OXIDE-ENCAPSULATED SILVER NPs EMBEDDED IN POLYMER FOR IMPROVED OPTICAL ABSORPTION

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Abstract

Enhanced electric fields associated with surface plasmons can enhance light absorption in the surrounding medium that the plasmonic materials are embedded in. The exploitation of these unique properties in organic solar cells is well documented. Organic solar cells suffer from inherently low photocurrent and surface plasmons have the ability to overcome this drawback by improving absorption in the semiconducting photoactive layer. As surface plasmons manifest in the immediate vicinity of the plasmonic nanostructures, their placement in the polymeric active layer (or at least in close proximity to the active layer) is preferred. As the nanostructures are usually metallic in nature, embedding them in the semiconducting layer may introduce recombination sites. This can be circumvented by introducing a thin continuous insulating shell around the nanostructures. An insulating encapsulation layer helps in isolating nanostructures from the polymer layer, hence, mitigating charge recombination.

In this thesis, the effect on optical enhancement in a polymer by embedding 50 nm Ag nanoparticles (NPs) encapsulated with various oxides is investigated. The focus will be placed on the use of aluminum oxide (Al_2O_3), hafnium oxide (HfO_2), molybdenum oxide (MoO_3) and silicon oxide (SiO_2). Modelling studies reveal that, at silver (Ag) NP resonance, optical enhancement in poly(3-hexythyophene):phenyl-C61-butyric acid methyl ester (P3HT:PCBM) depends primarily on the position of peak extinction cross section relative to the polymer absorption. Photoinduced absorption (PIA) studies show an increased polaron yield when Ag NPs are protected with a sheath of Al_2O_3 . In fact, an optimal Al_2O_3 thickness of 3 – 5 nm exists to generate maximum polaron concentration. At this range, absorption enhancement within the polymer film by the plasmonic electric field and the spatial separation of charge carriers from recombination centers are balanced. Absorption gains/losses in the photoactive layer are examined by calculating with reference to AM1.5G solar spectrum. Through the additional use of simulation models, it is divulged that overall absorption in the polymer can be improved by incorporating oxide-encapsulated Ag NPs. Assuming a continuous shell is sufficient in mitigating charge recombination, a 2 nm thickness, regardless of the choice of oxide,

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should be enough to induce optical enhancement in the polymer with respect to a control P3HT:PCBM.

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Abbreviations

A	Absorptance
$A(\lambda)$	Absorbance
AFM	Atomic Force Microscopy
AM1.5G	Air Mass 1.5 Global
Ag	Silver
Ag NPs	Silver Nanoparticles
Al_2O_3	Aluminum Oxide
ALD	Atomic Layer Deposition
A_{weighted}	Absorption Weighted Against AM1.5G
B	Magnetic Flux Density
BPhen	Bathophenanthroline
C_{60}	Fullerene
C	Carbon
Ca	Calcium
$C_{\text{absorption}}$	Absorption Cross Section
CCD	Charge Coupled Diode
$C_{\text{extinction}}$	Extinction Cross Section
$C_{\text{scattering}}$	Scattering Cross Section
CuPc	Copper Phthalocyanine
DCB	1,2-dichlorobenzene
DDT	Dodecanethiol
DSSCs	Dye-sensitized Solar Cells
e	Elementary Charge
E	Electric Field or Photon Energy
FF	Fill Factor
FIB	Focused Ion Beam
h	Planck's Constant
H	Magnetic Field
HDA	Hexadecyl Amine

Abbreviations

HfO ₂	Hafnium Dioxide
HOMO	Highest Occupied Molecular Orbital
I	Intensity of Transmitted Beam
IEA	International Energy Agency
I _{MPP}	Maximum Power Point of Current
InGaAs	Indium Gallium Arsenide
I ₀	Dark Current or Intensity of Illuminated Beam
ITO	Indium Tin Oxide
j	$\sqrt{-1}$
j(0)	Displacement Current of the Capacitance of PhotoCELIV
J	Current Field Density
J _{sc}	Short Circuit Current Density
J-V	Current-Voltage
k	Boltzmann Constant or Wave Vector
k _{diss}	Polaron Dissociation Rate
k _f	Non-radiative Monomolecular Recombination Rate
LED	Light Emitting Diode
L ₀	Light Power Intensity
LSPs	Localized Surface Plasmons
LT-ITO	Low Temperature Processed Indium Tin Oxide
LUMO	Lowest Unoccupied Molecular Orbital
MoO ₃	Molybdenum Trioxide
MEH-PPV	Poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene)
MIM	Metal-Insulator-Metal
MPP	Maximum Power Point
n	Diode Ideality Factor
NIL	Nanoimprinting Lithography
NaOH	Sodium Hydroxide
NCPV	National Center for Photovoltaics
NREL	National Renewable Energy Laboratory
OPV	Organic Photovoltaic

Abbreviations

OSC	Organic Solar Cell
P3HT ⁺	Poly(3-hexythiophene) holes
P3HT:PCBM	Poly(3-hexythiophene):phenyl-C61-butyric acid methyl ester
PCE	Power Conversion Efficiency
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) Polystyrene Sulfonate
PhotoCELIV	Photoinduced Charge Extraction by Linearly Increasing Voltage
PIA	Photoinduced Absorption Spectroscopy
P _{MAX}	Maximum Power
PML	Perfectly Matched Layer
PMMA	Poly(methyl methacrylate)
Pt	Platinum
PVP	Polyvinylpyrrolidone
R	Reflectance
R _S	Series Resistance
R _{SH}	Shunt Resistance
SEM	Scanning Electron Microscopy
S	Term used for scaling PIA signals
Si	Silicon
SiO ₂	Silicon Dioxide
SPPs	Surface Plasmon Polaritons
S(λ)	AM1.5G Intensity Flux
T	Temperature or Transmittance
TEM	Transmission Electron Microscopy
T _g	Glass Transition Temperature
THF	Tetrahydrofuran
TiO ₂	Titanium Dioxide
t _{max}	Time at the maximum of extraction peak in PhotoCELIV
UV	Ultraviolet
UV-vis	Ultraviolet-Visible
VASE	Variable Angle Spectroscopic Ellipsometer
V _{MPP}	Maximum Power Point of Voltage

Abbreviations

V_{oc}	Open Circuit Voltage
X	Rate of Change of Polaron Concentration
Xe	Xenon
ZnO	Zinc Oxide
$ZnPc$	Zinc Phthalocyanine
α	Polarisability or linear weight denoting the relative absorption strengths of the Ag NPs
β	Linear weight denoting the relative absorption strengths of P3HT
ΔE	Absorption Red-shift
Δj	Extraction Peak of PhotoCELIV
ΔT	Fractional Change in Optical Transmission
$\Delta T/T$	Term used to quantify polaron yields in PIA measurements
$\Delta T/(TS)$	Scaled $\Delta T/T$
ϵ_0	Permittivity of Free Space
ϵ_i	Imaginary Part of the Relative Permittivity
ϵ_r	Relative Permittivity
$\eta_{absorption}$	Absorption Cross Section Efficiency
$\eta_{extinction}$	Extinction Cross Section Efficiency
$\eta_{scattering}$	Scattering Cross Section Efficiency
λ	Wavelength
ω	Frequency

Chapter 1

Introduction

The development of organic photovoltaic (OPV) or organic solar cell (OSC) technology has proven to be a promising alternative to meet global energy demand. Unfortunately, the semiconducting layer in OPV devices has very low charge mobility. Taking into account this drawback, a very thin organic semiconducting layer must be adopted. Inevitably, solar absorption will be compromised, which results in poor charge carrier generation, poor charge collection and poor power conversion efficiency (PCE). To overcome this, surface plasmons arising from plasmonic nanostructures are one of the many methods to boost absorption. Since plasmonic nanostructures are usually metallic, incorporating them into the organic layer will inevitably lead to the introduction of charge recombination sites. These charge recombination sites can be reduced drastically by introducing a protective sheath around the nanostructures. At plasmonic resonance, it is expected that optical absorption will be enhanced when the nanostructures are encapsulated with a protective shell. This is due to an increase in the polarisability of the photoexcited material. It is believed that an optimal shell thickness exists such that charge carrier population is maximized while charge recombination suppression is enforced. When these buffer-encapsulated plasmonic nanostructures are incorporated into a polymer film, overall absorption is expected to be enhanced when the structure is illuminated by the Air Mass 1.5 Global solar spectrum.

1.1 Hypothesis/Problem Statement

The use of plasmonic nanostructures in an OPV device is one of the many possible routes undertaken to improve device performance.^{1,2} At resonance, plasmonic materials possess strong optical scattering and large localized field enhancement properties.³ This is due to the presence of surface plasmons. Primarily, these positive qualities are exploited for their ability to enhance light absorption. An increase in the light absorption will correspondingly lead to an improvement in photogeneration. This will in turn boost device performance. Produced at the optical resonance of the plasmonic nanostructures, surface plasmons generate electric field enhancements which are highly localized at the metal/dielectric interface. In order to take advantage of this, placement of the plasmonic nanostructures in the polymeric layer is preferred. On the flip side, being metallic in nature, the introduction of plasmonic materials in the polymeric layer means that they will also double up as recombination sites. Free charge carriers, more specifically, free holes will recombine with the free electrons on the metallic/plasmonic material surfaces instead of being captured by the electrodes for photogeneration. The most straightforward method to mitigate charge recombination is to encapsulate plasmonic materials with an encapsulating shell.⁴⁻⁶ This will isolate the plasmonic materials from the active layer. To function its role, the encapsulating shell must either be insulating or semiconducting. Oxides such as Al_2O_3 and SiO_2 should be appropriate. At the optical resonance of the plasmonic nanostructures, incorporating oxide-encapsulated nanostructures into a polymer film should increase its optical absorption. This is due to an increase in the polarisability. As a direct function of extinction cross section, increasing the polarisability improves the chance of a photon being trapped within the polymer film via scattering means. Correspondingly, this will result in an increase in optical absorption in the film. An oxide with a higher relative permittivity should induce higher absorption in the polymer. However, this approach will also shield the active layer from the enhanced electric fields associated with the surface plasmons. As the extent of the electric field is localized at the immediate vicinity of the optically resonating plasmonic nanostructures, a thick shell will trap most of this field enhancement within the oxide layer. Hence, there must be a balance between photogeneration and charge recombination. This must be

realised by determining the optimal thickness of the insulating layer that protects the plasmonic materials. Upon incorporating oxide-encapsulated nanostructures into a polymer film, overall absorption in the film is expected to be improved when calculated with reference to AM1.5G intensity flux. There should be a limit to the shell thickness before the presence of the oxide-encapsulated nanostructures becomes detrimental to the overall absorption in the polymer film.

To summarize, as plasmonic nanostructures are usually metallic in nature, incorporating them into a semiconducting layer introduces charge recombination sites. Encapsulating the plasmonic nanostructures with a thin protective sheath should mitigate charge recombination. The protective layer should be insulating or semiconducting. Hence, it is hypothesized that:

- a) At the optical resonance of the plasmonic nanostructure, introducing a protective layer will increase its extinction cross section. This should be observed in the form of improved absorption in the polymer layer. A protective layer with a high relative permittivity can potentially improve the absorption in the polymer layer.
- b) For buffer-encapsulated plasmonic nanostructures, an optimal shell thickness exists to maximize field enhancement effects while suppressing charge recombination.
- c) For buffer-encapsulated plasmonic nanostructures incorporated in a polymer film, overall polymer absorption, when calculated with reference to AM1.5G intensity flux, should improve. However, when a limit is exceeded, overall absorption in the polymer will fall into the negative regime.

1.2 Objectives and Scope

To test the hypothesis, a set of objectives and scope was formulated:

- a) Shells must be insulating or semiconducting to function as effective medium for charge suppression. Hence, oxides of Al_2O_3 , HfO_2 , MoO_3 and SiO_2 are investigated. At optical resonance, the magnitude of absorption enhancement in poly(3-hexythiophene):phenyl-C61-butyric acid methyl ester (P3HT:PCBM) due to the presence of Ag NPs will be investigated. The type of oxide and its thickness will dictate the degree of enhancement.
- b) To prove an optimal shell surrounding Ag NPs exist. This optimum balances maximum field enhancement effects with charge recombination. By monitoring polaron population using photoinduced absorption (PIA) spectroscopy, the optimal shell thickness for Al_2O_3 can be determined.
- c) To determine the overall absorption in P3HT:PCBM if the oxides with different shell thicknesses are embedded in the polymer. This is to allow the projection of expected optical yields if these oxide-encapsulated Ag NPs are incorporated into an OSC.

1.3 Dissertation Overview

The thesis is divided into seven different chapters.

Chapter 1 highlights the problem pertaining to incorporating metallic nanostructures with plasmonic properties in a polymer layer. A solution in the form of a protective shell encapsulating the nanostructures is proposed. A hypothesis with respect to this approach is presented together with its corresponding objectives.

Chapter 2 summarizes the history and theory of photovoltaic technology. The motivation behind improving organic solar cells is presented and the use of plasmonic materials is

highlighted.

Chapter 3 discusses the different techniques that were employed for this project. Simulation models, fabrication methods and characterization means will be given an overview.

Chapter 4 describes the use of modelling studies to investigate the use of oxides with different relative permittivity (Al_2O_3 , HfO_2 , MoO_3 and SiO_2) as the protective shell on 50 nm Ag NPs in a poly(3-hexythiophene):phenyl-C61-butyric acid methyl ester (P3HT:PCBM) film. Absorption studies were calculated based on the resonance of the Ag NP.

Chapter 5 explains the existence of an optimal shell thickness on 50 nm Ag NPs. This optimum is necessary to maximize field enhancement effects while suppressing charge recombination. This is determined by monitoring P3HT^+ polaron population using a PIA spectroscopy setup.

Chapter 6 analyzes the overall absorption in P3HT:PCBM, through the use of modelling studies, when oxide-encapsulated Ag NPs are introduced into the polymer film. Calculated with reference to AM1.5G intensity flux, calculations will reveal the degree of absorption improvement when integrated throughout the absorption range of the polymer. A small discussion point is also raised with the use of oxide-encapsulated Ag NPs in $\text{CH}_3\text{NH}_3\text{PbI}_3$.

Chapter 7 concludes the findings of the thesis. It illustrates how adequately the hypotheses were verified. A brief future work, is proposed. Reconnaissance studies encompassing initial findings are included.

1.4 Findings and Outcomes/Originality

At Ag NP resonance, when the encapsulating shell is sufficiently thick, oxides with a

high relative permittivity will induce high absorption in P3HT:PCBM while oxides with a low relative permittivity will induce low polymer absorption. Extinction cross section alone does not determine the degree of absorption gains in the polymer. Instead, an important parameter is to look at the extent in which electric field enhancement arising from surface plasmons can penetrate into the polymer. Primarily, the magnitude of the extinction cross section depends on peak Ag NP absorption relative to the polymer. The findings are optically deduced. Electronic effects such as non-radiative recombination are not considered.

By monitoring P3HT^+ polaron population using a PIA spectroscopy setup, the ideal thickness of an insulating Al_2O_3 layer surrounding Ag NPs was found to be 3 – 5 nm. With such a shell thickness around the Ag NPs, the absorption enhancement within the P3HT film by the plasmonic electric field and the spatial separation of charge carriers from recombination centers are balanced to give the maximum polaron concentration.

When spectral absorption of Ag NPs encapsulated with various oxide thicknesses for wavelengths spanning 350 nm to 650 nm are calculated, secondary peaks that manifest from ~570 nm onwards can be observed. This can be attributed to near field interaction between the Ag NP and the polymer. However, this peak has a suppressed contribution once the extinction cross section efficiency is plotted. This is especially true for thicker oxide shells. In fact, the magnitude of the secondary peak can be taken as an indirect measure of oxide shell thickness. Absorption in the polymer is calculated with reference to AM1.5G spectrum and normalized with respect to the volume. Calculated absorption values reveal that optical enhancement is expected in P3HT:PCBM when bare Ag NPs are introduced. The presence of a thin shell around Ag NPs reduces absorption enhancement in the polymer. Absorption of Ag NPs will dominate as the shell thickness is increased. There is a shell thickness limit of ~5 nm for MoO_3 and SiO_2 before polymer absorption loss is induced for oxide-encapsulated Ag NPs. For Al_2O_3 and HfO_2 , the shell should not exceed ~10 nm.

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Chapter 2

Literature Review

Our sun is an attractive source of energy. The use of solar cells to harvest solar energy has been ongoing for decades. The solar energy market is dominated by inorganic solar cells. Emerging photovoltaic technologies such as OPV devices have shown great promise as an alternative to their inorganic counterparts. Numerous groups have investigated different ways to improve device performance in OPV devices and the use of plasmonic materials has proven to be a viable method. However, the use of plasmonic materials in OPVs has come with its own unique set of challenges; in particular, the need to alleviate losses associated with charge recombination.

2.1 Overview

Forecasts of dwindling fossil fuel supplies such as crude oil make for grim reading¹⁻³. The supply of fossil fuels is finite and it cannot be relied upon as a sustainable source of energy. According to an annual report released by the International Energy Agency (IEA), the world's energy supply is still dominated by the use of fossil fuels⁴. In 1973, global supply of energy is primarily driven by crude oil, as shown in Figure 1. Although this share has fallen considerably by 2013, the use of fossil fuels still constitutes about 81 % of the world's consumption. Besides these supply issues, the environmental consequences of burning fossil fuels to quench our energy needs are well-documented^{5,6}. There is ample evidence that burning hydrocarbons contribute massively to climate change. A paradigm shift in harnessing energy is imperative. As global demand for energy continues to grow, alternative forms of energy are needed to address the eventual shortfall of cheap oil that has driven the world economy for the past century and a half⁷.

There is no shortage of alternative forms of energy that we can fall back on^{8,9}. In fact, most of these energy sources are clean, green and renewable. Collectively, they have the potential to provide sufficient energy to satisfy accelerating worldwide demand. Renewable energy can be derived from natural resources such as wind, tides, precipitation, geothermal, solar, etc. Nuclear power in the form of fission or fusion is also a bright prospect. However, following the Fukushima Daiichi Nuclear Power Plant meltdown back in 2011, sentiments against nuclear energy have grown considerably¹⁰. On the other hand, nuclear fusion is touted as the energy of the future^{11,12}.

Approximately 1.05×10^5 TW of solar power strikes the Earth's surface continuously¹³. To put this in another perspective, the amount of energy Earth receives in an hour is enough to meet mankind's demand for the entire year¹⁴! If 10 % efficient solar panels were to cover 1 % of the Earth's surface, it will produce a power output equivalent to 105 TW. This is substantial, considering that the projected global energy demand is expected to be 25-30 TW in 2050¹³. This highlights the immense potential of solar energy. Despite this, solar energy contributes less than 1.7 % of the global energy supply in 2013 (Figure

2.1). Primarily, this is due to the relative high prices of energy generated by solar power as compared to conventional sources. However, as the cost of solar panels continue to fall tremendously over the past decade or so, the cost to produce photovoltaic electricity per Watt has reached levels similar to that of electricity generated from conventional fossil fuels¹⁵. This is largely due to aggressive marketing which has pushed down prices significantly. Hence, the time is ripe to promote the use of photovoltaic technology to satisfy mankind's burgeoning energy needs.

Figure 2.1 Since 1973, the world's supply of energy is still mainly from burning fossil fuels. (Source: International Energy Agency, 2014 Key World Energy Statistics)

In 1839, Alexandre-Edmond Becquerel became the first person in the world to stumble upon the photovoltaic effect¹⁶. Since then, progress in photovoltaic technology has improved tremendously. Currently, commercialized photovoltaic technology is dominated by inorganic panels¹⁷. Generally, these solar panels are based on silicon. The early silicon-based solar cells had an efficiency of about 6 %. As technology improved, present-day silicon-based solar cells have efficiencies of more than 20 %.

Broadly speaking, solar cells can be divided into inorganic and organic. They can also be classified as first generation (silicon-based), second generation (thin film based) and third

generation (organic-based) photovoltaic cells. The National Center for Photovoltaics (NCPV) at National Renewable Energy Laboratory (NREL) further refined the classification into the following categories:

- 1) Multi-junction cells
- 2) Single junction gallium arsenide (GaAs) cells
- 3) Crystalline silicon (Si) cells
- 4) Thin film technology
- 5) Emerging solar cells

Figure 2.2 The latest solar cell efficiencies of various solar cells as of 2014. The current record holder for organic solar cell is Mitsubishi Chemical at 11.1 %. (Source: National Center for Photovoltaics (NCPV), National Renewable Energy Laboratory (NREL)¹⁹)

Established in 1977, this categorization was introduced by NREL to keep abreast of the latest photovoltaic developments¹⁸. With its expertise mainly in solar energy, it maintains and publishes annual efficiency charts of the latest solar cell efficiency. The data points in NREL's chart were verified by NREL, National Institute of Advanced Industrial Science and Technology (AIST)¹⁹. Multi-junction and single junction GaAs are typically

expensive and mainly used in space satellites. Being cheaper, the most common ones are crystalline Si and thin film cells. Also known as crystalline inorganic semiconductors, these 4 types of inorganic photovoltaic cells have been around since the 1970s (Figure 2.2). It was not until the early 1990s that dye-sensitized solar cell technology appeared. Called emerging solar cells, this category includes organic, quantum dots and perovskite cells. These cells are radically different in the way they are fabricated. The absorbing active layers are chemically synthesized and solution processed, which gives them a production cost advantage over their inorganic counterparts^{16,20-23}. In this respect, emerging solar cells are attractive since this translates to significant design flexibility and cost savings. With cheap processing techniques such as spin-coating and doctor-blading, high volume production can be easily realized. In this thesis, organic materials will be used as the backbone of the investigations.

