. D.; Xie, H. X.; de Boer, B.; Koster, L. J. A.; Blom, P. W. M. *Adv. Funct. Mater.* **2006**, *16*, 699.
- (151) Gan, Q.; Bartoli, F. J.; Kafafi, Z. H. *Advanced Materials* **2013**, *25*, 2385.
- (152) Topp, K.; Borchert, H.; Johnen, F.; Tunc, A. V.; Knipper, M.; von Hauff, E.; Parisi, J.; Al-Shamery, K. *J. Phys. Chem. A* **2010**, *114*, 3981.
- (153) Mandoc, M. M.; Kooistra, F. B.; Hummelen, J. C.; de Boer, B.; Blom, P. W. M. *Appl Phys Lett* **2007**, *91*, 263505.
- (154) Nalwa, K. S.; Mahadevapuram, R. C.; Chaudhary, S. *Applied Physics Letters* **2011**, *98*, 093306.
- (155) Street, R. A.; Schoendorf, M.; Roy, A.; Lee, J. H. *Phys Rev B* **2010**, *81*, 205307.
- (156) Rauh, D.; Deibel, C.; Dyakonov, V. *Advanced Functional Materials* **2012**, n/a.
- (157) Koster, L. J. A.; Mihailitchi, V. D.; Ramaker, R.; Blom, P. W. M. *Applied Physics Letters* **2005**, *86*, 123509.
- (158) Maurano, A.; Hamilton, R.; Shuttle, C. G.; Ballantyne, A. M.; Nelson, J.; O'Regan, B.; Zhang, W.; McCulloch, I.; Azimi, H.; Morana, M.; Brabec, C. J.; Durrant, J. R. *Advanced Materials* **2010**, *22*, 4987.
- (159) Cowan, S. R.; Roy, A.; Heeger, A. J. *Physical Review B* **2010**, *82*, 245207.
- (160) Wetzelaer, G. A. H.; Kuik, M.; Lenes, M.; Blom, P. W. M. *Applied Physics Letters* **2011**, *99*, 153506.
- (161) Kirchartz, T.; Pieters, B. E.; Kirkpatrick, J.; Rau, U.; Nelson, J. *Physical Review B* **2011**, *83*, 115209.
- (162) Topp, K.; Borchert, H.; Johnen, F.; Tunc, A. V.; Knipper, M.; von Hauff, E.; Parisi, J.; Al-Shamery, K. *The Journal of Physical Chemistry A* **2009**, *114*, 3981.
- (163) Giebink, N. C.; Wiederrecht, G. P.; Wasielewski, M. R.; Forrest, S. R. *Physical Review B* **2010**, *82*, 155305.
- (164) Cowan, S. R.; Leong, W. L.; Banerji, N.; Dennler, G.; Heeger, A. J. *Advanced Functional Materials* **2011**, *21*, 3083.
- (165) Guo, J. M.; Ohkita, H.; Bente, H.; Ito, S. *Journal of the American Chemical Society* **2010**, *132*, 6154.
- (166) Jiang, X. M.; Österbacka, R.; Korovyanko, O.; An, C. P.; Horovitz, B.; Janssen, R. A. J.; Vardeny, Z. V. *Adv. Funct. Mater.* **2002**, *12*, 587.
- (167) Hodgkiss, J. M.; Albert-Seifried, S.; Rao, A.; Barker, A. J.; Campbell, A. R.; Marsh, R. A.; Friend, R. H. *Adv Funct Mater* **2012**, *22*, 1567.
- (168) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *The Journal of Physical Chemistry* **1996**, *100*, 13148.
- (169) Shuttle, C. G.; Treat, N. D.; Douglas, J. D.; Frechet, J. M. J.; Chabinyc, M. L. *Adv. Energy Mater.* **2012**, *2*, 111.
- (170) Rauh, D.; Deibel, C.; Dyakonov, V. *Adv. Funct. Mater.* **2012**, 3371.
- (171) Monroe, D. *Phys. Rev. Lett.* **1985**, *54*, 146.