An organic photovoltaic (OPV) or OSC has numerous advantages over inorganic semiconductors due to its light weight, ease of fabrication, cost-effectiveness, significant reduction of production energy consumption and environmental friendliness^{16,20,22}. The original OPV technological breakthrough happened in 1979 when C. W. Tang pioneered the donor/acceptor bilayer planar heterojunction to OPV devices^{24,25}. By adopting a bilayer configuration consisting of copper phthalocyanine and a perylene tetracarboxylic derivative, Tang was able to achieve a power conversion efficiency of around 1 %. In 1992, Hiramoto et al. improvised the heterojunction by thermally co-evaporating donor and acceptor organic small molecules, thus, forming a bulk heterojunction²⁶. Although this configuration did not improve its efficiency as compared to its planar heterojunction predecessor, it paved the way for solution processed bulk heterojunction. In 1995, Heeger's group invented the polymer/fullerene bulk heterojunction OPV system²⁷. Entirely solution processed, an efficiency of 2.9 % was attained for an OPV consisting of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). Polymer/fullerene devices since dominated bulk heterojunction systems, due to the superior solubility of polymeric molecules compared to "small" molecules. According to the latest solar cell efficiency

chart published by NREL (Figure 2.2), as of 2014, Mitsubishi Chemical is the current record holder for organic bulk heterojunction solar cells at 11.1 % efficiency.

An OPV material can be further divided into 2 categories: small molecules and polymers. The principal distinction lies in the different molecular weight and size of both material groups. Polymers have large constituent molecules while small molecules are named due to their relatively short chain lengths. The long chains of a polymer have more attached solubilizing groups, which allow high solubility in organic solvents. On the other hand, small molecules have short chains which make them less soluble. However, they have a lower evaporation temperature. Due to these properties, polymers are fabricated using solution process methods such as spin-coating while small molecules are processed using thermal evaporation. This relative ease of fabrication means that polymers are much favoured over small molecules. Despite their numerous advantages over inorganic semiconductors, OPV cells present a host of disadvantages as well. Firstly, the typical lifetime of an OPV is much shorter than that in Si-based solar cells. Most degradation studies are based on a poly(3-hexylthiophene):[6,6]-phenyl C₆₁-butyric acid methyl ester (P3HT:PCBM) system, given the in-depth understanding of this well-studied bulk heterojunction system^{28,29}. Secondly, carrier mobilities in organic semiconductors are generally lower. At room temperature, carrier mobilities in inorganic materials can be 100 to 10⁴ cm² V⁻¹ s⁻¹³⁰ while the best carrier mobilities can only reach 14.4 cm² V⁻¹ s⁻¹.³¹ Low carrier mobility induces slow charge carrier extraction and high charge carrier recombination.³² This severely restricts the performance of OPV devices. Thirdly, the solar spectral response of Si cells are superior as its absorption range cover from visible light to >1000 nm³³ while the best organic varieties have a narrower absorption spectral range^{34,35}. Lastly, unlike inorganic semiconductors, the primary photoexcited state in organic semiconductors is the exciton, which is a tightly bound electron-hole pair³⁶. This arises from their low dielectric constants ($\epsilon_r \approx 2 - 4$). Bound by strong Coulomb interaction, the excitons must dissociate into free charge carriers before they recombine³⁷. The tendency for excitons to recombine gives rise to short exciton diffusion lengths, which are about 10 – 20 nm.^{38,39} Due to low charge mobility, the active layer thickness is

about 100 – 200 nm^{33,40} as a thick photoactive layer results in an increase in recombination losses³³.

These disadvantages are the reason that current OPV efficiencies are still lower than those of the well-established inorganic solar cells. Encapsulation technology capable of prolonging the lifetime of an OPV device is still improving. Tuning intrinsic material properties like the carrier mobility and the exciton binding energy requires extensive investigation. Other approaches to improving device performance include tandem structures⁴¹, improving bulk heterojunction morphology⁴², novel device architectures⁴³ and optimising light absorption⁴⁴.

The use of plasmonic nanostructures in an OPV device is one of the many possible routes to improve device performance^{44,45}. When exhibiting surface plasmon resonance, plasmonic nanostructured materials strongly scatter light and can greatly enhance the local electromagnetic field⁴⁶. Primarily, these properties are exploited to enhance light absorption in solar cells. An increase in the light absorption can boost device performance. There are, however, drawbacks to introducing plasmonic nanostructures into OPVs; in particular, these metallic structures tend to promote charge carrier recombination. This interplay between the gains made by improved light harvesting and the losses due to increased recombination is a topic that shall be explored in detail in this thesis.

2.1.1 A Primer on Organic Semiconductors

Organic polymers are made up of repeating chains of carbon atoms. Originally considered as strictly insulators, it was in 1977 when Heeger, MacDiarmid and Shirakawa discovered a way to vary the electrical conductivity of polyacetylene over a range of eleven orders of magnitude.⁴⁷ In their pristine state, organic polymer can behave either as insulators or semiconductors. Upon doping, they become conducting and in some instances, may reach the metallic regime. Hence, doping paved the way for remarkable developments in the field of organic electronics.

Figure 2.3 The three different types of orbital hybridisation. Image taken from Generalic, Eni. " sp^2 hybrid orbital." Croatian-English Chemistry Dictionary & Glossary. 31 July 2014. KTF-Split. 11 Dec. 2014.

The ground state of a carbon atom has an electronic configuration of $1s^2 2s^2 2p^2$.⁴⁸ The two unpaired p electrons in the outer electronic shell can form four chemical bonds with different kinds of atoms, by forming single, double or triple bonds. A single bond is known as a σ -bond while a double bond consists of a σ and a π -bond. A triple bond has one σ and two π -bonds. The bonding between different atoms can be described by hybridisation. There are three types of hybridisation for carbon atoms: sp , sp^2 and sp^3 hybridisation. In sp hybridisation, the 2s orbital and one 2p orbital hybridise to form two sp orbitals, forming a 180° bond angle between the two orbitals (Figure 2.3a), with the two remaining p orbitals available to form two π -bonds with a neighbouring atom. In sp^2 hybridisation, the 2s orbital and two 2p orbitals hybridise to form three sp^2 orbitals which are oriented at 120° to one another (Figure 2.3b), with the one remaining p orbital available for π -bonding. In sp^3 hybridisation, one 2s orbital and three 2p orbitals hybridise to form four sp^3 orbitals, which take on a 109.5° bond angle with respect to one another (Figure 2.3c). When a chain of carbon atoms form π -bonds through overlap of their unhybridized p orbitals, electrons in the molecular π -orbital can be delocalised over several atoms. The extension of the delocalised electrons determines the conjugation length of the organic molecule.

A π -conjugated system is shaped by the overlap of the 2p orbitals of the carbon atoms. As depicted in Figure 2.4, The quantum mechanical overlap of the orbitals produces a bonding orbital (π -orbital) and an anti-bonding orbital (π^* -orbital). The bonding π -orbital and anti-bonding π^* -orbital have a lower and higher energy, respectively, than the original atomic orbital. In the ground state the bonding π -orbital will be occupied by electrons, while the anti-bonding π^* -orbital is left unoccupied. As more carbon atoms are introduced, quasi-continuous bands will be formed from the ensemble of bonding and anti-bonding states. When the molecule is in the ground state, the bonding states will be occupied up to the Highest Occupied Molecular Orbital (HOMO) while the states that have energies larger than or equal to the Lowest Unoccupied Molecular Orbital (LUMO) will be unoccupied. These ensembles of states below the HOMO and above the LUMO are analogous to the valence and conduction bands, respectively, in inorganic crystalline

semiconductors. The separation between the HOMO and LUMO is called the bandgap, and is one of the intrinsic properties of organic semiconductors.

Figure 2.4 The quasi-continuous energy bands comprise of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO).

The analogy of bands in organic semiconductors extends to excited states as well. Electrons occupying the HOMO may be excited (electrically or through photon absorption) to the LUMO. The excited electron is delocalized over the molecule and may even ‘hop’ to a neighbouring molecule and this constitutes free charge carrier transport. Promotion of an electron from the HOMO to LUMO leaves behind a hole in the HOMO, which is effectively a positive charge carrier and also exhibits transport phenomena similar to that of a free electron. Some organic semiconductors tend to transport electrons more effectively than they do holes, and are known as n-type semiconductors. Those that tend to transport holes more effectively are known as p-type.

2.1.2 Organic Semiconductors for Organic Photovoltaic Cells

As mentioned in the earlier section, OPV materials (and organic semiconductors in general) can be classified as either small molecules or polymers. Polymers, which consist

of large constituent molecules made of many repeated units, can be solution processed with methods such as spin-coating and slot-die coating. Small molecules, with their short chain lengths, are generally deposited using thermal evaporation/sublimation.

Figure 2.5 The different types of materials used commonly in OPV cells. From left to right, CuPc, C₆₀, PCBM and P3HT.

Some of the more well-known small molecules for OPV are derived from phthalocyanine and buckminsterfullerene (or C₆₀). Phthalocyanines such as zinc phthalocyanine (ZnPc) and copper phthalocyanine (CuPc) are p-type (donor) or hole conducting semiconductors while C₆₀ and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) function as n-type (acceptor) or electron transporting semiconductors. For polymers, poly(3-hexylthiophene) or P3HT is no doubt the most well-studied p-type OPV material. Figure 2.5 shows some different types of OPV materials. The choice of materials for use in OPV cells is important since it has to be spectrally matched with the solar spectrum. Generally, OPV materials absorb in the range 350 – 800 nm. The measured solar spectrum on Earth reveals that the contribution from the UV region is not significant. Air Mass 1.5 Global (AM 1.5G), the spectral irradiance that is considered as a fair representation of natural sunlight, is plotted in Figure 2.6. The normalised absorbance of CuPc:C₆₀ and P3HT:PCBM are also superimposed, showing the absorption of both OPV systems relative to AM 1.5G. A better overlap means that there is a higher amount of absorption from the solar spectrum. P3HT:PCBM covers mainly the shorter wavelengths while

CuPc:C₆₀ absorbs in the longer wavelengths. This leaves much of AM 1.5G unutilized since it can extend beyond 2000 nm. A good solar cell will optimize the coverage of the AM 1.5G spectrum. This is to maximise the number of photons absorbed by the solar cell. Some of the ways to improve the absorption range of an OPV cell include synthesising low bandgap materials and incorporating plasmonic nanostructures.

Figure 2.6 The absorption of CuPc:C₆₀ and P3HT:PCBM is compared relative to AM 1.5G solar spectrum. A large part of the solar spectrum is not utilized for both OPV systems.

2.1.3 Excitonic Conversion Steps

Most OPV devices adopt a donor-acceptor configuration. A donor-acceptor structure comprises an electron donating material and an electron accepting material. In a working OPV device, the donor-acceptor layer is sandwiched between an anode and cathode. This device structure is adopted due to the intrinsic properties of organic polymers. Here, it is important to introduce the excitonic conversion steps in an OSC device.

Five steps are involved in an OPV cell when light is converted into electricity: Photon absorption, exciton generation, exciton diffusion, charge separation and charge migration⁴⁹. These steps determine the overall photocurrent efficiency of an OPV cell. The conversion steps, together with the corresponding loss mechanisms can be represented by the schematic diagram in Figure 2.7.

Figure 2.7 The five basic excitonic conversion steps in an OPV device. The corresponding loss mechanisms are also represented.

a) Photon absorption. Generally, most OPV materials have a high absorption coefficient of $\geq 10^5 \text{ cm}^{-1}$. One of the requirements for a semiconducting material to be suitable for light harvesting demands the incident photon energy to be equal to or greater than the energy bandgap of the semiconducting material. If the photon energy is less than the energy bandgap, the photon will pass through the organic material, as it is transparent. In an OPV system, reflection loss at the interface between two materials can be quite substantial. This loss will be significantly multiplied in a multilayer solar cell. This will

reduce light absorption in the active layer. The reflection loss stems from the difference in the refractive indices when light travels from one medium to another medium. Typically, most OPV devices are fabricated on a glass substrate. A glass substrate contributes about 4 % reflection loss at the glass-air interface. This loss can be mitigated by applying an anti-reflection coating or texturing the glass surface to increase its surface area. Another loss mechanism arising from photon absorption is due to spectral mismatch. As mentioned in section 2.1.2, a good selection of semiconducting materials ensures that the utilization of the solar spectrum is optimized. The well-studied P3HT:PCBM system absorbs mainly the shorter wavelengths. This spectral mismatch leaves the longer wavelengths largely unused. The loss mechanisms can be further mitigated by improving photon absorption in the form of incorporating plasmonic nanostructures. This will be discussed in the later part of this chapter.

b) Exciton generation. Upon excitation by light, an electron is transferred from the HOMO to the LUMO in the donor, leaving behind a hole in the HOMO. This creates an exciton in the process. In organic semiconductors, these excitons are known as Frenkel excitons, while they are known as Wannier excitons in inorganic semiconductors.⁵⁰ Due to the low dielectric constant ($\sim 3 - 4$), Coulomb interaction, ranging from 0.1 – 1.4 eV, between the electron and hole is strong.⁵¹ These excitons also tend to be small, usually within the same order as a unit cell. In contrast, Wannier excitons are produced in inorganic semiconductors as they generally have large dielectric constants. The exciton binding energy is weak and is typically a few millielectron volts. Hence, Wannier excitons are large and their radii extend to a few lattice spacing. Frenkel excitons will recombine if they are not dissociated within their lifetimes.

c) Exciton migration. Upon the creation of an exciton, it will normally drift to an interface where there is a sufficient electric potential energy difference for exciton dissociation. This interface spans the donor and acceptor region. However, this must take place within the lifetime of the exciton. Hence, exciton diffusion length, which is 10 – 20 nm in an organic material, limits the thickness of the bilayer heterojunction in an OPV device.⁵² This is the reason bilayer heterojunctions are not common while a bulk

heterojunction configuration is preferred instead. The difference between a bilayer and a bulk heterojunction structure will be discussed in the next section. In an OPV cell adopting a bulk heterojunction structure, a good nanophase separation in a donor-acceptor system should be within the same order of magnitude of the exciton diffusion length. Otherwise, the excitons will recombine via radiative or non-radiative means.

d) Exciton dissociation or charge separation. The donor is a material with low electron affinity while the acceptor is a material with high electron affinity. In a heterojunction system, once the excitons drift to the donor-acceptor interface within its lifetime, efficient photoinduced charge transfer from the donor to acceptor will occur. At this interface, an electric potential gradient exists. This gradient is determined by the difference between the HOMO of the donor and the LUMO of the acceptor. Here, the exciton dissociates into a free electron and a free hole. The difference in the electron affinity gives rise to the driving force for the dissociation. In a fullerene conjugated polymer system, the photoinduced charge transfer from the donor to the acceptor happens within a time scale of 45 fs.⁵³ On the other hand, the electron transfer from acceptor to donor is extremely slow. Hence, the quantum efficiency of this dissociation process is close to 100 %. Similar to the previous excitonic conversion steps, free charges may recombine.

e) Charge migration. Once an exciton dissociates into a free electron and a free hole, the carriers will migrate to the respective electrodes. These free charges cannot move independently so they drift under the influence of an electric field. The built-in electric field is manifested when asymmetrical contacts are used. This is realised by using a cathode with a low work function for electron collection and a high work function for hole collection at the anode. The higher the number of charges the electrodes collects, the higher the electric current. It is important to note that free charge carriers will recombine if they cannot find a percolation pathway to travel to the corresponding electrodes. Hence, morphology control is paramount as it dictates the degree of nanophase separation. This also explains why a bulk heterojunction system is preferred over a bilayer structure.

The energy diagram which represents the five excitonic conversion steps in a generic donor-acceptor OSC device is depicted in Figure 2.8.

Figure 2.8 Energy diagram showing photon absorption, exciton creation in the donor, exciton migration to the donor-acceptor interface, exciton dissociation at the donor-acceptor interface and charge migration to the respective electrodes in an OPV device.

2.1.4 Device Structures

Figure 2.9 shows a simplified diagram of the working principle of an OPV cell. The working principle is based on the five excitonic conversion steps that are discussed in the previous section. Consider the simple case of the donor-acceptor semiconducting layer sandwiched between the cathode and an anode. When the device is photoexcited, electron-hole pairs or excitons are created in the semiconducting layer. The excitons dissociate into free holes and free electrons once they reach the donor-acceptor interface. From the interface, electrons will drift to the cathode while holes will migrate to the anode where they will be collected as electrical charges.

Figure 2.9 Cross section of an OPV device showing the simplified working principle based on the excitonic conversion steps.

Most OSC devices adopt either a bilayer or a bulk heterojunction configuration. The first bilayer system was created by C. W. Tang.^{24,25} An example of a bilayer heterojunction is depicted in Figure 2.10a, in which a standard device comprises of two distinct layers of the P3HT donor and PCBM acceptor. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) functions as a hole-transporting layer while the indium tin oxide (ITO) and Al electrodes function as the anode and cathode, respectively. ITO is commonly used as the anode as it is highly conductive and has a high transparency of >80 % in the visible range.³³ However, there are flaws to this design. As mentioned in the previous section, there is a limitation imposed by exciton migration and charge migration. Since only excitons created within 10 – 20 nm of the interface will migrate to the heterojunction interface, excitons that are created further away from the interface will eventually recombine. This leads to a substantial loss in the quantum yield. This can usually be circumvented by depositing thin layers. Thick layers give rise to an appreciable optical filter effect and the amount of excitons that manifests will be even lower. This drives down quantum yield even more.

Figure 2.10 An example of a a) bilayer heterojunction and b) bulk heterojunction for a P3HT donor and PCBM acceptor.

Taking into account the short exciton diffusion length of 10 – 20 nm, adopting a bulk heterojunction system can overcome this limitation. In this configuration, as shown as an example in Figure 2.10b, the donor-acceptor system is blended together to produce a single layer, instead of forming two distinct layers in a bilayer heterojunction. Due to the intermixing nature, the donor-acceptor interface is significantly increased. In a well-mixed system, the nanoscale interpenetrating network dictates that an exciton does not have to migrate more than its diffusion length before it arrives at a donor-acceptor interface.

Depending on the type of OPV material used, a bilayer heterojunction and bulk heterojunction can be deposited using a solution method such as spin-coating or by thermal evaporation/sublimation, or a combination of both.

2.1.5 Current-Voltage Characteristics

One standard technique to characterise solar cells, including OPV devices, is to measure their current-voltage scan while irradiating the sample under experimentally simulated

AM 1.5 G illumination.⁵⁴ The sample must be at a temperature of 25 °C. Besides characterising under illuminated conditions, the behaviour of an OPV cell is also measured under dark conditions. To explain the current-voltage characteristics of an OPV cell, we can model the cell as a metal-insulator-metal (MIM) structure.³⁰ In this model, consider a solar cell comprised of the semiconducting material sandwiched by two metallic contacts, the anode and the cathode. In most cases, indium tin oxide (ITO) functions as the anode while silver or aluminium is commonly used as the cathode. Figure 2.11 illustrates the energy diagram for each corresponding point of the current-voltage characteristics of an OPV device.

Under an applied reverse bias (i.e. ITO anode biased negatively with respect to Al cathode), a negligible amount of current is injected under dark conditions. Under illumination, strong internal electric fields dictate that free charge carriers can drift to their respective electrodes; the holes will drift to the anode while the electrons will move to the cathode. Under reverse bias, the current in the OPV cell flows in the same direction (Figure 2.11a) as the applied voltage. In the absence of an applied voltage, no net current can flow in the dark. The built-in electric field, which results from the difference in the work functions of the anode and cathode, is almost equally distributed (Figure 2.11b). Under illuminated conditions at this point, the maximum photocurrent that can be generated reaches its maximum. This is called the short circuit current or I_{sc} . In this situation, free charge carriers will drift to their respective electrodes. At this point, the power generated by the solar cell $P = IV = I_{sc} \times 0 = 0$. As an increasing forward bias is applied, the photocurrent will decrease, but the solar cell will reach a point at which the power extracted from the solar cell is maximum. This is the maximum power point (MPP) and it is denoted by $P_{max} = V_{MPP} \times I_{MPP}$. When the forward bias is applied further, the current becomes zero, as shown in Figure 2.11c. This applied voltage corresponds to the open circuit voltage (V_{oc}) and no free charge carriers can drift since the net driving force is zero. As a result, no photocurrent is generated. Upon further application of the forward bias, there will be charge injection from both electrodes into the semiconducting material (Figure 2.11d).

Figure 2.11 The metal-insulator-metal (MIM) model can be used to explain the current-voltage characteristics of an OPV cell. a) Reversed bias; b) Short circuit condition; c) Flat band or open circuit condition; d) Forward bias greater than open circuit condition. The energy diagram at each corresponding condition is accompanied by a current-voltage characteristics curve. The dotted line denotes measurement at dark conditions while the solid line is characterized under illuminated conditions.

To determine the efficiency of an OPV cell, the maximum power extracted from the device, $P_{\max}$, has to be compared with the incident light intensity. This is calculated by taking the ratio of the maximum power derived from the cell to the power intensity emanating from the light source. In the case of AM1.5G illumination, the intensity is 1000 W/m^2 . The efficiency, known more appropriately as the power conversion efficiency (PCE), is calculated as:

$$\text{PCE}, \eta = \frac{P_{\text{out}}}{P_{\text{in}}} = \frac{I_{\text{MPP}} \times V_{\text{MPP}}}{P_{\text{in}}}$$

Another important parameter to note is the fill factor (FF). This is taken as $\text{FF} = V_{\text{MPP}} \times I_{\text{MPP}} / (V_{\text{OC}} \times I_{\text{SC}})$. Therefore, the equation for PCE can be rewritten as:

$$\text{PCE}, \eta = \frac{P_{\text{out}}}{P_{\text{in}}} = \text{FF} \times \frac{I_{\text{sc}} \times V_{\text{oc}}}{P_{\text{in}}}$$

As illustrated in Figure 2.12, Air Mass (AM) is defined as the amount of atmosphere that solar radiation has to traverse before arriving on the Earth's surface. AM 1.5 Global or AM 1.5G for short, takes into account absorption and scattering of solar radiation by air molecules in the atmosphere while AM 1.5 does not. However, AM 1.5 is naturally referred to as AM 1.5G. This is the international standard for the characterisation of all types of solar cells. AM 1.5G is derived from the solar radiation making an angle of 48.2° with respect to the zenith. Mathematically, this is simply calculated as $\cos 48.2^\circ \approx 1/1.5$. Many solar installations lie in major population centres such as Europe, Japan and the USA. Hence, taking into account their temperate latitudes, AM 1.5G is adopted as an international measurement standard. AM 1.0 refers to the solar radiation arriving on the Earth's surface from the Sun's zenith position. It is a useful standard for measuring solar cells installed in equatorial countries such as Singapore. AM 0 is used for characterisation of solar panels on Earth-orbiting satellites. At this standard, solar radiation does not penetrate Earth's atmosphere.

Figure 2.12 The different types of Air Mass (AM) measurements. For measurements of solar cells, the international standard is AM 1.5G.

The current-voltage (I-V) characteristics of an OPV cell can be described by:

$$I = I_0 \cdot \left\{ \exp \left(\frac{e}{nkT} (V - IR_S) - 1 \right) \right\} + \frac{V - IR_S}{R_{SH}} - I_{PH}$$

where I_0 is the dark current, e the elementary charge, n the diode ideality factor, k the Boltzmann constant, T the temperature, V the applied voltage, R_S the series resistance, R_{SH} the shunt resistance and I_{PC} the photocurrent. A circuit diagram, which is electrically equivalent to the equation above, is modelled in Figure 2.13. In this model, a current source is in parallel with a diode. The shunt resistance and series resistance components are also added to complete the model. The series resistance represents the total accumulated resistance that arises from bulk transport and interfacial effects. Recombination of electrons and holes near the donor-acceptor interface is represented by the shunt resistance. A good OPV device requires a high FF. This is attained by a combination of a very high shunt resistance and a very low series resistance. I_{PC} is the

photocurrent which is generated after the free electrons and holes are collected from the corresponding electrodes. Recombination is not taken into account. The diode depicts the asymmetric conductivity in an OPV cell due to the built-in electric field of the semiconducting material.

Figure 2.13 A model showing a circuit diagram equivalent of a solar cell.

2.1.6 Improving Device Performance Using Plasmonic Materials

Performance of an OPV device can be improved through several ways. Through chemical tailoring, the development of efficient OPV based on polymers and small molecules is an ongoing process.⁵⁵⁻⁵⁷ In the area of device engineering, a myriad of methods have been investigated, some of which involve trapping light within the active layer of a solar cell. Light trapping strategies increase the path length of photons without increasing the distance that photogenerated charge carriers must travel to get extracted at the electrodes. Such strategies can make use of diffraction gratings,^{58,59} V-shaped reflective structures,^{60,61} photonic crystals⁶² and surface plasmon resonant nanostructures, for example.

Surface plasmons are attractive as they have unique optical properties in the form of localized field enhancement and strong light scattering ability. As confined electromagnetic waves propagating at the metal/dielectric interface, surface plasmons can improve light absorption in a photoactive layer and hence, photogeneration of carriers.⁶³ Localized electric field enhancement associated with surface plasmons can increase the optical path length of a photons due to elevated scattering conditions.

Materials that support surface plasmon resonance are usually called plasmonic materials. Surface plasmons are created when incident light interacts with free electrons at a metal/dielectric interface. Under the surface plasmon resonance condition at the interface, the conduction electrons in the metal are driven to oscillate in resonance with the frequency of the impinging light, which increases light absorption at specific wavelengths.⁶⁴ Energy arising from plasmon excitations is strongly localized at the metal/dielectric interface. The phenomenon can be classified into surface plasmon polaritons (SPPs) and localized surface plasmons (LSPs). SPPs propagate at the interface between a metal and a dielectric while LSPs are localized on metal nanoparticles.⁶⁵ In this thesis, special focus will be placed on the use of spherical nanoparticles, which generate LSPs under resonance conditions.

As illustrated in Figure 2.14, LSPs arise from the presence of conduction electrons in metallic spheres mediating in a background of fixed positive ions, forming a free electron plasma (Figure 2.14). This is achieved when the frequency of the incident light matches that of the resonance frequency of the nanoparticles (NPs). The plasma frequency of this free-electron plasma determines the optical properties of a metal. At resonance, optical properties in the form of absorption and scattering effects will change. The composition of both optical terms defines the extinction behaviour of plasmonic nanoparticles. Extinction behaviour is dependent on the size of the spherical nanoparticles.

Polarisability can be determined using the quasi-static approximation.⁴⁶ The mathematical theory is sufficient in predicting particle sizes as long as the dimensions do not significantly exceed 100 nm. Consider a plasmonic NP with a radius r , embedded in

an infinitely large absorbing medium (P3HT). The NP has dimensions much smaller than the wavelength of light ($r \ll \lambda$). Polarisability is a parameter which dictates optical absorption and optical scattering due to a change in the refractive index between two media. Since an applied field induces a dipole moment inside a NP, polarisability α can be defined as

$$\alpha = 4\pi r^3 \frac{\epsilon_{NP} - \epsilon_{P3HT}}{\epsilon_{NP} + 2\epsilon_{P3HT}}$$

where ϵ_{NP} and ϵ_{P3HT} are the relative permittivity of the Ag NP and P3HT:PCBM respectively. Consider a NP core with an oxide shell, embedded in an infinitely large P3HT medium. Polarisability can be rewritten as

$$\alpha = 4\pi r_2^3 \frac{(\epsilon_{oxide} - \epsilon_{P3HT})(\epsilon_{NP} + 2\epsilon_{oxide}) + f(\epsilon_{NP} - \epsilon_{oxide})(\epsilon_{P3HT} + 2\epsilon_{oxide})}{(\epsilon_{oxide} + 2\epsilon_{P3HT})(\epsilon_{NP} + 2\epsilon_{P3HT}) + f(2\epsilon_{oxide} - 2\epsilon_{P3HT})(\epsilon_{NP} - \epsilon_{oxide})}$$

where ϵ_{oxide} is the relative permittivity values of the oxide, r_1 is the inner radius, r_2 is the outer radius and $f = r_1^3/r_2^3$, which is the fraction of the total particle volume occupied by the inner sphere.

The scattering cross section and the absorption cross section can be expressed as

$$C_{scattering} = \frac{k^4}{6\pi} |\alpha|^2$$

$$C_{absorption} = k \text{Im}[\alpha]$$

respectively. k is the wave vector defined by $k = 2\pi/\lambda$. Both terms are essential in determining the absorption and scattering of plasmonic NPs and hence, imparting a direct influence on optical absorption in a photoactive layer. Take for example, a small Ag NP in air. Under the surface plasmon resonance condition, the scattering cross section can be up to ten times the cross sectional area of the particle.⁶⁶

Figure 2.14 Under resonance, surface plasmons are created. These comprise of an oscillating free electron density with respect to a metallic sphere.

Surface plasmon resonances are highly localized and the strength of the localized electric field decays rapidly with distance from the metal/dielectric interface. In order to leverage on the advantages of surface plasmons, it is hence intuitive to place plasmonic nanostructures within the photoactive layer of an OPV cell or at least, as close to the photoactive film as possible.

Plasmonic materials are usually nanostructured. Introducing them in OPV devices can help to enhance photon absorption within the active layer, while keeping the photovoltaic absorber layers thin. These plasmonic nanostructures can take the form of zero-dimensional (plasmonic nanoparticles), one-dimensional (plasmonic gratings) or two-dimensional (plasmonic periodic array) structures.⁴⁴

H.A. Atwater and A. Polman outlined several ways these plasmonic materials can help to improve absorption in a solar cell.⁴⁵ As sketched in Figures 2.15a and 2.15b, plasmonic nanoparticles, plasmonic gratings and plasmonic periodic arrays can act as subwavelength scattering centres to efficiently couple impinging light into a solar cell via forward scattering. Due to the increased angle of incidence, photons are trapped within the semiconducting active layer, resulting in an increase in the optical path length. When plasmonic nanoparticles and plasmonic periodic arrays are embedded within the active

layer, they function as subwavelength antennas (Figure 2.15c). At resonance, near field enhancement at the metal/semiconductor interface, arising from LSPs, is coupled into the active layer, thus, increasing the effective absorption cross section. Plasmonic gratings which are embedded within the active layer also perform as subwavelength antennas (Figure 2.15d). In this case, at resonance, SPPs modes are created at the metal/semiconductor interface when impinging light is coupled into the solar cell. These SPPs modes travel in a direction parallel to the active layer, hence, boosting light absorption in a photovoltaic cell. In OPV devices, plasmonic nanostructures have been placed in the active region,⁶⁷⁻⁷¹ or in the hole-transporting layer.^{72,73} Introducing a combination of two different types of plasmonic materials has also been carried out.^{71,74,75}

Figure 2.15 There are several ways in which plasmonic nanostructures can aid in improving the performance of solar cells. a) Placement of plasmonic nanoparticles and b) plasmonic periodic array at the hole-transporting layer function as light scattering centres. This will effectively trap light within the active layer. At resonance, the effective absorption cross section can also be enhanced by incorporating c) plasmonic nanoparticles and d) plasmonic gratings in the active layer.

2.1.7 Problem with Plasmonic Materials in OSCs and its Solution

The surface plasmon resonance is a near field effect. This means that, under resonance, the immediate vicinity around the metal/dielectric interface experiences an enhanced electric field, with its intensity decaying exponentially as the distance from the interface increases. Depending on the relative permittivity of the dielectric, the decay length can range from tens to hundreds of nanometres.⁴⁴ At resonance, electrons on the plasmonic material surface are forced to oscillate and this increases the effective interaction area. This interaction area is also known as the absorption/scattering cross section. The sum of both terms constitutes extinction cross section. Due to an increase in the extinction cross section, localized electric fields associated with surface plasmons in plasmonic materials can enhance light absorption in the active medium of a solar cell. To fully leverage on this effect, the placement of the plasmonic nanostructures is ideally in the active layer of an OPV cell, or at least as close as possible to its active region.

Numerous groups have investigated the impact on device performance by incorporating plasmonic nanostructures within the photoactive layer.^{44,76,77} Although they are demonstrated to improve device performance, positioning the plasmonic materials within the active layer of an OPV cell has its drawbacks. As plasmonic materials are typically metallic in nature, incorporating them into the polymer layer could result in increased charge recombination at the metal/semiconductor interface. In a well-optimized OSC, once excitons are dissociated at the donor/acceptor interface, free electrons will migrate to the cathode while free holes will drift to the anode. As the holes encounter plasmonic materials, the presence of free electrons at the metallic surface will cause charge injection.^{78,79} This process of charge injection can be interpreted as charge recombination. Gains made in photogeneration can be offset by losses due to free charge recombination.

Figure 2.16 The presence of Ag NPs in a polymer layer introduces charge recombination sites (L). Dissociated free holes will recombine with the free electrons on the metal surface. This can be mitigated by protecting Ag NPs with a shell (R).

To overcome this recombination problem, a protective sheath around the plasmonic materials can be introduced.⁸⁰⁻⁸² As depicted in Figure 2.16, the absence of a shell around Ag NP allow dissociated free holes to recombine with delocalized electrons on the surface of the Ag NP. With the introduction of a protective shell around the Ag NP, the free electrons at the NP surface will be shielded from free holes in the polymer. In order for the protective layer to be effective, the shell must be in insulating or semiconducting. For the purpose of this thesis, four different oxides will be used. They are Al_2O_3 , HfO_2 , MoO_3 and SiO_2 .

2.1.8 Monitoring Polarons in a Photoinduced Absorption (PIA) Setup

Upon photoexcitation, charges are created in the polymer backbone. The presence of these charges imparts a force on their immediate vicinity. As the polymer backbone is

rather soft, the charges induce localized elastic distortions. The presence of a charge and its accompanying polymeric distortion, is called a polaron.⁸³ A visual representation of a polaron is illustrated in Figure 2.17, where a free charge imparts a distortion on a polymer plane.

Figure 2.17 A simple visual representation of a polaron, which arises from the presence of a free charge with its accompanying polymeric distortion.

Photoexcited P3HT produces different types of polarons and they can be monitored using a Photoinduced Absorption (PIA) setup. The setup is an optical measurement system which measures small changes in the transmission of a P3HT film. The presence/absence of photoexcited species create a transmission profile that is unique to P3HT. This transmission profile or PIA signal has a characteristic spectrum which is indicative of the different polaron transitions in the polymer. In this thesis, attention shall be focused on the ~ 1.25 eV (~ 1000 nm) peak/dip, which is attributed to the P2 transition.⁸⁴⁻⁸⁸ Change in magnitude of this signal is a measure of the concentration of photogenerated charge carriers. Based on this principle, the effectiveness of having a protective shield around Ag NPs are monitored using a PIA setup. It does not measure charge recombination directly, but rather, it measures photogenerated charge carriers arising from P3HT^+

species (from P2 polaron transition). The degree of charge recombination suppression can be indirectly inferred by monitoring the magnitude of the P2 transition.

In the PIA measurement setup, the film sample is photoexcited by a blue 470 nm or red 625 nm LED. The blue LED photoexcited both the polymer and the Ag NPs while the red LED photoexcited the polymer film only.

2.2 Questions to answer based on literature

While the problem of having plasmonic nanostructures in a polymer layer is being resolved by proposing a continuous protective shell, there are certain key points pertaining to the use of oxide shells to circumvent charge recombination.

- a) What are the main factors that contribute to absorption enhancement in a polymer layer upon incorporating oxide-encapsulated Ag NPs?

Ag NPs protected by an oxide shell can be expected to be an effective measure to mitigate charge recombination at the metal/dielectric interface. At optical resonance, for oxide-encapsulated Ag NPs embedded in a polymer layer, absorption enhancement in the polymer will improve due to an increase in the extinction cross section. This is due to an increase in a Ag NP's interaction area, which allows light to be efficiently scattered into the polymer. Assuming that a thin continuous shell is sufficient to quench recombination at the metal/dielectric interface, it is interesting to discern the degree of optical enhancement in the polymer layer. Shell thickness and relative permittivity should contribute to the outcome.

- b) Is there an optimal shell thickness for encapsulating Ag NPs?

Since electric field enhancement associated with surface plasmons is highly localized at the metal/dielectric interface, the presence of the encapsulating shell around Ag NPs will limit the amount of photogenerated charge carriers in the polymer. Hence, it is hypothesized that an optimal thickness may exist to maximize field enhancement effects while suppressing charge recombination.

- c) How much is absorption expected to improve in a solar cell when encapsulated Ag NPs are introduced in the semiconducting active layer?

In the context of oxide-encapsulated Ag NPs introduced in an OSC, the magnitude of absorption improvement will depend on the type of oxide and its corresponding thickness used. The degree of improvement needs to be investigated.

2.3 PhD in context of literature

- a) Assuming that a thin insulating shell is sufficient in suppressing charge recombination, four different oxides will be investigated via simulation studies. Oxides with varying thicknesses will protect 50 nm Ag NPs. The oxides under study are Al_2O_3 , HfO_2 , MoO_3 and SiO_2 . They are selected to provide a wide range of relative permittivity (from ~ 2 to ~ 5). At optical resonance, the effect of the type of oxide and shell thickness protecting Ag NPs on absorption enhancement in a polymer layer will be investigated. Poly(3-hexyothiophene):phenyl-C61-butyric acid methyl ester (P3HT:PCBM) will be used as the polymer layer as its absorption range overlaps with the peak absorption of 50 nm Ag NPs.
- b) Although it is proven that the use of encapsulated NPs embedded in a photoactive layer will improve photogenerated carriers as compared to the use of bare NPs⁸⁰⁻⁸², a systematic study on the role of varying shell thicknesses on NPs is yet to be carried out. In this thesis, the use of Al_2O_3 as the encapsulating shell for Ag NPs is emphasized. To prove experimentally that the existence of a shell plays a significant role in mitigating charge recombination, 50 nm Ag NPs will be encapsulated with varying thicknesses of Al_2O_3 using Atomic Layer Deposition (ALD). These oxide-encapsulated Ag NPs will be coated with a 25 nm layer of P3HT. By monitoring polaron population using a Photoinduced Absorption (PIA) spectroscopy setup, an optimal Al_2O_3 thickness is determined. This optimal thickness balances maximum field enhancement effects with charge recombination. Field enhancement associated with surface plasmons is expected to improve absorption in the polymer.

- c) Numerous groups have leveraged on the use of plasmonic nanostructures in OSC devices to improve device performance.^{44,76,77} However, incorporating bare plasmonic materials in the photoactive layer offsets photogenerated carrier gains with recombination losses. The knowledge of using various oxide-encapsulated nanostructures in OPV devices remain limited. Here, simulation studies will be undertaken to determine optical gains/losses in P3HT:PCBM. Absorption will be adjusted with respect to AM1.5G intensity flux. Oxides investigated will encompass Al_2O_3 , HfO_2 , MoO_3 and SiO_2 . As these oxides are predominantly non-absorbing, extinction cross section should be dominated by scattering effects. Assuming that charge recombination at the metal/dielectric interface is completely quenched in the presence of an oxide layer, Ag NPs with thin protective shells should improve absorption gains in the polymer layer. However, absorption improvement is not expected to increase infinitely when the shell thickness is further increased.

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Chapter 3

Experimental Methodology

Experimental results are complemented by simulation models. Modelling studies were performed using COMSOL Multiphysics® Modelling Software version 4.4. The chief fabrication method used was Atomic Layer Deposition (ALD) for the deposition of Al_2O_3 while spin-coating was chosen for the deposition of poly(3-hexylthiophene) (P3HT). Nanoimprinting was used to create plasmonic gratings. UV-ozone treatment was employed for the removal of ligands on the Ag NPs. Experimental analyses were undertaken using Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), Ellipsometry, UV-vis Absorption Spectroscopy, Photoinduced Absorption (PIA) spectroscopy and current-voltage (J-V) characterization.

3.1 Rationale for Selection of Methods/Materials/Simulations

This project relies primarily on optical studies through the use of simulation and experimental methods. In this chapter, the principles underlying the fabrication, characterization and modelling techniques employed will be examined. In addition, methods of data analysis will be discussed. The rationale for the selection techniques will be highlighted.

3.2 Simulations: COMSOL Multiphysics® Modelling Software Version 4.4

Modelling studies of the optical effects on the use of four different oxides with different relative permittivity values as the encapsulating buffer in Ag NPs embedded in a polymer layer were investigated. Simulations are not meant to replace experimental results but they serve as an excellent guideline to design experiments.

COMSOL Multiphysics® Modelling Software version 4.4¹ was used to solve Maxwell's equations,

$$\nabla \times E = -j\omega B \quad \text{----- 1}$$

$$\nabla \times H = J + j\omega \quad \text{-----2}$$

for monochromatic, normally incident plane waves. Here, E , B , H and J are the electric field, magnetic flux density, magnetic field, current density field, respectively. As the equations are frequency dependent, j is $\sqrt{-1}$ while ω is the associated frequency domain. In the model, oxide-encapsulated Ag NPs were positioned on a glass substrate. These discrete NPs were embedded in a poly(3-hexylthiophene):phenyl-C61-butyric acid methyl ester (P3HT:PCBM) film. Figure 3.1 below depicts the structure subjected to modelling studies. P3HT:PCBM or P3HT was used as the semiconducting polymer layer due to its well-studied popularity among the organic solar cell research community, and therefore ready availability of its optical data.

Figure 3.1 Cross section of a structure comprising of oxide-encapsulated Ag NPs embedded in P3HT:PCBM.

In the model, Ag NPs with 50 nm diameter, spaced 200 nm apart, were positioned on a glass substrate. The NPs were encapsulated with a uniform oxide buffer layer. The size of the NPs was selected on the basis of $r \ll \lambda$, where r is the radius of the NP while λ is the wavelength of visible light (350 nm being the shortest wavelength). A 25 nm thick P3HT:PCBM completed the structure yielding glass/Ag NP/oxide/P3HT:PCBM.

The model's polymer layer was deliberately made thin so as to maximize the volume fraction of polymer that interacts with the surface plasmon fields, so that any simulated absorption enhancements become more readily apparent. Due to the thickness of the semiconducting layer relative to the size of the Ag NP, P3HT:PCBM was modelled to conform to the contours of the oxide-encapsulated Ag NP. As shown in Figure 3.2a, the top and bottom boundaries of the structure were perfectly matched layers (PMLs). The role of the PMLs was to ensure that any light that emerges from the structure is not reflected back into the model. For a qualitative investigation, the modelled structure was a quarter unit cell with half-periodicity of 100 nm. This was chosen to minimize simulation time while assuming that inter-NP interactions were negligible. This assumption is valid when negligible changes to the peak positions are observed to the simulated results when the half-periodicity was increased to 150 and 200 nm. The initial mesh for the simulations is shown in Figure 3.2b. The mesh was made finer in the vicinity of the metal/oxide and oxide/polymer interfaces for higher accuracy.

Figure 3.2 (a) Model of the structure set up in COMSOL Multiphysics® Modelling Software version 4.4 interface; (b) Mesh distribution of the model; (c) Example of the electric field distribution plot normalized with respect to incident electric field. The extra boundary between glass and PML is where the incoming plane wave enters the structure.

The four different oxides investigated are Al_2O_3 , HfO_2 , MoO_3 and SiO_2 . These oxides were selected as they have a broad range of relative permittivity, ranging from ~ 2 to 5.5 . The value of the oxide relative permittivity affects the surface plasmon resonance and the corresponding electric field distribution. The direction of illumination was that of plane waves propagating from air into glass, i.e. from top to bottom in Figure 3.2.