-
- (172) Tanase, C.; Meijer, E. J.; Blom, P. W. M.; de Leeuw, D. M. *Physical Review Letters* **2003**, *91*, 216601.
 - (173) Noolandi, J. *Phys. Rev. B* **1977**, *16*, 4466.
 - (174) Cowan, S. R.; Banerji, N.; Leong, W. L.; Heeger, A. J. *Adv. Funct. Mater.* **2012**, *22*, 1116.
 - (175) Christ, N.; Kettlitz, S. W.; Zuefle, S.; Valouch, S.; Lemmer, U. *Phys. Rev. B* **2011**, *83*, 195211.
 - (176) Kim, K.; Carroll, D. L. *Applied Physics Letters* **2005**, *87*, 203113.
 - (177) Kim, C.-H.; Cha, S.-H.; Kim, S. C.; Song, M.; Lee, J.; Shin, W. S.; Moon, S.-J.; Bahng, J. H.; Kotov, N. A.; Jin, S.-H. *ACS Nano* **2011**, *5*, 3319.
 - (178) Atwater, H. A.; Polman, A. *Nat Mater* **2010**, *9*, 205.
 - (179) Gan, Q.; Bartoli, F. J.; Kafafi, Z. H. *Adv. Mater.* **2013**, n/a.
 - (180) Wang, C. C. D.; Choy, W. C. H.; Duan, C.; Fung, D. D. S.; Sha, W. E. I.; Xie, F.-X.; Huang, F.; Cao, Y. J. *Mater. Chem.* **2012**, *22*, 1206.
 - (181) Dunbar, R. B.; Pfadler, T.; Schmidt-Mende, L. *Optics Express* **2012**, *20*, A177.
 - (182) Ye, Z.; Chaudhary, S.; Kuang, P.; Ho, K. M. *Optics Express* **2012**, *20*, 12213.
 - (183) Chen, L. Z.; Choy, W. C. H.; Sha, W. E. I. *Applied Physics Letters* **2013**, 102.
 - (184) Zhu, X.; Zhang, J.; Xu, J.; Yu, D. *Nano Letters* **2011**, *11*, 1117.
 - (185) Ameling, R. *Appl. Phys. Lett.* **2010**, *97*, 253116.
 - (186) Williamson, A.; McClean, E.; Leipold, D.; Zerulla, D.; Runge, E. *Appl. Phys. Lett.* **2011**, 99.
 - (187) Manolatu, C. R., F.; *IEEE Journal of Quantum Electronics* **2008** *44*, 435
 - (188) Amit, M. L.; et al. *Semiconductor Science and Technology* **2011**, *26*, 014013.
 - (189) Manolatu, C.; Rana, F. *IEEE J. Quantum Electron.* **2008**, *44*, 435.
 - (190) Lakhani, A. M.; Yu, K.; Wu, M. C. *Semicond. Sci. Technol.* **2011**, 26.
 - (191) Balanis, C. A. *Antenna Theory: Analysis Design*; Third Edition ed.; John Wiley & Sons, Inc., 2005.
 - (192) Kuttge, M.; de Abajo, F. J. G.; Polman, A. *Nano Lett.* **2010**, *10*, 1537.
 - (193) Catchpole, K. R. *Appl. Phys. Lett.* **2008**, *93*, 191113.
 - (194) Diukman, I.; Tzabari, L.; Berkovitch, N.; Tessler, N.; Orenstein, M. *Opt. Express* **2011**, *19*, A64.
 - (195) Kuttge, M.; García de Abajo, F. J.; Polman, A. *Nano Letters* **2009**, *10*, 1537.
 - (196) Hägglund, C. *Appl. Phys. Lett.* **2008**, *92*, 053110.
 - (197) Beck, F. J.; Verhagen, E.; Mokkaapati, S.; Polman, A.; Catchpole, K. R. *Opt. Express* **2011**, *19*, A146.
 - (198) Beck, F. J. *J. Appl. Phys.* **2009**, *105*, 114310.
 - (199) Ferry, V. E.; Verschuuren, M. A.; Li, H. B. T.; Verhagen, E.; Walters, R. J.; Schropp, R. E. I.; Atwater, H. A.; Polman, A. *Opt. Express* **2010**, *18*, A237.
 - (200) Catchpole, K. R.; Polman, A. *Applied Physics Letters* **2008**, 93.
 - (201) Hoppe, H.; Sariciftci, N. S.; Meissner, D. *Molecular Crystals and Liquid Crystals* **2002**, *385*, 113.
 - (202) Monestier, F.; Simon, J.-J.; Torchio, P.; Escoubas, L.; Flory, F.; Bailly, S.; de Bettignies, R.; Guillerez, S.; Defranoux, C. *Solar Energy Materials and Solar Cells* **2007**, *91*, 405.
 - (203) Dennler, G. *J. Appl. Phys.* **2007**, *102*, 123109.
 - (204) Koster, L. J. A.; Smits, E. C. P.; Mihailetschi, V. D.; Blom, P. W. M. *Phys. Rev. B* **2005**, 72.
 - (205) Kumar, P.; Jain, S. C.; Kumar, V.; Chand, S.; Tandon, R. P. *J. Phys. D: Appl. Phys.* **2009**, 42.
 - (206) Knapp, E.; Hausermann, R.; Schwarzenbach, H. U.; Ruhstaller, B. *J. Appl. Phys.* **2010**, 108.
 - (207) Trukhanov, V. A.; Bruevich, V. V.; Paraschuk, D. Y. *Phys. Rev. B* **2011**, 84.

-
- (208) MacKenzie, R. C. I.; Kirchartz, T.; Dibb, G. F. A.; Nelson, J. J. *Phys. Chem. C* **2011**, *115*, 9806.
- (209) Soldera, M.; Taretto, K.; Kirchartz, T. *Physica Status Solidi a-Applications and Materials Science* **2012**, *209*, 207.
- (210) Selberherr, S. *Analysis and simulation of semiconductor devices*; Springer-Verlag: Wien, Austria ; New York, 1984.
- (211) Gummel, H. K. *IEEE Trans. Electron Devices* **1964**, *Ed11*, 455.
- (212) Fredriksson, H.; Alaverdyan, Y.; Dmitriev, A.; Langhammer, C.; Sutherland, D. S.; Zäch, M.; Kasemo, B. *Advanced Materials* **2007**, *19*, 4297.
- (213) Park, S. H.; Roy, A.; Beaupre, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat Photon* **2009**, *3*, 297.
- (214) Wang, H.; Shah, M.; Ganesan, V.; Chabinyk, M. L.; Loo, Y.-L. *Advanced Energy Materials* **2012**, n/a.
- (215) Yamamoto, S.; Ohkita, H.; Benten, H.; Ito, S. *J. Phys. Chem. C* **2012**, *116*, 14804.
- (216) Tessler, N.; Roichman, Y. *Organic Electronics* **2005**, *6*, 200.
- (217) Bakulin, A. A.; Martyanov, D. S.; Paraschuk, D. Y.; Pshenichnikov, M. S.; van Loosdrecht, P. H. M. *J. Phys. Chem. B* **2008**, *112*, 13730.

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