The relative permittivity of the Ag NP was derived from refractive index values by Johnson and Christy.² Optical constants of Al_2O_3 , HfO_2 , MoO_3 and SiO_2 were obtained from Malitson & Dodge³, Wood⁴, Lajaunie⁵ and Lemarchand⁶ respectively. The real and imaginary part of the oxides' relative permittivity, ϵ_r and ϵ_i respectively, are plotted in

Figure 3.3. All the oxides are non-absorbing (*i.e.* imaginary component ≈ 0) in the visible range, with the exception of MoO_3 , which is slightly absorbing for wavelengths <400 nm.

The relative permittivity values of the oxides vary with wavelength throughout the 350 – 550 nm range. This is especially so for MoO_3 which shows a considerable increase in its relative permittivity values for the shorter wavelengths. JA Woollam Variable Angle Spectroscopic Ellipsometer (VASE) was used to measure the optical constants of P3HT:PCBM while poly(3-hexylthiophene) (P3HT) values were derived from digitizing the plot from René A. J. Janssen et. al.⁷

Figure 3.3 Real part of the relative permittivity values (left y-axis) of Al_2O_3 , HfO_2 , MoO_3 and SiO_2 . With the exception of MoO_3 , all oxides are non-absorbing (right y-axis). MoO_3 is slightly absorbing for wavelengths <400 nm.

Electric field distribution plots were normalized against the normal incident electric field. An example is shown in Figure 3.2c. This allowed the identification of regions with enhancement, where values are bigger than unity. Since absorption is a direct function of

electric field (proportional to $|E|^2$), regions with electric field enhancement will experience a corresponding increase in absorption. Absorption spectra were calculated for neat Ag NPs to determine the magnitude of the absorption peak and its wavelength. This absorption peak is attributed to surface plasmon resonance. Based on the relationship $A + R + T = 1$, where A is absorptance, R is reflectance and T is transmittance, an absorptance value of 1 means that absorption is 100 % with no reflectance and transmittance.

It has to be highlighted that the modelling studies only encompassed optical effects. Electronic effects such as charge transport and recombination are not taken into account as they are beyond the scope of the simulation model.

3.3 Sample Fabrication Techniques

In the experiments, Ag NPs and the photoactive layer were prepared using spin-coating. The Ag NPs were treated using UV-ozone treatment. Ag NPs were encapsulated with an insulating buffer using atomic layer deposition (ALD).

3.3.1 Spin-coating

This technique is probably the most popular approach to deposit solution-processable polymers onto sample substrates. It is a cheap and efficient way to prepare thin polymer films. In addition, this method enabled the deposition of Ag NPs with a reasonable distribution. Ag NP solution was spin-coated in ambient conditions while P3HT and P3HT:PCBM solutions were spin-coated in an inert glovebox environment.

Ag NPs from Nanocomposix⁸ were dissolved in ethanol at a concentration of 10 mg/ml for samples meant for TEM imaging; 1 mg/ml for samples meant for Photoinduced Absorption (PIA) spectroscopy measurements. Next, the substrates were annealed at 165 °C for 10 min to remove the residual solvent.

P3HT from Rieke Metals Inc⁹ were prepared in a dichlorobenzene (DCB) solution at a

concentration of 5 mg/ml. After spin-coating, the film was allowed to dry for 2 hr before annealing it at 120 °C for 10 min. This yielded a polymer film thickness of ~25 nm. As mentioned in the previous section, a thinner polymer film is preferred due to interaction volume arising from plasmonic effects.

For a P3HT:PCBM solution, 40 mg of P3HT was mixed with 32 mg of PCBM from Nano-C¹⁰ in 2 ml of DCB. Similarly, after spin-coating, the film was allowed to dry for 2 hr before annealing it at 120 °C for 10 min. This yielded a polymer film thickness of ~200 nm.

3.3.2 Nanoimprinting Lithography (NIL)

Nanoimprinting Lithography (NIL) is a process where patterns in the nanoscale regime are transferred from a mold to a substrate.¹¹ The mold, typically silicon, has a predefined pattern with topographical features of high resolution. It is a low cost process with high throughput. The process flow is illustrated in Figure 3.4.

This technique creates patterns by leveraging on the mechanical deformation of poly(methyl methacrylate) (PMMA). Firstly, a layer of PMMA was spin-coated onto a glass substrate. Next, the Si mold was positioned over the substrate and a pressure of 60 bars at a temperature of 160 °C was applied during the imprinting process. This elevated temperature, which is above the glass transition temperature (T_g) of PMMA, was necessary to ensure that the polymer attains a viscous flow state. This enables the PMMA to flow in between the nanostructures, allowing it to conform to a pattern which is determined by the mold. Lastly, the temperature was cooled down to 40 °C before the mold was released.

NIL was chosen as the preferred technique to create grating structures. They have good reproducibility with high throughput. These patterned structures formed the basis of gratings-incorporated solar cells.

a) Spin-coating of PMMA on substrate

b) Position Si mold over substrate

c) Imprint with pressure and elevated temperature

d) Remove Si mold

Figure 3.4 The nanoimprinting steps for creating high resolution patterns on the substrates.

3.3.3 Atomic Layer Deposition (ALD)

Ag NPs were coated with Al_2O_3 by Atomic Layer Deposition (ALD) using a Beneq TFS 200. It is a thin film deposition technique where samples are exposed to alternate gaseous species. It is a self-limiting process in which reaction will cease once all surface reactive sites are adsorbed. This approach is undertaken since a precise oxide encapsulation thickness is necessary for the experiments.

Figure 3.5 ALD involves a sequential deposition of gaseous species (a-d). Since the process is self-limiting, thickness control is highly controllable. A TEM image of the thickest deposited Al_2O_3 is also shown.

ALD fulfilled two crucial experimental aspects of this study: 1) Al_2O_3 thickness is highly controllable (to the Ångström level) due to the self-limiting nature of the deposition reaction. The number of cycles directly determines oxide thickness, thus, allowing accurate attainment of the required thickness. 2) The gaseous precursors chemisorb in a conformal and uniform manner on the surface of the Ag NPs, ensuring no direct contact between the P3HT and Ag NPs. Figure 3.5 shows the schematic diagram of the ALD process. Precursors A are first introduced into the reaction chamber and they adsorb on the substrate surface (Figure 3.5a). Excess precursors are purged from the chamber once all surface reactive sites are adsorbed. Next, precursors B are introduced into the reaction chamber where they chemisorb onto the first deposited layer from precursors A (Figure 3.5b). Similarly, excess precursors are purged from the chamber once all surface reactive sites are adsorbed. This process is repeated (Figure 3.5c) until a desired thickness is attained (Figure 3.5d).

The ALD deposition consisted of 0.1 s pulse of water, 3 s soaking, 40 s purge, 0.1 s pulse of trimethylaluminum, 3 s soaking and 20 s purge per cycle. Different thicknesses of the insulator were investigated (0, 0.2, 0.8, 2, 3, 8, 15 and 30 nm). The oxide thickness of the thickest sample ($30 \pm \sim 0.5$ nm) was measured from a Transmission Electron Microscope (TEM) image (Figure 3.5), and the thicknesses of the thinner samples were determined by linear interpolation from the cycle numbers. The thicknesses were reported to either one significant figure (if <10 nm), or to the nearest nm (>10 nm).

3.3.4 UV-Ozone Treatment

Typically, organic contamination/compounds can be removed using UV-ozone treatment. In the experiments, Ag NPs are stabilized with polyvinylpyrrolidone (PVP) ligands. To ensure that the spacing between the Ag NP and P3HT was determined by the Al_2O_3 thickness, the ligands were removed by subjecting the spin-coated Ag NPs to a UV-ozone treatment using Novascan PSD UVT Series for 1 min at room temperature.

Figure 3.6 summarizes the process of ozone generation. Ozone is produced when air is irradiated by UV, which splits oxygen molecules (O_2) into oxygen atoms ($O^\cdot$). Oxygen atoms will attach to unreacted oxygen molecules, forming ozone (O_3). Ozone oxidizes readily with organic compounds and by this principle, PVP can be effectively removed.

Figure 3.6 Upon UV irradiation, oxygen molecules are split into oxygen atoms, which then combine with unreacted oxygen molecules to form ozone.

The harsh conditions imposed by UV-ozone treatment could lead to oxidation of the Ag NPs. Hence, a minimum treatment time of 1 min was considered to be just sufficient in removing the ligands, while minimizing unwanted oxidation. Different UV-ozone treatment timings were investigated and the treated Ag NPs were observed under a TEM. Under TEM imaging, no additional layer could be detected for Ag NPs subjected to a 1 min UV-ozone treatment, thus, confirming the removal of PVP without subsequent oxidation of the Ag surface. As ozone is a powerful oxidant, a longer UV-ozone is undesirable since it is almost a foregone conclusion that oxidation of Ag NPs will take place.

3.4 Characterization

A wide variety of characterization tools were used to investigate the samples. Quantitative and qualitative analysis techniques were used. Imaging methods such as

Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM) assisted in Ag NP characterization. Optical analysis in the form of UV-vis spectroscopy and Photoinduced Absorption (PIA) spectroscopy were attempted. Solar cells devices were characterized using a solar simulator setup.

3.4.1 Transmission Electron Microscope (TEM)

Samples were imaged using a Philips CM300 (Figure 3.7) high resolution Transmission Electron Microscope (TEM). Operating at 300 kV, images were obtained in bright field TEM imaging mode. The use of TEM is an important tool in allowing the determination of the average Ag NP size, as well as determining the presence of polyvinylpyrrolidone (PVP) ligands around the Ag NPs. It is also used to evaluate the thickness of Al_2O_3 , which was deposited using Atomic Layer Deposition (ALD).

Figure 3.7 A Philips CM300 high resolution TEM system used for imaging Ag NPs and Al_2O_3 thickness.

A TEM displays magnified images of a thin sample in the range 10^3 to 10^6 . Behaving as negatively charged particles, electrons penetrate thin samples and are focused by the use of electric and magnetic fields. A TEM instrument can be divided into three different sections: 1) Illumination system; 2) Specimen stage and 3) Imaging system.

Electrons are produced and accelerated in the illumination system via a system of lenses. Samples are loaded into the specimen stage. Positioned in between the illumination system and the imaging system, specimens are loaded via an air-lock antechamber. TEM images are created on the phosphorus screen in the imaging system. A charge coupled diode (CCD) camera converts the image on the phosphorus screen into digital images. The resolution of a modern TEM is about 0.2 nm.

In order to image the size of the Ag NPs and their ligands, Ag NPs were prepared in solution form. The NPs were prepared by dissolving 10 mg of Ag NPs in 1 ml of ethanol. Next, several drops of the Ag NP solution were dripped onto holey Cu TEM grids and allowed to dry overnight before they were sent for TEM imaging. Some grids were exposed to various UV-ozone treatment timings for the removal of ligands.

To image the conformance of Al_2O_3 on the Ag NPs, cross sectional TEM imaging was needed. Ag NP solution, dissolved in ethanol with a concentration of 10 mg/ml, was spin-coated on a Si substrate. A high Ag NP concentration was needed since the task of imaging a cross section showing the conformance of Al_2O_3 on Ag NPs was a challenging undertaking. The spin-coated Si samples were milled down to a mere 100 nm thick using Focused Ion Beam (FIB) milling before transferring for TEM imaging. Sample milling was performed in a dual-beam FIB using FEI Helios Nanolab 600. Si substrates were used rather than glass due to charging concerns during the FIB process.

3.4.2 Scanning Electron Microscope (SEM)

The maximum operating voltage in a SEM is typically 30 kV, which is smaller than that of TEM. While a TEM imaging works by electron penetration of samples, SEM uses the scanning principle, in which primary electrons are focused into a small diameter electron probe. The probe scans across the specimen by the use of magnetic fields. This is called raster scanning. Through raster scanning, secondary electrons are ejected from the sample surface. Sample image is formed by collecting secondary electrons emanating from the

specimen.

Figure 3.8 Ag NP distribution on the substrates was imaged using JEOL FESEM 7600F.

A reasonable distribution of Ag NPs was needed for optical measurements. Scanning Electron Microscopy (SEM) imaging was useful in helping to quantify this. JEOL FESEM 7600F (Figure 3.8) was used to image the Ag NP distribution on the samples. Images were obtained at 5 kV. The concentration of Ag NPs in solution determines the distribution of the Ag NPs. Obviously, a higher Ag NP solution concentration produces a higher concentration of Ag NPs to be deposited on the substrates. After a series of iterations, the final solution concentration was set at 1 mg/ml in ethanol for samples that were subjected to Photoinduced Absorption (PIA) spectroscopy measurements.

3.4.3 Ellipsometry

Optical constants of P3HT:PCBM were measured using a J.A. Woollam Variable Angle Spectroscopic Ellipsometer (VASE) (Figure 3.9). Ellipsometry is an optical technique

that uses polarized light to characterize the optical constants $n(\lambda)$ and $k(\lambda)$ of thin film stacks. These values are needed for modelling studies.

To prepare the samples for ellipsometric measurements, polymer films were deposited by spin-coating a P3HT:PCBM solution onto Si substrates. After allowing the films to dry for 2 hr, they were annealed at 120 °C for 10 min. The thickness obtained was about 200 nm.

Figure 3.9 Optical constants of P3HT:PCBM films were obtained by using a JA Woollam Variable Angle Spectroscopic Ellipsometer (VASE).

The thickness and n , k values of the film are not directly measured. Instead, the change in the polarization of light as it is reflected at different angles off the sample is measured. The measured polarization change has two components: the amplitude ratio Ψ , and the phase difference Δ . Data for both components were acquired for 65°, 70° and 75° angles of incidence. The wavelength range was scanned in the 300 – 800 nm range. The measured ellipsometric data was fitted using the Cauchy model to infer the wavelength dependent refractive index, $n(\lambda)$, and the extinction coefficient $k(\lambda)$ and film thickness.

3.4.4 UV-VIS Absorption Spectroscopy

A Shimadzu UV 3101PC (Figure 3.10) was used to measure the absorption spectra of the samples. This technique is primarily relied on to quantify the position of the surface plasmon resonance wavelength of Ag NPs. It also aided in determining the Ag NP solution concentration to prepare by observing the magnitude of the surface plasmon peak. In addition, the absorption of P3HT films were also measured. The absorption spectra were needed for the fitting calculations, which will be covered in the later chapters.

Figure 3.10 Absorption of the samples are measured using a Shimadzu UV 3101PC.

Absorbance of the samples was measured in terms of the negative logarithm of transmittance. Transmittance is affected by a combination of absorption and scattering and to a lesser extent, reflection. Absorbance is determined by the equation:

$$A(\lambda) = -\log \frac{I}{I_0} = -\log T$$

where $A(\lambda)$ is the absorbance, I is the intensity of the transmitted beam, I_0 is the intensity of the illuminating beam and T is the transmittance. The amount of Ag NPs deposited onto the substrates cannot be too low as absorption enhancement arising from surface plasmons will be insignificant in causing an overall absorption improvement in the polymer layer. On the other hand, the amount of Ag NPs deposited on the substrate cannot be too high either since the photons will be reflected away from the polymer layer.

3.4.5 Photoinduced Absorption (PIA) Spectroscopy

Net photo-generated charge concentrations were monitored using a Photoinduced Absorption (PIA) Spectroscopy setup. Built in-house, it is an optical measurement system which detects miniscule light-induced changes in the transmission of a sample.

Figure 3.11 Schematics of the PIA setup. The pump used was either a blue 470 nm or red 625 nm LED.

In P3HT, hole polarons were monitored in a PIA setup. These polarons exhibit a broad absorption peak/dip centered at ~ 1.25 eV (~ 1000 nm). This absorption peak/dip is

assigned as a P2 transition.¹² Changes in the magnitude of this peak is a measure of net photo-generated charge concentration.

The optical setup is shown in Figure 3.11. In the PIA measurements, the probe light was provided by a 720 nm long pass filtered quartz tungsten halogen lamp. The filter ensures that the sample will not be photo-excited by wavelengths below this threshold. A focused light emitting diode (LED), square-wave modulated at 233 Hz, was used as the pump. The probe light was passed through a monochromator and was detected by a cooled indium gallium arsenide (InGaAs) detector. The total signal from the detector was measured using a Keithley 2400 source-meter, while the 233 Hz modulated signal was measured with a SR830 lock-in amplifier. Only the in-phase signal (i.e. 'X-channel') was used as data. PIA signals were corrected for photoluminescence emission from P3HT by repeating the measurement with no probe light.

Figure 3.12 The pump photoexcites the sample, creating P3HT⁺ carriers. However, when the pump is in the OFF mode, no P3HT⁺ carriers are created. Correspondingly, a change in the transmission of the sample is induced.

The working principle of a PIA setup can be explained by the diagram in Figure 3.12. When the LED pump is in the OFF mode, the film has transmittance T . No P3HT⁺ carriers are formed. When the LED pump is in the ON mode, new P3HT⁺ species are created. Absorption increases due to their presence and this is reflected as a dip in transmittance values. The change in transmittance is defined as photoinduced T , which is given by $T + \Delta T$. ΔT has a very small value and this is detected by a lock-in amplifier.

3.4.6 Current-Voltage Characterizations

The current-voltage (J-V) characteristics were measured using a solar simulator (SAN-EI Electric XES-301S 300W Xe Lamp JIS Class AAA). The performance of a solar cell is determined by the power conversion efficiency (PCE), which is defined by:

$$PCE = FF \frac{J_{sc} V_{oc}}{L_o}$$

where V_{oc} is the open circuit voltage, J_{sc} is the short circuit current density, FF is the fill factor and L_o is the light power intensity (1000 W/m² for standard solar cell characterizations). Any increase in FF , J_{sc} and V_{oc} will have a direct impact on the eventual PCE. In device engineering aspects, applying light trapping methods by leveraging on surface plasmons can improve the J_{sc} since the average optical path length is increased.

A schematic diagram of the solar characterization setup is shown in Figure 3.13. Light from the xenon lamp passes through a AM1.5G filter, allowing the spectrum of the output light source to match the solar spectrum. The measurement was carried out by applying a bias across the OPV devices and sweeping its J-V characteristics from -1 to 1 V. Solar cell devices were illuminated under the calibrated AM1.5G solar simulator and the photocurrent generated was detected using a Keithley 2400 source-meter. The light source intensity was calibrated using a KG-5 filtered photodiode and is adjusted to 100 mW/cm². All the measurements were performed in an inert glove box environment.

Figure 3.13 A solar simulator setup with its corresponding electronic components (L). The solar simulator from SAN-EI (R).

3.5 Overview of Methodologies

A heavy emphasis has been placed on the use of simulation models. It is crucial in the designing of the experimental setup which involves the use of PIA spectroscopy to monitor polaron signals and UV-vis spectroscopy to determine surface plasmon peaks. The use of ALD ensures a superior control of deposited oxide thickness. Other analysis tools such as SEM and TEM play a supporting role to image Ag NPs.

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Chapter 4

Polymer Absorption at Ag NP Resonance Due to Different Oxide Thicknesses – A Theoretical Study

Incorporating plasmonic nanoparticles (NPs) in an OSC can improve device performance. As plasmonic materials are usually metallic in nature, positioning the NPs within the polymeric semiconducting layer introduces additional charge recombination sites. This can be circumvented by encapsulating the NPs with a continuous buffer layer. However, the surface plasmon peak of a Ag NP and its intensity evolve with respect to oxide thickness and relative permittivity. In these modelling studies, the use of four different oxides with different relative permittivity (Al_2O_3 , HfO_2 , MoO_3 and SiO_2) as the encapsulating buffer in a poly(3-hexyothiophene):phenyl-C61-butyric acid methyl ester (P3HT:PCBM) film are investigated. Electric field distribution plots reveal how absorption in the semiconducting layer is affected by the choice of oxide and its corresponding thickness. At resonance, the polymer layer experiences very minimal absorption enhancement for thin oxide-encapsulated Ag NPs. However, as the oxide thickness is increased, absorption is observed to significantly improve for buffer layers with high relative permittivity values. It is believed that a high dielectric contrast can induce a highly localized electric field enhancement but this effect is primarily determined by its Ag NP peak position position relative to P3HT:PCBM, which is an absorbing medium. This chapter explores how the choice of oxide and its thickness can affect light distribution in a polymer at Ag NP resonance.

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4.1 Introduction

Chapter 2 introduces the concept of improving device performance by incorporating plasmonic nanoparticles in the active layer of an OSC. However, as these NPs are usually metallic in nature, undesirable charge recombination sites are introduced. This problem can be worked around by introducing a continuous buffer layer around the NPs. Upon incorporating the buffer-coated NPs into the polymeric semiconducting layer, the NPs are effectively isolated away from the polymer. The Ginger group has demonstrated that introducing a very thin SiO_2 layer of 2.5 nm around Ag nanoprisms enhances the absorption properties of poly(3-hexythiophene):phenyl-C61-butyric acid methyl ester (P3HT:PCBM).¹ This thickness is sufficient in completely suppressing charge recombination without having to compromise plasmonic enhancement. Encapsulated NPs also has the added benefit of better surface plasmon peak tunability as compared to bare NPs.² As encapsulating NPs with an oxide layer will induce changes to the surface plasmon peak position of Ag NPs and its corresponding magnitude,²⁻⁹ a measured approach is crucial in selecting a suitable oxide with the right thickness.

Obviously, the buffer layer should be insulating/semiconducting to prevent any further charge recombination losses. Oxides such as HfO_2 and MoO_3 should be sufficient to serve their function. Using oxides such as TiO_2 and ZnO is not ideal since they are conducting. This will defeat the purpose of isolating the NPs from charge recombination losses. Hence, in these simulation studies, focus will be placed on the use of insulating oxides Al_2O_3 , HfO_2 , MoO_3 and SiO_2 as the buffer layer. While there is a minimum buffer thickness requirement to completely suppress charge recombination, there is a limit in which the thickness can attain. As the electric field enhancement associated with surface plasmons are highly localized, having an excessively thick insulating layer limits the extent in which the localized field can extend into the semiconducting layer. Hence, there is an optimal layer which will effectively balance charge recombination and maximizing field enhancement. This is reinforced in an earlier study which quantified an existence of an optimal Al_2O_3 layer around Ag NPs in order to generate the maximum absorption.¹⁰ However, it must be highlighted that in this chapter, the modelling only encompasses

optical studies. Fortunately, charge recombination in the bulk can be directly inferred by studying electric field distribution. On the other hand, it is beyond this chapter's scope to calculate charge recombination on the Ag NP surface.

Charge recombination in the bulk polymer can be accounted for by the relation:

$$k_{diss}X - R = \frac{\pi\epsilon_2\epsilon_0}{h} |E|^2 - k_f X \quad (1)$$

where k_{diss} is the polaron dissociation rate, X is rate of change of polaron concentration, R is bimolecular recombination rate, ϵ_2 is the imaginary component of the ϵ_r of P3HT:PCBM, ϵ_0 the permittivity of free space, h is Planck's constant, E is the electric field component and k_f is the non-radiative monomolecular recombination rate.¹¹ Note that this formula does not take into account, charge recombination at the NP/polymer interface. By rearranging equation 1, both R and k_f are dependent on the electric field. Since $|E|^2$ is a direct function of both terms, it can be safely assumed that charge recombination increases linearly with the square of electric field. Regions of enhanced electric field will equate to higher absorption, which in turn, results in higher charge recombination. Hence, charge recombination in the bulk polymer will not be calculated but rather, inferred indirectly from electric field distribution. To keep the investigation simple, oxide thickness is kept thin so as to ensure that the plasmonic field effect can propagate into the active layer and at the same time, assuming that the insulating layer is sufficient in keeping out charge recombination at the NP/polymer interface.

In this chapter, the effects of having different oxide thicknesses with different relative permittivity values on the electric field distribution in P3HT:PCBM at Ag NP resonance will be tackled. Electric field distribution plots reveal regions of absorption and charge recombination in the bulk polymer. They present a good visual representation of how absorption and recombination are distributed in a P3HT:PCBM system embedded with an oxide-encapsulated Ag NP. This will be correlated with polarisability of an encapsulated Ag NP arising from different oxides with different shell thicknesses. This polarisability parameter will be determined by calculating its extinction cross section, which is a

measure of the sum of probability of absorption and scattering of Ag NPs. It measures the ability of a Ag NP to distribute light and hence, a direct relation to absorption gains/losses in the polymer. Finally, absorption in P3HT:PCBM will be tabulated at various oxide conditions.

4.2 Simulation Setup

Modelling studies of the optical effects on the use of the four oxides as the encapsulating buffer in Ag NPs embedded in a polymer layer were investigated. The detailed simulation model setup has already been presented in Chapter 3.

4.3 Results

Although charge recombination at the NP/polymer interface can be controlled by encapsulating Ag NPs with an oxide, the surface plasmon peak of the NP and its magnitude will evolve with changes in the relative permittivity contrast and oxide shell thickness. Hence, the choice of insulating oxide will influence absorption enhancement in a semiconducting layer. Although nanoparticles with dielectric core and metallic shell are well-studied,⁶⁻⁹ very limited studies have been undertaken for metallic cores with dielectric shells.

4.3.1 Surface plasmon peak due to different oxides with different shell thicknesses

Relative permittivity or dielectric constant is related to the refractive index of a material. Non-transparent materials such as silver have a complex refractive index while oxides are mostly transparent and non-absorbing. The real part of the relative permittivity determines the magnitude of the red-shift of the surface plasmon peak of Ag NPs. This observation is already well-established and verified by numerous groups.²⁻⁵

The absorption spectra in Figure 4.1 shows the surface plasmon peak position of oxide-encapsulated Ag NPs in a 25 nm thick P3HT:PCBM layer. The Ag NP was encapsulated

with the four different oxides with varying shell thicknesses (0, 2, 5, 10, 20, 30 nm). Bare Ag NP has a peak absorption position of ~ 410 nm. The surface plasmon peak red-shifts when the real part of the relative permittivity is increased. Oxides with higher relative permittivity values will red-shift more. MoO_3 , with a relative permittivity ~ 5 red-shifts the absorption peak by 93 nm when the oxide thickness is increased from 0 nm to 30 nm. On the other hand, SiO_2 , with a relative permittivity of ~ 2 red-shifts by a mere 26 nm when the oxide thickness is increased by the same magnitude. Sandwiched in between, HfO_2 ($\epsilon_r \sim 4$) and Al_2O_3 ($\epsilon_r \sim 3$) red-shifts by 51 nm and 28 nm respectively.

Figure 4.1 Absorption spectra of oxide-encapsulated Ag NPs embedded in P3HT:PCBM. MoO_3 , with the highest relative permittivity values of ~ 5 , red-shifts the most while SiO_2 , with the lowest relative permittivity of ~ 2 , red-shifts the least.

The plots were rearranged to observe the change in the magnitude of the absorption peak

intensity of the Ag NPs by fixing the oxide thickness while varying the relative permittivity values. Oxides with a 2 nm thickness produce Ag NP absorption intensities which are very similar (Figure 4.2a). However, as the oxide thickness is increased, the distinction between different oxides becomes clear. Besides an observed red-shift with increasing relative permittivity, a decrease in the surface plasmon peak intensity is expected. In Figure 4.2b, once the oxide thickness attains 5 nm, the absorption magnitude of Ag NPs encapsulated with SiO_2 is about twice that of MoO_3 . At a thickness of 10 nm (Figure 4.2c), this magnitude widens about 2.5 times. As the oxide thickness is increased to 20 and 30 nm (Figures 4.2d & 4.2e), the magnitude is further increased to three times. Absorption peak intensity is a direct result of electric field strength. At Ag NP resonance, electric field enhancement is particularly strong at the metal/oxide interface. For oxides with low relative permittivity values (SiO_2 and Al_2O_3), the P3HT:PCBM polymer has a dampening effect on the electric field enhancement strength. This dampening effect is due to the absorbing nature of the polymer while oxides are almost non-absorbing. As the oxide thickness is increased, the dampening effect of the polymer on the Ag NP diminishes as the electric field enhancement at the metal/oxide dominates. As a result, absorption magnitude of Ag NPs increases.

Figure 4.2 By plotting similar thicknesses together, the effect of having different relative permittivity values on the absorption magnitude of Ag NPs can be observed. Different oxides are plotted for (a) 2 nm; (b) 5 nm; (c) 10 nm; (d) 20 nm; (e) 30 nm.

4.3.2 Electric field distribution due to different oxides with different shell thicknesses

In the previous section, simulation studies have demonstrated the ease in which the surface plasmon peak position is tuned with different relative permittivity values and with different oxide thicknesses. However, electric field distribution plots within a P3HT:PCBM system embedded with oxide-encapsulated system presents a more insightful view. Since absorption is a direct function of electric field ($\text{Absorption} \propto |E|^2$), regions of enhanced electric field intensity equates to higher absorption and elevated charge recombination in the polymer bulk. By relying on electric field distribution plots, there is a better understanding on the effects of the presence of encapsulated Ag NPs on the absorption in the polymer layer.

The corresponding electric field distribution within a P3HT:PCBM system for a Ag NP at resonance is plotted in Figures 4.3 (a)-(f). The electric field distribution was obtained by normalizing electric field with respect to incidence. Since electric field has a direct relationship with absorption, regions with a high concentration of electric field intensity will experience a high absorption. A series of oxide thicknesses was investigated: a) no Al_2O_3 shell; b) 2 nm Al_2O_3 shell; c) 5 nm Al_2O_3 shell; d) 10 nm Al_2O_3 shell; e) 20 nm Al_2O_3 ; f) 30 nm Al_2O_3 . In order to ensure that the semiconducting polymer was able to reap the optimal benefits of enhanced electric field enhancement, modelling of thicker shells (> 30 nm) was not undertaken.

Figure 4.3 Electric field distribution plots for Al_2O_3 -encapsulated Ag NPs embedded in P3HT:PCBM. The electric field strength was obtained by normalizing electric field intensity with incident field strength. The resonant wavelength for each oxide thickness is indicated. The oxide thicknesses are (a) 0 nm; (b) 2 nm; (c) 5 nm; (d) 10 nm; (e) 20 nm and (f) 30 nm.

As highlighted in Figure 4.3, the effect of having an oxide shell has a clear effect on the electric field distribution in the P3HT:PCBM. In Figure 4.3a, in the absence of an insulating shell, absorption in the immediate vicinity of the Ag NP has an exceptionally high absorption. This decays rapidly as the distance is increased. When a 2 nm thick Al_2O_3 shell is introduced (Figure 4.3b), most of the electric field enhancement is localized within the shell, although regions at the Ag NP/P3HT:PCBM interface are still

benefitting from the increase in absorption. As the shell thickness is further increased to 5 nm and 10 nm (Figure 4.3c & 4.3d respectively), an increasing amount of the electric field enhancement is confined in the Al_2O_3 shell. At a thickness of 10 nm (Figure 4.3d), the localized electric field around the Ag NP is hugely amplified but absorption in P3HT:PCBM is not correspondingly improved. A further increase in the oxide thickness to 20 nm (Figure 4.3e) and 30 nm (Figure 4.3f) reveals that most of the electric field enhancement is trapped within the shell instead of encroaching into the polymer layer.

The relative permittivity contrast between the Ag NP and oxide determines the strength of the electric field enhancement at the metal/oxide interface. The strength of the electric field enhancement has a direct impact on the absorption in the semiconducting layer. A stronger electric field intensity at the metal/oxide interface will ensure that its enhancement will extend through the thickness of the oxide and penetrate into P3HT:PCBM. In order to investigate the effect of changing refractive indices (and hence, relative permittivity) on the electric field distribution, results for different oxides were computed.

As depicted in Figure 4.4, thin Al_2O_3 layers are sufficient to allow a considerable amount of electric field enhancement to extend into P3HT:PCBM. Based on the assumption that a continuous oxide encapsulation of Ag NPs is enough to suppress charge recombination at the NP/polymer interface, oxide thickness was maintained at 2 nm. The oxide buffer coating was changed to HfO_2 , MoO_3 and SiO_2 . As highlighted in Figure 4.4d, at Ag NP resonance, the SiO_2 shell induces a particularly strong electric field enhancement, which substantially extends into P3HT:PCBM. However, in the case of MoO_3 , the absorption is significantly weaker (Figure 4.4c). Barring charge recombination and other external factors, it is clear that the only parameter which causes changes in the electric field intensity is the change in the relative permittivity values of the oxide. The relative permittivity is lowest for SiO_2 while it is highest for that of MoO_3 . At this point, it appears that at Ag NP resonance, lowering an oxide's relative permittivity will induce a higher electric field enhancement and hence, giving rise to an improved absorption in P3HT:PCBM.

Figure 4.4 Normalized electric field distribution plots for 2 nm thick oxides, (a) Al_2O_3 ; (b) HfO_2 ; (c) MoO_3 and (d) SiO_2 . The resonant wavelength for each oxide thickness is indicated.

4.3.3 Polarisability

From the modelling above, it can be easily discerned that the intensity of the electric field associated with surface plasmons is sensitive to the thickness of the oxide shell. This is in addition to the well-known fact that peak Ag NP absorption due to surface plasmons are sensitive to the relative permittivity contrast at the metal/dielectric interface.²⁻⁵ This is due to NP polarisability arising from an external dielectric medium. It measures the ability of an oxide-encapsulated Ag NP to scatter light into P3HT:PCBM by taking into account scattering cross section and absorption cross section.

Polarisability can be determined using quasi-static approximation.¹² Consider a plasmonic NP with a radius r , embedded in an infinitely large P3HT:PCBM medium. The NP has dimensions much smaller than the wavelength of light ($r \ll \lambda$). Since an applied field induces a dipole moment inside a nanoparticle, polarisability α can be defined as

$$\alpha = 4\pi r^3 \frac{\epsilon_{NP} - \epsilon_{P3HT}}{\epsilon_{NP} + 2\epsilon_{P3HT}} \quad (2)$$

where ϵ_{NP} and ϵ_{P3HT} are the relative permittivity values of the Ag NP and P3HT:PCBM respectively.

Consider a Ag NP core with an oxide shell, embedded in an infinitely large P3HT medium. Polarizability will be rewritten as

$$\alpha = 4\pi r_2^3 \frac{(\epsilon_{oxide} - \epsilon_{P3HT})(\epsilon_{NP} + 2\epsilon_{oxide}) + f(\epsilon_{NP} - \epsilon_{oxide})(\epsilon_{P3HT} + 2\epsilon_{oxide})}{(\epsilon_{oxide} + 2\epsilon_{P3HT})(\epsilon_{NP} + 2\epsilon_{P3HT}) + f(2\epsilon_{oxide} - 2\epsilon_{P3HT})(\epsilon_{NP} - \epsilon_{oxide})} \quad (3)$$

where r_1 is the inner radius, r_2 is the outer radius and $f = r_1^3/r_2^3$, which is the fraction of the total particle volume occupied by the inner sphere.

The scattering cross section can be calculated as

$$C_{scattering} = \frac{k^4}{6\pi} |\alpha|^2$$

$$= \frac{8\pi}{3} k^4 r_2^6 \left| \frac{(\epsilon_{oxide} - \epsilon_{P3HT})(\epsilon_{NP} + 2\epsilon_{oxide}) + f(\epsilon_{NP} - \epsilon_{oxide})(\epsilon_{P3HT} + 2\epsilon_{oxide})}{(\epsilon_{oxide} + 2\epsilon_{P3HT})(\epsilon_{NP} + 2\epsilon_{P3HT}) + f(2\epsilon_{oxide} - 2\epsilon_{P3HT})(\epsilon_{NP} - \epsilon_{oxide})} \right|^2 \quad (4)$$

while its absorption cross section is

$$C_{absorption} = k \text{Im}[\alpha]$$

$$= 4\pi k r_2^3 \text{Im} \left[\frac{(\epsilon_{oxide} - \epsilon_{P3HT})(\epsilon_{NP} + 2\epsilon_{oxide}) + f(\epsilon_{NP} - \epsilon_{oxide})(\epsilon_{P3HT} + 2\epsilon_{oxide})}{(\epsilon_{oxide} + 2\epsilon_{P3HT})(\epsilon_{NP} + 2\epsilon_{P3HT}) + f(2\epsilon_{oxide} - 2\epsilon_{P3HT})(\epsilon_{NP} - \epsilon_{oxide})} \right] \quad (5)$$

where k is the wave vector defined by $k = 2\pi/\lambda$.

Equations 4 and 5 can be combined to yield the extinction cross section, which is the sum of scattering cross section and absorption cross section.

$$C_{\text{extinction}} = C_{\text{scattering}} + C_{\text{absorption}} \quad (6)$$

If the shell thickness is small ($f \rightarrow 1$), polarisability becomes very large when $\text{Re}[\epsilon_{\text{NP}}] = -2\epsilon_{\text{P3HT}}$. This occurs at wavelengths close to the resonant enhancement. At this condition, it is possible for light to interact with an area which is larger than the geometrical cross section of the NP. Changes in the oxide shell thickness contribute to the polarisability as well. Absorption in P3HT:PCBM is dictated by the polarisability of the oxide-encapsulated Ag NPs. Since polarisability is a function of extinction cross section, a high polarisability means that photons have a higher tendency of getting trapped in the polymer layer. This usually takes place at the resonant frequencies of Ag NPs. Equation 6, which relates to extinction cross section, is valid for particle sizes which are much smaller than the wavelength of light. This quasi-static approximation is sufficient for particle sizes less than 100 nm. If the incident wavelength is in the visible wavelength to the near infrared range, this formula loses its accuracy once particle sizes approach 100 nm and beyond.¹²

Extinction cross section spectra for the oxide-encapsulated Ag NPs are plotted in Figure 4.5. The imaginary component of the relative permittivity of P3HT:PCBM is also plotted. The extinction spectra are directly related to the absorbance spectra of Figure 4.1. Peaks in the absorbance and extinction cross section spectra are related to surface plasmon peaks. Spectra in both figures display a similar red-shifting trend as the shell thickness for each oxide increases. With the exception of a shell thickness of ≥ 20 nm, the peak positions for both sets of figures (Figures 4.1 and 4.5) are representative of each other. As mentioned earlier, equation 6 loses its accuracy for larger particle sizes. This is especially so for oxide thicknesses of 20 nm and 30 nm. This explains why the extinction cross section peak is slightly misaligned from the absorption peak. For the studies, the maximum NP diameter is 110 nm (diameter of Ag NP + oxide shell thickness). However, it is assumed that equation 6 is reasonably good in assisting in the investigations as Ag NPs with other oxide shell thicknesses have diameters that can be adequately addressed by the quasi-static approximation.

Figure 4.5 Computed extinction cross section based on the sum of absorption cross section and scattering cross section.

4.3.4 Absorption in P3HT:PCBM at Ag NP resonance

It must be noted that strong surface plasmon peak intensity does not necessarily translate to enhanced absorption in P3HT:PCBM. In order to quantify that, absorption in the polymer layer at Ag NP resonance is calculated. This data is summarized in Figure 4.6. Here, absorption per unit volume is calculated to give a better gauge of absorption gain/loss in P3HT:PCBM. The oxides are grouped according to their thicknesses. The dotted line represents absorption per unit volume arising from the absence of an insulating shell.

Figure 4.6 Calculated absorption per unit volume at Ag NP resonance in P3HT:PCBM.

When $f \rightarrow 1$ (low shell thicknesses of up to 5 nm), absorption gains in P3HT:PCBM are mostly in the negative region. At 2 nm thicknesses, absorption in P3HT:PCBM appears to dip slightly for all oxides. A further increase in the thickness to 5 nm only shows an increase in absorption for MoO₃. However, as the shell thickness increases to 10 nm, absorption gains are clearly observed for all oxides except for SiO₂. At this point, oxides with high relative permittivity (MoO₃ and HfO₂) appear to be more useful in improving light absorption in the polymer layer. Both oxides induced a big increase in the absorption while Al₂O₃ and SiO₂ registered very little improvement. Light absorption seems to benefit from a minimum thickness of ~10 nm for most oxides. For thicker oxides beyond 10 nm (i.e. 20 nm and 30 nm), further enhancements can be observed for buffer layers with high relative permittivity values. Interestingly, although SiO₂, with the lowest relative permittivity, produces the highest electric field enhancement at the metal/oxide interface, it causes the lowest absorption in the polymer layer. The reverse is true for MoO₃, which has the highest relative permittivity. Across all oxides, the trend

appears to suggest that absorption improvement will plateau once a threshold thickness is reached. Primarily, what determines the extinction cross section magnitude is the Ag NP plasmon peak position relative to the absorption range of P3HT:PCBM. This magnitude is also determined by a NP's proximity to P3HT:PCBM, which is an absorbing medium.

It is worthy to note that the position of the extinction cross section peak will determine the degree of absorption enhancement in the P3HT:PCBM. Intuitively, lining the extinction peaks within the polymer blend will improve absorption. This is well-represented by MoO₃ in Figure 4.5. Correspondingly, absorption gains in the polymer due to MoO₃-encapsulated Ag NPs are reflected in Figure 4.6. For SiO₂-encapsulated Ag NPs, since most of the extinction peaks do not lie within the absorption range of the polymer (Figure 4.5), absorption gains are either in the negative region or very minimal (Figure 4.6). However, there is no simple explanation to the observed optimum shell thickness as the maxima in absorption per unit volume is an interplay of both relative permittivity contrast (of Ag NP and the oxide shell) and the extinction cross section peak of Ag NP in the oxide shell or P3HT:PCBM.

4.4 Discussions

In this section, the assumptions in the theoretical and numerical models presented in this Chapter will be discussed.

Firstly, it has to be pointed out that the choice of 50 nm Ag NPs is to restrict the resonant influence of the Ag NPs to its fundamental resonant mode. This is to ensure that the higher order modes due to larger Ag NP sizes do not come into play for the interested wavelengths of between 350 nm to 700 nm. As for the P3HT:PCBM active layer, a thin 25 nm layer was chosen for two reasons. First, the main aim of incorporating plasmonic NPs is to enable the use of less active material (equating to lower costs). Therefore a much thinner active layer is chosen as compared to that of a typical P3HT:PCBM thickness of 100 – 200 nm. Second, plasmonic enhancement due to the presence of the oxide-encapsulated Ag NPs is highly localized in the vicinity of the NPs. Hence, the

presence of a sufficiently thin active layer is desired to capture the improvement in optical absorption specifically due to the localized field enhancement induced by the oxide-encapsulated Ag NPs.

Secondly, quasi-static approximation has been used to derive extinction cross section in Section 4.3.3. This approach is good in predicting extinction trends for NP diameters less than 100 nm. In the studies, an oxide shell thickness of 30 nm will give rise to a NP diameter of 110 nm. Strictly speaking, a modified equation leveraging on Mie theory is preferred when dealing with larger particle sizes. However, it is beyond the scope of this paper to derive a modified equation for the core-shell system. Furthermore, taking into consideration that the largest NP size does not significantly exceed the requirement for quasi-static approximation, the calculations are still well-placed to explain extinction trends.

Thirdly, it is worthy to revisit the basic assumption that was made earlier with regard to calculating absorption per unit volume for P3HT:PCBM. The geometrical setup of the model means that the active layer volume will increase with increasing oxide thickness. Abide being a useful gauge, calculating absorption per unit volume means that active layer volume geometry effect has been neglected. A thicker oxide produces a more corrugated active layer volume geometry, which by itself, is adept at light trapping. Perhaps a more useful gauge will be realized if the total active layer volume is kept constant regardless of shell thickness. This will involve thinning the thickness of the active layer to compensate for the increase in oxide thickness. From an experimental point of view, this may yet be challenging to undertake.

Last but not least, it must be stressed that the simulation studies only encompass optical models. Other electronic effects such as charge recombination and other non-radiative recombination in the polymer bulk can only be indirectly inferred from electric field distribution. However, the results can be used as a benchmark for light management in the use of OSCs.

4.5 Conclusions

Optical effects arising from oxide-encapsulated 50 nm diameter Ag NPs are investigated. Oxide shell thickness and the choice of oxide will inadvertently affect light absorption in a polymer layer and this can be explained by the polarisability of an oxide-encapsulated Ag NPs. The modelling studies show that increasing oxide shell thickness will expectedly red-shift the surface plasmon peak of Ag NPs. The red-shifting nature of the surface plasmon peak of encapsulated Ag NPs is also observed by increasing the shell's relative permittivity. In order to improve light absorption at Ag NP resonance in P3HT:PCBM, a shell thickness of ~ 10 nm is sufficient for Al_2O_3 , HfO_2 and MoO_3 . Assuming that extinction cross section peaks are aligned with the absorption range of P3HT:PCBM, an oxide with low relative permittivity (SiO_2) does not appear to be a good candidate for encapsulating Ag NPs while an oxide with high relative permittivity (MoO_3) appears to be the most attractive.

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Chapter 5

Optimal Shell Thickness for Al_2O_3 -encapsulated Ag NPs for Enhancing Polaron Generation in P3HT – An Experimental Study

Embedding metal nanoparticles in the active layer of organic solar cells has been explored as a route to improving charge carrier generation, with localized field enhancement as a proposed mechanism. However, embedded metal nanoparticles can also act as charge recombination sites. To suppress such recombination, the metal nanoparticles are commonly coated with a thin insulating shell. At the same time, this insulating shell limits the extent that the localized enhanced electric field influences charge generation in the organic medium. It is presumed that there is an optimal thickness which maximizes field enhancement effects while suppressing recombination. Atomic Layer Deposition (ALD) was used to deposit Al_2O_3 layers of different thicknesses onto silver nanoparticles (Ag NPs), in a thin film of P3HT. Photoinduced absorption (PIA) spectroscopy was used to study the dependence of the photogenerated P3HT^+ polaron population on the Al_2O_3 thickness. The optimal thickness was found to be 3-5 nm. This knowledge can be further applied in the design of metal nanoparticle-enhanced solar cells.

5.1 Introduction

Localized electric fields associated with surface plasmons on metallic nanoparticles can enhance light absorption in surrounding organic media. While enhancing light absorption, metal nanoparticles also act as centers for charge carrier recombination, so that the gains made in photogeneration can be offset by losses due to recombination. Coating the metal nanoparticles with an insulating layer (e.g. silica¹⁶⁻¹⁸) is a common strategy to reduce recombination losses. Unfortunately, this insulating layer also limits the extent to which the localized plasmonic electric field extends into the active organic medium. Therefore, it is hypothesized that an optimal insulator thickness exists in such metal@insulator nanoparticle systems that maximizes photogeneration of charge carriers while suppressing carrier recombination.

In this chapter, photoinduced absorption (PIA) spectroscopy is used to study the hole polaron concentration in poly(3-hexylthiophene) (P3HT) films, as enhanced by Ag NPs. The rationale of using P3HT instead of P3HT:PCBM will be discussed later in this section. A series of samples were made in which Ag NPs were coated with different thicknesses of aluminum oxide (Al_2O_3) deposited by atomic layer deposition (ALD). This allowed for the study of the effect of insulator shell thickness on the concentration of photogenerated charge carriers. Other oxides such as HfO_2 , MoO_3 and SiO_2 , which were mentioned in the previous chapter, were not undertaken due to experimental limitations.

PIA is a pump-probe technique that is used to investigate photoexcited states in organic solar cells. The optical absorption of P3HT^+ hole polarons shows a well-documented characteristic peak around 1000 nm (1.25 eV).¹⁹⁻²³ Ginger's group has investigated the role of plasmonic materials in organic solar cells using PIA.²⁴ Their experiments on silver nanoprisms in poly(3-hexylthiophene):phenyl-C61-butyric acid methyl ester (P3HT:PCBM) films revealed an increase of photocharge generation by up to 3 times. In a follow-up experiment, the group also underlined the importance of an insulating shell on the silver nanoprisms to prevent metal-mediated losses in plasmon-enhanced solar cells.¹⁷ In a more recent development, polaron yield enhancements of ~ 7 were observed

for edge-gold-coated silver nanoprisms.²⁵

The main objective of this chapter is to find an optimal thickness of Al_2O_3 insulating layer for maximizing photogenerated polaron concentrations in P3HT films that incorporate Ag NPs. The rationale for an optimal thickness is as follows: The strength of the localized electric field decays rapidly with distance from the nanoparticle. Therefore, polaron generation may be expected to be higher for thin oxide layers compared to thick oxide layers. On the other hand, thicker oxide layers increase the separation between metal nanoparticle and polarons and thus, thick oxide layers are more effective at preventing charge carrier recombination.

Due to the spherical geometry of the Ag NPs, it is beyond the scope to describe the electric field decay length by an analytical expression. This is made even more challenging by the non-radial symmetrical nature of the electric field distribution and the refractive index changes with position. However, this attenuation length can be visually represented by simulating the electric field distribution of an oxide-encapsulated Ag NP embedded in P3HT.

Figure 5.1 shows the simulated electric field distribution plot of an Al_2O_3 -encapsulated Ag NP at peak resonance, embedded within a P3HT layer. The structure rests on a glass/ITO substrate. This was calculated using COMSOL 4.4, for monochromatic, linearly polarized plane waves, normally incident on the ITO/glass face. In the absence of Al_2O_3 shell, the plasmonic field extends ~ 10 nm into the P3HT. This extension diminishes as the shell thickness increases, such that when the shell reaches 10 nm, the plasmonic field is nearly non-existent in the P3HT. Regions nearer to the nanoparticle experience a higher electric field enhancement, but the electric field decays rapidly in the oxide shell before reaching the polymer, such that absorption would probably not be enhanced significantly.

Figure 5.1 Simulated plot of the electric field strength distribution of surface plasmon resonance in a quarter unit of Al_2O_3 -encapsulated Ag NP embedded in P3HT. The resonance wavelength at each corresponding shell thickness is indicated. The wavelength used corresponded to the wavelength at which the Ag NPs in each structure showed peak resonance. The structure rests on top of a glass/ITO substrate. When there is no shell, the enhanced electric field extends well into the P3HT. This extension of the plasmonic field into the P3HT diminishes as the shell thickness increases. When the shell is 10 nm thick, there is almost no plasmonic field in the P3HT.

In the previous chapter, the polymer was modelled in the form of a P3HT:PCBM blend. However, the model in Figure 5.1 utilizes a neat P3HT film instead. Simulation studies had to be aligned with PIA characterizations, which will be discussed later in this chapter. Obviously, in terms of polaron yield, a P3HT:PCBM blend will be much more efficient and more relevant in OSC devices. As demonstrated by Kulkarni et al., significant PIA signal enhancement in the P3HT:PCBM blend was observed.²⁴ Although the results are insightful, this technique does not allow clear differentiation of polaron contribution between Ag NPs and the polymer blend. In effect, enhancement in polaron population

contributed by Ag NPs will be drowned out by the P3HT:PCBM's inherent PIA signal. On the contrary, by replacing P3HT:PCBM with neat P3HT films, polaron enhancement attributed from the presence of Ag NPs will be much more discernible and quantifiable. In view of this, simulation studies were modelled for P3HT films.

Figure 5.2 Slight modifications to the simulation model were made in order to reflect experimental setup. a) Initial structure that was investigated in Chapter 4. b) An additional ITO/ Al_2O_3 layer was added. The P3HT:PCBM blend was replaced by a neat P3HT film.

Another slight modification was made to the simulation structure, as compared to the previous chapter. As depicted in Figure 5.2a, the initial model comprised of discrete oxide-encapsulated Ag NPs positioned on a glass substrate. From an experimental point of view, the oxide-encapsulated Ag NPs can be prepared via a synthesis route and spin-coated onto glass substrate. Difficulties were encountered when Ag NPs were spin-coated on bare glass, hence, the switch to an ITO/glass substrate was made. This was added into the simulation structure in Figure 5.2b. For the preparation of Ag NPs, there is a limit in which these NPs can be prepared. Theoretically, it is possible to tune the oxide thickness

through modification of the synthesis process. A careful approach should allow for the attainment of Ag NPs with different Al_2O_3 thicknesses. However, a superior approach to shell thickness adjustment is ALD, where precise control of different Al_2O_3 thicknesses is unparalleled. Unfortunately, not only does this method deposit a conformal layer of Al_2O_3 on the Ag NPs, any surface, including the substrate, will be subjected to an equal thickness of deposited oxide. As a result, an additional layer of Al_2O_3 appears on the substrate surface. The modified structure is represented in Figure 5.2b.

5.2 Experimental

Ag NPs capped with polyvinylpyrrolidone (PVP) were purchased from Nanocomposix in powder form and were prepared by dispersing them in ethanol at a concentration of 1 mg/ml. In order for the Ag NPs to disperse in ethanol, the Ag NPs were functionalized with PVP. Figure 5.3 shows the TEM image of a cluster of Ag NPs. The average diameter of the nanoparticles is 50 nm. TEM imaging clearly reveals a monolayer of PVP encapsulating the Ag NPs. The PVP ligands ensure that the NPs are well-dispersed so that they do not agglomerate.

Figure 5.3 TEM image of a cluster of Ag NPs with their PVP ligands clearly visible.

Regioregular (>98%) Sepiolid™ P200 P3HT was acquired from Rieke Metals and used

as received. Indium tin oxide (ITO) substrates purchased from Xin Yan Technology Ltd were cleaned by sonicating in Hellmanex solution, DI water, acetone and isopropanol alcohol sequentially. After drying in a 60 °C oven, the substrates were treated with argon plasma before spin-coating the Ag NPs in an inert environment. Subsequently, they were annealed at 165 °C for 10 min to remove residual solvent. The samples were treated in a UV-ozone cleaner for 1 min to remove the PVP from the Ag NPs. The PVP capping was removed so that the spacing between the metal and P3HT was determined solely by the thickness of the Al_2O_3 layer.

Figure 5.4 A series of TEM images showing the state of PVP removal at different UV-ozone treatment times. A 1 min treatment is sufficient enough to ensure complete PVP removal.

A series of UV-ozone treatments were undertaken to determine the minimum time required to remove the PVP. It appears counter-intuitive to perform such a treatment,

which may easily oxidize Ag NPs under such a harsh UV-ozone environment. However, it is a necessary step to completely strip PVP from the NPs. Assuming that negligible oxidation were to take place on the Ag NPs, a UV-ozone treatment time of no more than 1 min should be sufficient. Figure 5.4 shows complete removal of PVP after subjecting Ag NPs to a 1 min treatment. Obviously, additional treatment time (5 & 10 min) will ensure PVP removal. Such a prolonged exposure to UV-ozone treatment was deemed unnecessary as it would be almost certain to induce surface oxidation of Ag NPs.

To ensure a reasonable amount of Ag NP coverage on the substrates, different concentrations of Ag NP solutions were prepared. It was determined that Ag NPs prepared with a concentration of 1 mg/ml in ethanol will produce a NP coverage of ~1 % on the substrates (Figure 5.5).

Figure 5.5 Spin-coating 1 mg/ml of Ag NP solution will give rise to a NP coverage of around 1-2 % on the substrates.

A layer of Al_2O_3 was deposited onto the spin-coated Ag NPs using Atomic Layer Deposition (ALD), which consisted of 0.1 s pulse of water, 3 s soaking, 40 s purge, 0.1 s pulse of trimethylaluminum, 3 s soaking and 20 s purge per cycle. Different thicknesses of the insulator were investigated (0, 0.2, 0.8, 2, 3, 8, 15 and 30 nm). The oxide thickness

of the thickest sample ($30 \pm \sim 0.5$ nm) was measured from a TEM image (Figure 5.6), and the thicknesses of the thinner samples were determined by linear interpolation from the cycle numbers. The thicknesses were reported to either one significant figure (if < 10 nm), or to the nearest nm (> 10 nm).

Figure 5.6 The conformal deposition of Al₂O₃ enables the precise control of the oxide thickness using ALD. a) Here, the cross-section TEM image shows an Ag NP encapsulated with a thin layer of Al₂O₃. The white contrast underneath Al₂O₃ is native SiO₂. b) Schematic of the different layers is illustrated for clarity.

As mentioned in Chapter 3, ALD produces a uniform and conformal coating of Al₂O₃ onto Ag NPs. This is crucial since it ensures no direct contact between P3HT and Ag NPs for charge recombination.^{16-18,26} TEM imaging was used to investigate the cross-section of the conformal layer of Al₂O₃ on Ag NPs. This image was used to determine the thickness of the insulating shell. Figure 5.6a illustrates the cross-section TEM image of an Al₂O₃-encapsulated Ag NP on a Si substrate. For clarity, Figure 5.6b shows the schematic of the different layers. Layers of C and Pt were sputtered onto the sample to protect it during the focused ion beam milling process and can be seen covering the Al₂O₃ layer. The Al₂O₃ can be seen to coat the Ag NP conformably and has a thickness of 30 nm. A thin layer of native SiO₂ can be seen on the Si substrate. The Al₂O₃ coating on top

of the Ag NP appears fuzzy due to that region being out of focus and because a much smaller depth of Al_2O_3 was imaged.

Neat P3HT (in dichlorobenzene) films were spin-coated in an inert environment onto the oxide-encapsulated Ag NPs. The thickness of the polymer films was about 25 nm. P3HT film was kept thin so that a significant volume fraction of the P3HT was in close proximity to the Ag NPs. The P3HT film thickness was measured with a surface profiler and found to be similar for all samples, regardless of the thickness of the Al_2O_3 . Lastly, the samples were encapsulated to prevent sample degradation, as the PIA experiments were performed in air.

To perform PIA measurements, the probe light was provided by a 720 nm long pass filtered quartz tungsten halogen lamp. A focused light emitting diode (LED), square-wave modulated at 233 Hz, was used as the pump. The role of the pump wavelength was investigated by using a blue 470 nm or red 625 nm LED. The blue LED photoexcited both the polymer (absorbance range of ~450 nm to 650 nm) and the Ag NPs (absorbance range of ~450 nm to 500 nm) while the red LED photoexcited the polymer film alone. The probe light was passed through a scanning monochromator and was detected by a cooled indium gallium arsenide (InGaAs) detector. The total signal from the detector was measured with a Keithley 2400 source-meter, while the 233 Hz modulated signal was measured with a SR830 lock-in amplifier. Only the in-phase signal (i.e. 'X-channel') was used as data. PIA signals were corrected for photoluminescence emission from P3HT; the photo-luminescence signal was determined by repeating the measurement with no probe light.

5.3 Results & Discussions

PIA measures changes in the absorption of samples due to photoexcitation. The absorption of light by semiconducting polymers typically results in the creation of excitons. In P3HT, it is known that a small fraction of excitons spontaneously dissociate to form polarons¹⁹, which can be detected by PIA. The characteristic absorption of the

hole polarons in P3HT manifests itself as a dip in the $\Delta T/T$ (fractional change in optical transmission) signal at ~ 1.25 eV. The magnitude of $\Delta T/T$ is directly proportional to the concentration of these polarons in the sample.²⁴

Figure 5.7 PIA spectra of samples excited with either a blue LED or red LED. a) Under blue light (which is near the resonance energy of the Ag NPs and is also absorbed by P3HT), PIA signal is highest for P3HT films with encapsulated Ag NPs, followed by a neat P3HT film and lowest for P3HT films with bare Ag NPs. b) Under red light (which is absorbed by P3HT only), PIA signal is highest for a neat P3HT film, followed by P3HT film with encapsulated Ag NPs and lowest for P3HT with bare Ag NPs.

Figure 5.7 shows the $\Delta T/T$ spectra for P3HT samples, photoexcited using a blue 470 nm LED and red 625 nm LED. The blue LED photoexcites both the Ag NPs and the P3HT film while the red LED only photoexcites the P3HT layer. Under blue light (Figure 5.7a), polaron concentrations are enhanced by Ag NPs insulated with Al_2O_3 . However, in the absence of the oxide layer, there is a decrease in the polaron concentration with respect to the neat P3HT film. Ag NPs can act as sites for exciton quenching as well as charge carrier recombination, processes which can be limited by an insulating shell.

Figure 5.7b shows the $\Delta T/T$ spectra for the same samples under red light. Polaron concentration is greatest for a neat P3HT film but decreases for samples incorporating Ag NPs, either encapsulated or bare. Off resonance illumination does not allow for any enhancement in polaron generation, hence, the Ag NPs behave solely as loss centers. These loss processes can be limited by the presence of an insulating shell. Hence, the film incorporating bare Ag NPs shows the lowest polaron concentration.

Figure 5.8 Normalized absorbance of the Ag NPs encapsulated with different thicknesses of Al_2O_3 . The red-shifting nature of the peak due to increasing oxide thickness is evident.

It is known that the surface plasmon resonance energy of metallic NPs will shift depending on the dielectric properties of the surrounding medium. This phenomenon has been observed by several groups²⁷⁻³⁰ and can be rationalized with effective medium approximations.³¹⁻³³ Figure 5.8 shows the normalized absorbance spectra of the Ag NPs with different Al₂O₃ thicknesses (0.2, 0.8, 2, 3, 8, 15, 30 nm), measured using a Shimadzu UV 3101PC spectrophotometer. Bare Ag NPs prepared on an ITO/glass substrate have a surface plasmon peak at 448 nm. This peak shifts from 448 nm to 482 nm when a 30 nm layer of Al₂O₃ is deposited. A further red-shift would be expected when there is a P3HT top layer changing the effective medium refractive index.

Quantitative comparison of polaron concentrations in these samples must account for the difference in the amount of pump light absorbed by the Ag NPs. This difference in the amount of absorbed pump light arises from the shift in Ag NP absorption spectra and varying fractional contribution of Ag NP absorption to total absorption across the different samples. Obtaining the scaling factor *S* involved 3 different measured spectra:

- 1) glass/ITO/P3HT (Figure 5.9a);
- 2) glass/ITO/Ag NP/Al₂O₃ (x nm)/P3HT (Figure 5.9a);
- 3) glass/ITO/Ag NP/Al₂O₃ (x nm) (Figure 5.9b).

The absorbance of ITO/Ag NP/Al₂O₃ (x nm)/P3HT, shown in Figure 5.9 for various thicknesses of Al₂O₃, was assumed to be a linear combination of the other two spectra.

Mathematically, this assumption is expressed as:

$$A_{AgNP/Al_2O_3/P3HT}(E) = \alpha A_{AgNP/Al_2O_3}(E + \Delta E) + \beta A_{P3HT}(E)$$

where *A* is the measured normalized absorbance, with the subscripts denoting the constituents and structure of the samples. Here, α and β are the linear weights, denoting the relative absorption strengths of the Ag NPs (insulated or not) and P3HT respectively.

E is the photon energy, and ΔE is the absorption red-shift when the Ag NP/ Al_2O_3 nanoparticles are covered by P3HT instead of air. The left side represents the measured sample absorbance, while the right side represents the predicted absorbance based on the linear combination assumption. The fitting procedure is to find the combination of α , β and ΔE that yields the smallest absolute difference between both sides of the equation. Therefore, the following function is minimized:

$$\varepsilon(\alpha, \beta, \Delta E) = \|A_{\text{AgNP}/\text{Al}_2\text{O}_3/\text{P3HT}}(E) - \alpha A_{\text{AgNP}/\text{Al}_2\text{O}_3}(E + \Delta E) - \beta A_{\text{P3HT}}(E)\|^2$$

Figures 5.9c-j are examples of optimized fits for 0, 0.2, 0.8, 2, 3, 8, 15 and 30 nm Al_2O_3 thicknesses respectively. Green and red lines represent measured absorbance of ITO/AgNP/ Al_2O_3 and ITO/P3HT respectively. The linear combination is shown in black, and the measured ITO/AgNP/ Al_2O_3 /P3HT absorbance is the blue dotted line. The quality of the fits are found to be excellent (Mean squared error of less than 0.001).

Figure 5.9 a) Measured absorbance of ITO/AgNP/ Al_2O_3 /P3HT samples, showing small changes in the 400-500 nm region due to increasing Al_2O_3 thickness. For reference, the absorbance of a neat P3HT film is also shown. b) Absorbance spectra of Ag NPs with different Al_2O_3 layers, showing the red-shift in the surface plasmon resonance as the Al_2O_3 thickness is increased. c-j) Fitted curves and fitting parameters for a 0, 0.2, 0.8, 2, 3, 8, 15 and 30 nm oxide shell.

The absorbance of the insulated/non-insulated Ag NPs relative to the total sample absorbance can be written as:

$$S = \frac{\alpha}{\alpha + \beta}$$

The quantity S can then serve as a scaling factor to fairly compare the $\Delta T/T$ data.

Absorbance spectra of Ag NPs in the air and in P3HT are quite different due to near field interactions between P3HT and Ag NPs.^{34,35} Unfortunately, in the experiment, it was impossible to directly discern the absorption characteristics of the Ag NPs when embedded in P3HT. In the fitting methodology to derive the quantity S , an implicit assumption was made that the shapes of the Ag NPs absorption spectra remain the same. The fits resulting from this assumption appear reasonably good, which suggests that the effect of changing the surrounding medium (from air to P3HT) on the NP absorption spectra appear to be minimal.

The scaled PIA data (under 470 nm blue light) are plotted in Figure 5.10a, which now shows an up-down trend in the $\Delta T/(TS)$ curves as Al_2O_3 thickness increases. In Figure 5.10b, this trend is shown clearly for the 980 - 1020 nm data points, with an obvious optimum Al_2O_3 thickness in the 3-5 nm range.

Under blue LED illumination, the polaron population increases sharply when a mere 0.2 nm of Al_2O_3 is deposited, as compared to the sample without an oxide layer. Polaron concentration is further enhanced as Al_2O_3 thickness is increased to 3 nm. This can be attributed to a decline in charge recombination as the free charge carriers in P3HT are better insulated from the Ag NPs. For Al_2O_3 thicknesses around 3-5 nm, peak polaron concentrations are observed. However, the polaron concentration starts to decrease for thicker Al_2O_3 layers, with a substantial drop once the oxide layer exceeds 8 nm. With an 8 nm separation between the Ag NPs and the polymer, the plasmonic field strength has decayed to an extent which has a limited influence on polaron generation. This is in agreement with the simulated electric field plots shown in Figure 5.1, where the plasmonic field is almost completely absent when Al_2O_3 thickness is 10 nm. At 30 nm, the polaron concentration is comparable to a sample with no oxide layer.

Dye-sensitized solar cells (DSSCs) enhanced by Ag NPs were previously studied by Standridge et al., in which TiO_2 was deposited onto Ag NPs by ALD and the photocurrent of the DSSC was found to depend on the TiO_2 thickness.³⁶ They reported a monotonic decrease in photocurrent enhancement starting from a TiO_2 thickness of 2 nm, placing a

bound on the location of a possible optimum at less than a few nanometers. In this respect, the quantified optimum of 3-5 nm fits into such a range.

Figure 5.10 a) Scaling factor is applied to the PIA spectra of films excited using a blue LED. The ideal Al_2O_3 thickness is about 3-5 nm. b) a plot of scaled $\Delta T/(TS)$ vs thickness, showing the ideal oxide thickness of 3-5 nm.

The optimum insulator shell thickness found here is likely to depend on factors such as:

- 1) Nanoparticle geometry: NPs with sharp edges (such as nanoprisms^{24,25} and nanorods^{4,10,11}) concentrate the plasmonic field where curvature is largest (i.e. at the vertices). It is possible that this further concentration of the electric field could lead to increased optimum shell thickness.
- 2) Absorber and shell material: The plasmonic field distribution is highly dependent on the optical constants of the medium surrounding the Ag NP. To create a working device, a semiconductor shell (such as MoO₃, TiO₂, ZnO or PEDOT:PSS)^{7,36,37} may be preferable to an insulating one, particularly if the shell also covers the electrode and must allow selective charge transport for the device to function, or to modify the electrode work-function. Electronic properties of the shell will also affect the optimal shell thickness.
- 3) Position with respect to the absorber layer: A device may be fabricated with NPs lying at one of the interfaces between the absorber layer and the two electrodes, or suspended within the absorber layer itself. Besides the obvious difference in the optical environment surrounding the NPs, electronic considerations include the charge carrier density profiles across the absorber layer.

The sample structure for PIA measurements has a contiguous insulator film, which is probably detrimental to a working solar cell, since the insulator film would act as a barrier to charge extraction. The contiguity of the Al₂O₃ film was an inevitable result of the experiment's requirement of fine thickness control. However, the information on the optimal shell thickness is still applicable to devices that incorporate NPs in the active layer itself.

In a working solar cell, electronic considerations beyond polaron concentrations are important. In particular charge transport, which the optical experiments do not account for, plays a crucial role. The manner in which embedded metal nanoparticles can affect

the extraction of photogenerated free charge carriers is still a subject under study.^{17,38-42} Simply put, maximum polaron concentrations do not necessarily translate to maximum device performance. Hence, the optimum shell thickness for maximizing polaron concentrations may not be what is needed for best conversion efficiency, although it is very likely to be a useful metric.

This chapter describes a systematic study to determine the optimal thickness of Al_2O_3 to achieve a maximum level of charge concentration. It cannot measure charge separation. Charge separation is crucial to charge concentration. A high charge separation efficiency will of course lead to higher charge concentration. But higher charge concentration does not necessarily mean higher charge separation efficiency. Higher charge concentration could also be due to a lower rate of free charge carrier recombination (which could be happening in the experiments due to the insulating effect of the shell), or a combination of both higher charge separation efficiency and lower charge recombination rate. PIA tracks the charge concentrations of photoexcited species. In the experiments, the (quasi-steady state) concentration of P3HT^+ hole polarons is monitored.

There is a limitation to what the simulation studies can perform. The model is unable to simulate the expected level of charge concentration enhancement. In a simple consideration, the concentration of free charge carriers is the result of:

- 1) Photon absorption;
- 2) Charge separation (exciton dissociation);
- 3) Recombination of free charge carriers both in bulk and at the NP surface.

The simulation model in this chapter can account for the absorption based on the calculated electric field, but the remaining two processes are beyond the means to be accounted for.

5.4 Conclusions

In conclusion, by comparing the strength of a photoinduced absorption signature (corresponding to hole polarons) in P3HT, the ideal thickness of an insulating Al_2O_3 layer surrounding Ag NPs was found to be between 3 and 5 nm. With such a thickness of Al_2O_3 around the NPs, the absorption enhancement within the P3HT film by the plasmonic electric field and the spatial separation of charge carriers from recombination centres are balanced to give the maximum polaron concentration. In Chapter 4, optical modelling revealed a similar trend for Al_2O_3 , which was determined to be ~ 10 nm. Hence, the experimental results derived from PIA studies were reasonably in line with theoretical expectations. This information is potentially useful to the design of solar cells that incorporate metal NPs as a strategy to improve optical absorption.

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Chapter 6

Optically-enhanced P3HT:PCBM Films Based on Oxide-encapsulated Ag NPs – A Theoretical Study

In the previous chapter, it was experimentally demonstrated that charge recombination can be mitigated at the polymer/NP interface by protecting Ag NPs with a sheath of Al_2O_3 . Polaron yields were maximized in P3HT through an optimal Al_2O_3 encapsulation. The yields were optimized at wavelength specific conditions. From an OSC point of view, it is more practical if absorption is calculated with reference to AM1.5G. Overall absorption in the polymer can be improved by incorporating oxide-encapsulated Ag NPs. However, polymeric absorption will be poorer than a neat P3HT:PCBM film when Ag NPs are protected by MoO_3 and SiO_2 shells which are thicker than 5 nm. For Al_2O_3 and HfO_2 , Ag NPs should not be encapsulated with shells thicker than 10 nm.

6.1 Introduction

In Chapter 4, optical effects arising from oxide-encapsulated 50 nm diameter Ag NPs were investigated. In order to improve light absorption at Ag NP resonance in 25 nm thick P3HT:PCBM films, modelling studies showed that a shell thickness of ~ 10 nm is sufficient for Al_2O_3 , HfO_2 and MoO_3 . This observation was verified through the use of PIA spectroscopy in Chapter 5. By comparing the strength of a photoinduced absorption hole polaron signature in P3HT, the ideal thickness of an insulating Al_2O_3 layer surrounding Ag NPs was found to be between 3 and 5 nm. With such a thickness of Al_2O_3 around the NPs, the absorption enhancement within the P3HT film by the plasmonic electric field and the spatial separation of charge carriers from recombination centres are balanced to give the maximum polaron concentration. This proved that the experimental results derived from PIA studies were reasonably in line with theoretical expectations. However, both studies were wavelength specific. A better insight will be achieved if overall photoactive layer absorption can be determined by integrating absorption gains/losses throughout the entire absorption range of the polymer. Henceforth, modelling studies are undertaken to determine optical absorption enhancement in P3HT:PCBM at Ag nanoparticle (NP) resonance for different encapsulated oxides. Studies will also extend to calculating total absorption in P3HT:PCBM when oxide-encapsulated Ag NPs are introduced. The focus will be the use of the four insulating oxides as the buffer layer.

6.2 Simulation Setup

In this chapter, the simulation model setup is identical to the one in Chapter 4. However, the theoretical investigation is extended to cover overall absorption calculated with respect to AM1.5G.

6.3 Results & Discussions

6.3.1 Absorption of oxide-encapsulated Ag NPs in P3HT:PCBM

Bare Ag NPs on glass have a peak absorption of ~ 400 nm. This peak can be attributed to surface plasmons. Encapsulating the Ag NPs with an oxide will shift the surface plasmon peak. Here, two factors will determine the degree of the shift: oxide thickness and relative permittivity value. Figure 6.1 shows the degree of red-shift of the Ag NP peak absorption in the lower wavelengths arising from increasing oxide thickness (0 nm to 30 nm) and different oxides. The peak position is a result of the plasmonic NPs embedded inside P3HT:PCBM. Regardless of oxide, an increasing shell thickness will induce a red-shift in the surface plasmon peak. Oxides with higher relative permittivity values will induce a higher magnitude of red-shift too. SiO_2 has the lowest relative permittivity and hence, Ag NPs experience the least red-shift. On the other hand, MoO_3 has the highest relative permittivity and hence, Ag NPs experience the most red-shift.

The manifestation of the secondary peaks for wavelengths above 570 nm is due to near field interactions between the Ag NPs and the polymer.^{1,2} The magnitude of these peaks is sensitive to oxide thickness and relative permittivity. As P3HT:PCBM is absorbing, its close proximity to the Ag NPs, which is dictated by the oxide thickness, will produce a small peak. However, once the oxide thickness is increased, the distance between the polymer and Ag NPs increases. This will manifest as a larger peak. The magnitude of this peak is also determined by the relative permittivity. The higher the relative permittivity, the larger the peak. In MoO_3 (which has the highest relative permittivity among the four oxides), the secondary peaks can be up to ~ 6 times stronger than the absorption peak due to surface plasmons. The importance of these secondary peaks, or lack of, will be discussed in succeeding sections.

Figure 6.1 The simulated absorbance peaks of the Ag NPs as a result of different oxide-encapsulated Ag NPs embedded in P3HT:PCBM. The plasmon peak is in the lower wavelength range while the manifestation of the secondary peaks above 570 nm is due to near field interactions with Ag NPs and the polymer.

6.3.2 Extinction cross section efficiency

Plotting the absorption peaks of the Ag NPs due to different thicknesses of oxides will give an idea the relative position of the surface plasmon peak and its corresponding strength. However, a better parameter to determine the effectiveness of these oxide-encapsulated Ag NPs is their extinction cross section, which is an indication of their absorption and scattering efficiency. Extinction cross section is the sum of absorption cross section and scattering cross section. It is usually written as:

$$C_{\text{extinction}} = C_{\text{scattering}} + C_{\text{absorption}}$$

Dividing each term by the geometrical cross section πr^2 yields:

$$\eta_{\text{extinction}} = \eta_{\text{scattering}} + \eta_{\text{absorption}}$$

where η is the efficiency of the respective terms defined by the subsets. Calculations of the extinction cross section efficiency will be the requisite for quantifying absorption performance in P3HT:PCBM.

Figure 6.2 Plots of absorption cross section efficiency for Al_2O_3 , HfO_2 , MoO_3 and SiO_2 . When a bare Ag NP is embedded in the polymer, the absorption efficiency can be up to almost four times its physical size.

Figure 6.2 shows the absorption cross section efficiency of the Ag NPs encapsulated in various oxide thicknesses. When a bare Ag NP is embedded in the polymer, the absorption efficiency can be up to almost four times its physical size. The efficiency drops to around two times as the shell is increased to 30 nm in all oxides. The red-shifting nature of the absorption efficiency upon increasing oxide shell thickness is similar to the trend in Figure 6.1

Figure 6.3 Plots of scattering cross section efficiency for Al_2O_3 , HfO_2 and SiO_2 . Scattering efficiency is significantly lower than that of absorption efficiency as absorption effects dominate for NPs smaller than 100 nm.

The scattering efficiency of the different oxides are plotted in Figure 6.3. As expected, the red-shifting trend upon increasing shell thickness is observed for all oxides. As compared to the absorption efficiency, scattering efficiency is significantly lower. A bare NP

incorporated into the polymer has a mere scattering efficiency of only ~ 0.35 . This is to be expected given that absorption effects will dominate for NPs with diameters which are less than 100 nm.

Figure 6.4 Plots of extinction cross section efficiency, which is derived by the addition of absorption cross section efficiency and scattering cross section efficiency.

For a more accurate representation of light distribution for Ag NPs with different oxides, the extinction cross section efficiency is calculated. This parameter is a useful parameter in projecting expected absorption trends in the polymer as it takes into account both absorption and scattering effects. The extinction cross section efficiencies of the different oxide-encapsulated Ag NPs are presented in Figure 6.4. The imaginary component of the relative permittivity of P3HT:PCBM is superimposed on each graph so as to give a better perception of overlap between polymer absorption and extinction cross section efficiency.

The strength of the extinction efficiency is dictated by the separation between the NP and the polymer. When a bare NP is introduced into the polymer layer, the extinction efficiency can be up to almost four times its physical size. As P3HT:PCBM is an absorbing medium, the NP's close proximity will result in a dampening of the extinction efficiency. This observation is particularly evident for the secondary peaks arising from near field interactions between Ag NPs and the polymer (Figure 6.4). When the shell thickness is thin enough (0 nm to 5 nm), they contribute to an extinction efficiency of similar magnitude as compared to the peaks arising from surface plasmons. In fact, for a Ag NP without any shell encapsulation, this extinction efficiency is just slightly lower than the extinction efficiency arising from surface plasmons. At thin shell thickness, Ag NPs are close enough to the polymer to induce localized interactions. In fact, a higher relative permittivity contrast at the NP/oxide interface induces a larger extinction cross section. However, upon further increase in the shell thickness, the extinction efficiency is almost negligible. This observation highlights that the secondary peaks are manifestations of near field interactions and they do not contribute substantially to extinction efficiency. The secondary peaks' participation effectively becomes negligible for larger shell thickness. However, the magnitude of the secondary peaks can be taken as an indirect measure of shell thickness.

For extinction efficiency arising from surface plasmons, attention is turned to the shorter wavelengths. As the oxide shell gets thicker, the extinction cross section drops progressively. This means that the electric field enhancement gets increasingly trapped within the oxide shell. Depending on the relative permittivity contrast at the NP/oxide interface, a higher contrast induces a larger red-shift. This observation is similarly observed in Figure 6.1. In addition, the position of the peak extinction efficiency relative to the polymer absorption must be taken into account. Consider the case of SiO₂. The absorption peaks of SiO₂-encapsulated Ag NPs are just under 450 nm (Figure 6.1d). Straddling at the absorption edge of P3HT:PCBM, a significant portion of the Ag NP absorption peak lies outside the absorption range of the polymer. The peak positions are located at regions where P3HT:PCBM is relatively less absorbing. As a result, the extinction efficiency appears higher than the rest of the oxide-encapsulated Ag NPs

(Figure 6.4d). For Al_2O_3 -encapsulated Ag NPs, the surface plasmon peak position red-shift progressively with increasing thickness, positioning its peaks in regions with significant overlap with the polymer's absorption range (Figure 6.4a). A similar trend is also observed for Ag NPs encapsulated with HfO_2 and MoO_3 . As the polymer imposes an absorbing effect on the oxide-encapsulated Ag NP, cross section extinction efficiency appears lower than that of SiO_2 encapsulation. Certain portions of the extinction efficiency fall in the negative regime. This is especially pronounced for Ag NPs encapsulated with 20 nm and 30 nm of oxides. As mentioned in Section 4.3.3, quasi-static approximation breaks down when the NP approaches a diameter of 100 nm and beyond. However, as the oxide thickness do not exceedingly stretch the limitations of the approximation, the extinction cross section results can be considered as a fairly good guideline.

6.3.3 Optical enhancements in P3HT:PCBM

Calculations have yielded useful information on the absorption and scattering efficiency of oxide-encapsulated Ag NPs in P3HT:PCBM. It is perhaps more interesting to understand how the effectiveness of these plasmonic nanostructures be translated into optical gains/losses in the polymeric layer. As discussed in Chapter 4, at Ag NP resonance, localized electric field enhancement is expected to improve optical absorption in the polymer. However, the calculations derived in Chapter 4 are wavelength specific. If oxide-encapsulated Ag NPs are meant to be incorporated into OSCs, total absorption in P3HT:PCBM should be integrated throughout its absorption range and calculated with reference to AM1.5G.

Absorption is integrated in the 350 – 700 nm range, which is the absorption range of P3HT:PCBM. For a more accurate gauge, polymer absorption is calculated with reference to AM1.5G by using the formula:

$$A_{\text{weighted}} = \frac{\int_{350\text{nm}}^{700\text{nm}} S(\lambda) \cdot A(\lambda) d\lambda}{\int_{350\text{nm}}^{700\text{nm}} S(\lambda) d\lambda}$$

where A_{weighted} refers to the absorption weighted against AM1.5G, $S(\lambda)$ denotes the AM1.5G intensity flux and $A(\lambda)$ is the calculated absorbance.³ A_{weighted} is further integrated with respect to wavelength within 350 nm to 700 nm to obtain integrated absorption, which is a measure of total absorption in the polymer. Another factor to consider is the total polymer volume. P3HT:PCBM was modelled to conform to the contours of the oxide-encapsulated Ag NP with a uniform thickness. Increasing the oxide thickness will lead to a corresponding increase in the surface area for the polymer to cover. As a result, polymer volume increases. An enlarged volume will naturally induce a higher absorption. The increased corrugation of the polymer topography will also contribute to more photons subjected to light trapping. In order to correct this anomaly, the integrated absorption is normalized with respect to total polymer volume to yield absorption per unit volume. Based on the assumption that the polymer absorbs equally regardless of volume geometry, this is a reasonably good approach to gauge the absorption trend.

Figure 6.5 Absorption trend in P3HT:PCBM due to different oxide-encapsulated Ag NPs shell thicknesses. Absorption per unit volume is a reasonable approach to gauge absorption trends. P3HT:PCBM control is represented by the dotted line.

Figure 6.5 depicts the expected absorption trend due to different oxide thicknesses. Absorption per unit volume is defined by the vertical axis. Note that absorption per unit volume has arbitrary units but nevertheless, it can be taken as having a direct relationship with absorption. The control, highlighted by the dotted line, denotes the absorption of a neat P3HT:PCBM film without any Ag NPs. Similarly, this is also normalized with respect to its volume. A 0 nm shell refers to bare Ag NPs. Incorporating them into the polymer film results in an absorption increase of ~8 %. Introducing a very thin shell of 2 nm causes a small absorption loss of ~3 % in all oxides. However, the degree of absorption loss is more evident if the oxide shell is increased. At a 5 nm thickness, both MoO₃ and SiO₂ shells result in a more pronounced absorption drop as compared to Al₂O₃ and HfO₂. Absorption losses appear to plateau for Al₂O₃, HfO₂ and MoO₃ for shell thicknesses beyond 10 nm. In fact, there is a slight rise in the absorption for MoO₃ when the shell thickness is increased from 20 nm to 30 nm. On the other hand, absorption loss is still substantial for SiO₂ as the shell thickness is increased from 10 nm to 20 nm before flattening out. For all oxides, absorption gains with respect to the control film are expected to be observed for shell thicknesses up to 5 nm. For Al₂O₃ and HfO₂, absorption enhancement can be observed up to a shell thickness of just under 10 nm before absorption losses kick in.

6.3.4 Optical enhancements in CH₃NH₃PbI₃

This modelling study is extended by replacing P3HT:PCBM with CH₃NH₃PbI₃. P3HT:PCBM has a short absorption range of ~350 nm – 650 nm versus CH₃NH₃PbI₃ with a wider absorption range of ~350 nm to 800 nm. All dimensions are held constant. CH₃NH₃PbI₃ is a perovskite material which is under intense research by numerous groups.⁴⁻⁶ Besides having advantages which are similar to those of OPV devices, perovskites are touted as alternatives to their organic counterparts due to their superior device performance. Hence, it is interesting to observe the absorption outcome if Ag NPs are incorporated into a perovskite layer. Absorption per unit volume is also plotted to determine absorption trends in CH₃NH₃PbI₃ films. The calculated values are represented

in Figure 6.6. The absorption trend is markedly different from that of P3HT:PCBM. Embedding bare Ag NPs in $\text{CH}_3\text{NH}_3\text{PbI}_3$ causes a slight dip of $\sim 1\%$ absorption as compared to the control film. This is probably due to absorption losses in the Ag NPs themselves. While P3HT:PCBM shows a continuous downward absorption trend, an optimal thickness exists for Al_2O_3 and HfO_2 at $\sim 20\text{ nm}$. At this thickness, the absorption is improved by $\sim 2.6\%$. The small increase could be due to the already absorbing nature of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and the net extinction efficiency is not sufficient to greatly improve perovskite absorption. P3HT:PCBM is much less absorbing than $\text{CH}_3\text{NH}_3\text{PbI}_3$, which explains the significantly lower absorption enhancement for the latter. On the other hand, the use of MoO_3 and SiO_2 as the oxide buffer layer induces absorption losses regardless of oxide thickness, although, at 20 nm , SiO_2 induces a very small absorption gain which is almost negligible.

Figure 6.6 Absorption per unit volume in $\text{CH}_3\text{NH}_3\text{PbI}_3$ due to different oxide-encapsulated Ag NPs shell thicknesses. The absorption trend is different from that of P3HT:PCBM, with only small enhancements observed for Al_2O_3 and HfO_2 .

6.4 Discussions

It is observed that the secondary peaks (for wavelengths > 570 nm) in the numerical simulation are much stronger than that predicted by the theoretical extinction cross section results for small oxide thickness of less than 5 nm. This mismatch is primarily due to two reasons: (a) The background medium (i.e. active layer) in the theoretical extinction cross section calculations presented in Section 6.3.2 is assumed to be much thicker as compared to the size of the oxide-encapsulated Ag NPs. In the numerical simulation, this is not entirely true, as the thickness of the conformal active layer (at 25 nm) is finite in thickness. (b) Within the theoretical extinction cross section calculations, the inter-reflections (or light trapping effects) due to the glass substrate and the active layer/air interface are not taken into account. On the other hand, the numerical simulations presented in Section 6.3.1 takes the light trapping effects into account and these light trapping influences seem to amplify the magnitude of the secondary peaks observed in the numerical simulation results in Figure 6.1. For the case of P3HT:PCBM, the secondary peaks do not have a significant impact on absorption trend of the polymer with increasing oxide thickness as the secondary peaks are found in the 600 nm range where the absorption of P3HT:PCBM is decreasing rapidly. However, this is not the case of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ active layer as the secondary peaks are found within its absorption wavelength range (350 nm to 800 nm). The presence of these peaks is most probably the main reason for the optimum 20 nm oxide thickness encapsulating the Ag NPs. This oxide thickness represents a much higher than the oxide thickness requirement for the P3HT:PCBM case. In addition, it has to be highlighted that although MoO_3 has a higher real relative permittivity as compared to SiO_2 , Al_2O_3 and HfO_2 , it is important to realize that MoO_3 is the only oxide that is absorbing in the UV regime. The UV absorbing nature accounts for the reduced enhancement in the absorption in the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ active layer even though a higher enhancement in absorption per unit volume from MoO_3 would be expected.

6.5 Conclusions

Simulation studies were undertaken for Ag NPs encapsulated with Al_2O_3 , HfO_2 , MoO_3 and SiO_2 . In absorbance calculations, the appearance of the secondary peaks were observed, probably due to inter-reflections at the glass substrate and active layer/air interface. These peaks are significantly lower when extinction cross section efficiency is computed and they are almost completely quenched when oxide thickness is more than 5 nm. This observation highlights that the secondary peaks are manifestations of near field interactions and they do not contribute substantially to extinction efficiency. However, they can be interpreted as an indirect measure of oxide shell thickness. Absorption in the polymer is calculated with reference to AM1.5G spectrum and normalized with respect to the volume. This method is reasonably good in predicting absorption trends. Calculated absorption values reveal that optical enhancement is expected in P3HT:PCBM bare Ag NPs are introduced. Encapsulating them with a 2 nm thin oxide shell will cause a slight absorption loss but optical enhancement is still superior to that of the control. However, a polymeric absorption loss is induced for oxide-encapsulated Ag NPs if MoO_3 and SiO_2 shells are more than 5 nm. For Al_2O_3 and HfO_2 , Ag NPs should not be encapsulated with shells thicker than 10 nm. The model was modified by replacing P3HT:PCBM with $\text{CH}_3\text{NH}_3\text{PbI}_3$. The use of Al_2O_3 and HfO_2 appeared to be the most useful, with an optimal oxide thickness at ~20 nm.

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Chapter 7

Conclusions and recommendations for future work

Modelling studies have revealed the optical advantage of incorporating 50 nm plasmonic Ag NPs in a 25 nm thin P3HT:PCBM layer. To prevent charge recombination at the NP surface, oxide shells (Al_2O_3 , HfO_2 , MoO_3 and SiO_2) are introduced. The amount of absorption enhancement in the polymer can be adjusted by changing the relative permittivity of the shell or by adopting different oxide thicknesses. An optimal shell thickness is observed in the PIA measurements on Al_2O_3 -encapsulated Ag NPs by monitoring net photogenerated P3HT^+ carriers. To further reinforce the observations, absorption in P3HT:PCBM is calculated with reference to AM1.5G spectrum. Absorption is expected to improve in the polymer if the shell thickness of oxide-encapsulated Ag NPs do not exceed a certain limit.

7.1 Conclusions

Leveraging on the advantages of surface plasmons to improve absorption in a polymer film is well-established. Generated at the optical resonance of plasmonic nanostructures, surface plasmons can improve the optical path length of a photon. Surface plasmons are highly localized at a metal/dielectric interface. Therefore, there is a preference to position nanostructures within the semiconducting polymer layer. However, plasmonic materials are usually metallic in nature. Placing them within the polymer layer will induce charge recombination at the metal/polymer interface. This problem can be avoided by protecting the metallic nanostructures with a thin encapsulating sheath. This protective shell must be insulating to perform its function and hence, Al_2O_3 , HfO_2 , MoO_3 and SiO_2 were chosen for the investigations.

Firstly, absorption trends were disclosed by zooming in on the optical resonance of Ag NPs. Simulation models were set up to analyze the effect on absorption in P3HT:PCBM due to 50 nm Ag NPs protected by Al_2O_3 , HfO_2 , MoO_3 and SiO_2 . The position and strength of the surface plasmon peak of Ag NPs are affected by the thickness of the oxide shell and its relative permittivity. Extinction cross section is dictated by the degree of overlap with the absorption range of the polymer. The absorbing nature of the polymer can damp the magnitude of surface plasmons. Plots of electric field distribution at Ag NP resonance reveal the extent in which P3HT:PCBM experiences enhanced absorption. The presence of an encapsulating shell changes the electric field profile in the polymer. Very minimal absorption improvements in P3HT:PCBM can be observed for oxide thicknesses below 10 nm. Al_2O_3 , HfO_2 and MoO_3 can induce absorption gains at a shell thickness of ~ 10 nm. As the oxide thickness is increased (20 – 30 nm), polymer absorption is observed to significantly improve for Ag NPs protected by oxides with high relative permittivity values.

However, as P3HT:PCBM is an absorbing medium, extinction cross section can be quenched by Ag NP peak position relative to polymer absorption. Although high relative permittivity oxides with sufficient shell thickness can induce a higher localized electric

field enhancement, extinction cross section magnitude can be quenched by its proximity to P3HT:PCBM, which is an absorbing medium.

Although the presence of an insulating shell around Ag NPs can suppress recombination, it limits the extent that the localized enhanced electric field influences charge generation in the polymer. This was experimentally investigated by monitoring P3HT⁺ polaron population using a PIA spectroscopy setup. Samples were prepared by encapsulating 50 nm Ag NPs with varying thicknesses of Al₂O₃ (0, 0.2, 0.8, 2, 3, 8, 15 and 30 nm) using ALD. Experiments concluded that an optimal thickness of 3 – 5 nm Al₂O₃ protecting the Ag NPs is sufficient in enhancing absorption in P3HT films by the plasmonic electric field while balancing the spatial separation of charge carriers from recombination centers. At this thickness range, maximum polaron population was measured.

While the initial two studies are centered at Ag NP resonance (i.e., wavelength specific), it is more insightful if the overall effect on the entire absorption range of P3HT:PCBM is investigated. According to theoretical calculations, absorption of oxide-encapsulated Ag NPs in P3HT:PCBM induces a significant secondary peak in the longer wavelengths. This can be attributed to near field interaction between the Ag NP and the polymer. However, this peak has a quenched contribution once the extinction cross section efficiency is plotted. This peak can also be taken as an indirect measure of oxide shell thickness. A shell thickness which is sufficiently thick enough will cause the secondary peak contribution to disappear. On the other hand, the primary peak, which is the result of surface plasmons, plays an important role in determining absorption trends. Extinction cross section efficiency is dominated by scattering cross section efficiency. Although the oxides are mostly non-absorbing, absorption losses in Ag NPs can still be observed. Absorption in the polymer is derived with reference to the AM1.5G spectrum and normalized with respect to the volume. Calculated absorption values reveal that optical enhancement is expected in P3HT:PCBM with respect to a control film when bare Ag NPs are introduced. The presence of a thin 2 nm shell will cause an absorption loss but optical enhancement is still higher than a control. However, there is a shell thickness limit of 5 nm for MoO₃ and SiO₂ before absorption loss is induced for oxide-encapsulated Ag

NPs. For Al_2O_3 and HfO_2 , the shell should not exceed 10 nm. Calculations are also performed for a perovskite layer by replacing P3HT:PCBM with $\text{CH}_3\text{NH}_3\text{PbI}_3$. As the Ag NP coverage is a sparse $\sim 4.9\%$ and because of the very absorbing nature of $\text{CH}_3\text{NH}_3\text{PbI}_3$, absorption enhancement is not as pronounced as what is observed in P3HT:PCBM.

Experimental Outcome vs. Hypothesis

In Chapter 1, several hypotheses were conceived. In order to gauge if the hypotheses were adequately verified, the experimental outcomes are compared against the hypotheses.

- a) It was hypothesized that relative permittivity contrast will determine the magnitude of the extinction cross section of a Ag NP. At optical resonance, Ag NPs protected with a shell that has a high relative permittivity will induce a higher absorption in P3HT:PCBM. A high relative permittivity produces a high relative permittivity contrast at the metal/dielectric interface. However, this hypothesis was true to a certain extent, that is, only if the shell is significantly thick enough. Primarily, peak Ag NP absorption relative to the absorption spectrum of P3HT:PCBM determines the magnitude of the extinction cross section and hence, the amount of optical enhancement in the polymer.
- b) Embedding Ag NPs can improve charge carrier generation due to localized field enhancement but the metallic nature of the NPs introduces charge recombination sites. Charge recombination can be reduced by coating the Ag NPs with an insulating shell but this limits the influence of the localized field enhancement. Hence, there should exist an optimal shell thickness, which balances electric field enhancement and suppression of charge recombination. By monitoring P3HT^+ polaron population through the use of PIA spectroscopy, the hypothesis was successfully verified through the finding of an optimal Al_2O_3 thickness of 3 – 5 nm.
- c) In the final hypothesis, it was theorized that overall absorption in P3HT:PCBM, when

calculated with reference to AM1.5G solar spectrum, should improve when oxide-encapsulated Ag NPs are introduced. There is a limit to the thickness that the oxide shell can attain before absorption losses in the polymer are encountered. This idea is confirmed through the simulation model. For optical enhancement in P3HT:PCBM, shell thickness in oxide-encapsulated Ag NPs should not exceed 5 nm for MoO_3 and SiO_2 while it is 10 nm for that of Al_2O_3 and HfO_2 . Therefore, the hypothesis was proven to be accurate.

7.2 Recommendations for Future Work

Based on the outcome of this thesis, several questions were encountered. For future work, three tasks are proposed that can take this PhD work further.

- a) It was not proven directly that an insulating shell around Ag NPs has the ability to control charge recombination at the metal/dielectric interface when the oxide-encapsulated Ag NP is embedded within a semiconducting polymer film. As part of the future work, the use of PhotoCELIV^{1,2} is proposed. In such a measurement, photogenerated carriers are formed throughout the film when the sample is excited with a pulsed laser. Photogenerated charge carriers can be extracted by an inverted triangular voltage pulse. Figure 7.1 shows a typical PhotoCELIV curve. Depending on the applied bias, photogenerated carriers can be calculated from the area under the extraction peak, which is shaded red. t_{max} is the time at the maximum Δj of the extraction peak, and $j(0)$ is the displacement current of the capacitance.

Figure 7.1 A typical PhotoCELIV curve. The number of charge carriers can be derived from the area shaded in red.

It is postulated that PhotoCELIV will register a drop in the hole concentration and an increase in the electron population upon the introduction of bare Ag NPs in P3HT. This is due to the recombination of free holes in the P3HT with the delocalized electrons on the Ag NP surface. When Ag NPs with a thin protective shell is introduced, the density of holes should increase as the free electrons on the Ag NPs are shielded from charge recombination. In the meantime, electron density should drop. The increase in the hole concentration is attributed to an improvement in the extinction cross section of the Ag NPs, which makes them efficient light scatterers. As the shell thickness is increased, enhanced electric field distribution associated with surface plasmons will be increasingly trapped within the shell. As a result, after crossing an optimal point, the number of holes collected will drop. Detected electron population could remain more or less unchanged regardless of shell thickness.

- b) To demonstrate that simulation and PIA studies are accurate, OSCs devices should be fabricated with oxide-encapsulated Ag NPs embedded in P3HT:PCBM. Simulation models show that each oxide-encapsulated Ag NP is discrete on its own. This can be easily prepared using a synthesis approach and the oxide-protected Ag NPs spin-coated onto the substrates. Theoretically, it is possible to prepare Ag NPs with

different oxide thicknesses. However, it lacks the accuracy of oxides deposited using ALD. This is the reason PIA studies were undertaken using ALD for oxide deposition. The use of ALD to deposit oxides presents a disadvantage. In ALD deposition, gaseous precursors chemisorbs in a conformal and uniform manner. Regardless of substrate geometry, every surface surface will be subjected to the same deposited thickness. The conducting anode, on which the Ag NPs will be positioned, will be covered with the same oxide thickness as the one surrounding Ag NPs. Since the anode is an essential component of a solar cell device (holes are collected after exciton dissociation), using ALD will insulate the anode from hole collection. Hence, ALD may not be a suitable method for oxide deposition. A synthesis approach, if feasible, will be more favorable.

- c) PIA studies can be taken further to encompass other oxides that were analyzed in the simulations. They include HfO_2 , MoO_3 and SiO_2 . Other semiconducting oxides such as TiO_2 and ZnO are also worth investigating.

7.3 Reconnaissance Studies

7.3.1 Gratings-incorporated Solar Cells

A grating structure was incorporated into P3HT:PCBM and ZnPc:C_{60} solar cells. Having a grating system within a solar cell has several advantages. When the light is incident at an angle, the optical path length is longer than the thickness of the photoactive layer. Thus, due to the diffraction effect of the grating structure, the average optical path length is increased. Furthermore, another promising scheme utilizes surface plasmons in plasmonic nanostructures. In a grating system, surface plasmon polaritons can assist in improving optical enhancement in the semiconducting layer.

Figure 7.2 a) The ITO layer conforms to a corrugated morphology when it is sputtered onto the PMMA grating; b) spin-coated P3HT:PCBM on the grating system; c) thermally evaporated ZnPc:C₆₀ on the grating system.

Gratings are fabricated by nanoimprinting poly(methyl methacrylate) (PMMA) before sputtering low-temperature processed ITO (Figure 7.2a). Next, a layer of the semiconducting active layer, P3HT:PCBM (Figure 7.2b) or ZnPc:C₆₀ (Figure 7.2c), was thermally deposited or spin-coated respectively onto the corrugated surface. The device structure of P3HT:PCBM system is glass/LT-ITO/PEDOT:PSS/P3HT:PCBM/Ca/Ag while it is glass/LT-ITO/ZnPc:C₆₀/C₆₀/BPhen/Ag for ZnPc:C₆₀.

The J-V characteristics are summarized in Table 7.1. Flat PMMA refers to a sample without any grating structures. Both P3HT:PCBM and ZnPc:C₆₀ solar cells were investigated. The V_{oc} remained unchanged, proving that the introduction of the PMMA (flat and gratings) did not affect the energy alignment of the photoactive layers. However,

enhancements were observed in the J_{sc} and FF. The J_{sc} in the P3HT:PCBM and ZnPc:C₆₀ cells were improved by a factor of 1.06 and 1.20 respectively. This is highlighted by the parentheses in Table 7.1. This could be due to the grating effect when the optical path lengths were increased, leading to higher absorption. Besides, surface plasmon polaritons generated by the grating structures could contribute to the higher absorption as well. Similarly, an increase factor of 1.13 and 1.08 in the FF were calculated for P3HT:PCBM and ZnPc:C₆₀ devices respectively. Overall, the PCE was improved from 2.06 % to 2.46 % in P3HT:PCBM and from 3.07 % to 3.93 % in ZnPc:C₆₀. Hence, the results supported the postulation that an improvement in the performance of the OPV devices (via the diffraction effect and surface plasmons) would be expected when grating structures were introduced.

Table 7.1 Photovoltaic performance data of a solar cell device based on P3HT:PCBM (top) and ZnPc:C₆₀ (bottom) on PMMA gratings. The flat PMMA, without any grating structures, functions as a control. The parentheses refer to the enhancement as compared to a control device.

Sample	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
P3HT:PCBM on flat PMMA	0.52	9.19	0.43	2.06
P3HT:PCBM on PMMA grating	0.52	9.70 (1.06)	0.49 (1.13)	2.46 (1.19)

Sample	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
ZnPc:C₆₀ on flat PMMA	0.54	13.04	0.43	3.07
ZnPc:C₆₀ on PMMA grating	0.54	15.68 (1.20)	0.47 (1.08)	3.93 (1.28)

7.3.2 Incorporating Ag NPs in P3HT:PCBM

Although the gratings can be duplicated with great reproducibility, nanoimprinting is not a technique which allows mass production. Hence, the switch to NPs was made. The ease of fabrication that comes with spin-coating a NP solution was a much more attractive option. Coverage of NPs on the substrates can be controlled with good reproducibility.

Solar cells having a structure of glass/ITO/PEDOT:PSS/Ag NPs/P3HT:PCBM/Ca/Ag are fabricated. Ag NPs were deposited using spin-coating. Table 7.2 summarizes the J-V characteristics of the cells.

A device without any Ag NPs yielded an open circuit voltage (V_{oc}) of 0.54 V, short circuit current density (J_{sc}) of 8.96 mA/cm² and a fill factor (FF) of 0.67. This works out to be a power conversion efficiency (PCE) of 3.27 %. With the introduction of Ag NPs, the figures of merits for the respective coverage were altered. The overall efficiencies dropped progressively with a steady increase in the coverage of Ag NPs. A similar situation was also observed in the V_{oc} . The decrease in V_{oc} can be attributed to the difference in the work functions.

Ag has a work function of 4.3 eV while PEDOT:PSS has a work function of 5.2 eV. This misalignment will inevitably result in a lower work function as compared to devices without Ag NPs. In addition, the presence of Ag NPs had caused a fall in the FFs of all devices. The FF of an OPV cell without Ag NPs had a typical value of 0.67. Adding Ag NPs into the polymeric matrix suppressed the FFs by 30 % to 0.45. This can be attributed to more electron-hole recombination as there is direct contact between the metallic NPs and the polymer. In addition, efforts were not made to ensure complete removal of the ligands that were attached to the Ag NPs. The presence of the ligands might have introduced additional charge recombination sites.

Table 7.2 Summary of the devices. By adding Ag NPs into the P3HT:PCBM system, a large drop in the FF is observed. This can be attributed to an increase in charge recombination as compared to a sample without any Ag NPs.

Surface coverage (%)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
0	0.54	8.96	0.67	3.27
1	0.45	13.46	0.45	2.74
2	0.44	13.34	0.45	2.62
5	0.42	12.83	0.46	2.44
8	0.39	12.66	0.45	2.22

7.3.3 Role of Organic Ligands³

Metallic NPs used in OPV processing typically contain an organic sheath of molecules that are weakly-moderately bound to the surface of the metal, rendering the metallic NPs soluble or dispersible in ink formulations using common organic solvents. Since the attachment of the ligands to the particle is reversible under the right conditions (various solvents, temperatures, etc.), there is a possibility for the ligands to be displaced and dispersed into the buffer or active layers during fabrication. Therefore, it is necessary to decouple ligand and NP effects and examine them individually to determine the result that each has on the final device performance.

The effects of various organic based ligands on the performance of polymer solar cells were examined. In general, the commonly used alkyl amine organic stabilizer, hexadecyl amine (HDA), drastically reduced solar cell performance when introduced at the PEDOT:PSS/P3HT:PCBM interface. Strong base (NaOH) has a deteriorating effect on the PEDOT:PSS buffer layer in polymer solar cells. On the other hand, it was found that other commonly used organic stabilizers, such as dodecanethiol (DDT), had little or no adverse effect on device performance.

Device structures of glass/ITO/PEDOT:PSS/ligands/P3HT:PCBM/Ca/Ag were prepared.

Control devices with an architecture of ITO/PEDOT:PSS/P3HT:PCBM/Ca/Ag containing no ligands were also fabricated for comparison.

Table 7.3 shows the J-V curves for the performance of the polymer solar cells having a ligand treated PEDOT:PSS buffer layer. The performance of the control cell without the ligand treatment shows an open-circuit voltage (V_{oc}) of 0.54 V, a short-circuit photocurrent (J_{sc}) of 9.80 mA/cm², a fill factor (FF) of 0.65 and a PCE of 3.47 % which is a typical performance of a standard P3HT:PCBM OPV device. The performance of the cells which were treated with HDA (0.1 wt%), shows a similar open-circuit voltage (V_{oc} = 0.54 V). However, the fill factor (FF = 0.46) dropped significantly when compared to that of the control cell leading to a significant overall reduction in PCE (2.35%).

In contrast, the performance of the DDT (0.1 wt%) treated cells shows only a slightly reduced PCE (3.25 %) compared to the control device. The open-circuit voltages of the DDT treated cells were similar to that of the control cell. The concentration of the HDA and DDT ligand solutions (above 0.2 wt% in THF) used to treat the PEDOT:PSS layer did not result in a further noticeable reduction in cell performance demonstrating that only a small amount of amine is needed to impact performance.

Table 7.3 Photovoltaic characteristics of OPV devices with and without ligands.

Surface coverage (%)	Ligand (wt%)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
Control	0.0	0.54	9.80	0.65	3.47
HDA	0.1	0.54	9.42	0.46	2.35
DDT	0.1	0.54	9.71	0.62	3.25

7.4 Outstanding Questions

While PhotoCELIV can probably assist in determining charge recombination reliably, it is assumed that no charge tunneling will occur for ultra-thin shells. There is a possibility

that charge tunneling may occur. In such an instance, the hole may migrate through the oxide from the polymer/shell interface to the metal/oxide interface to recombine with the delocalized electrons on the NP surface. Likewise, free electrons on the NP surface may tunnel through the oxide from the metal/oxide interface to the oxide/polymer interface to recombine with the free holes. Hence, this may challenge the observation that a thin shell allows a significant portion of the electric field enhancement to encroach into the polymer and hence, inducing high polaron yields. PhotoCELIV may be able to find a minimum oxide thickness to completely quench charge recombination but this may not necessarily be the optimal shell thickness.

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