



**UNIVERSITY OF
KWAZULU-NATAL** TM

**INYUVESI
YAKWAZULU-NATALI**

**Plasmon as a mechanism to improve performance of
bulk-heterojunction organic solar cells**

**Mr Wiseman Mpilo Dlamini
209 522 932**

A thesis submitted in fulfilment of
the requirements for the degree of Doctor of Philosophy (Physics)

School of Chemistry and Physics,
College of Agriculture, Engineering and Science,
University of KwaZulu-Natal,
Pietermaritzburg Campus, South Africa

Supervisor: Prof. Genene Tessema Mola

July 28, 2022

Plasmon as a mechanism to improve performance of bulk-heterojunction organic solar cells

Ph.D Thesis

by

Mr WISEMAN MPIOLO DLAMINI (209522932)

Under the supervision of

Prof. Genene Tessema Mola

University of KwaZulu-Natal,
Pietermaritzburg Campus, South Africa

2021

Submitted in fulfilment of the academic requirements for the degree of Doctor of Philosophy in the School of Chemistry and Physics, College of Agriculture, Engineering and Science, University of KwaZulu-Natal, Pietermaritzburg.

As the candidate's supervisor, I have/have not approved this thesis for submission.

Signature (Supervisor): _____ Date: _____

Preface

The work described in this thesis was carried out in the School of Chemistry & Physics, University of KwaZulu-Natal from July 2016 to April 2022 under the supervision of Prof. G. T. Mola.

This study represents original work by the author and has not been submitted in any form for any degree or diploma to any other tertiary institution. Where use was made of the work of others, it has been duly acknowledged in the text.

Signature (Student):

Date: 28 July 2022

Signature (Supervisor):

Date: 28 July, 2022

Declaration of Non-Plagiarism

I, Mr Wiseman Mpilo Dlamini, declare that:

1. The research reported in this thesis, except where otherwise indicated, is my original research.
2. This project has not been submitted for any degree or examination at any other university.
3. This project does not contain other persons data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.
4. This project does not contain other persons' writing, unless specifically acknowledged as being sourced from other researchers. Where other written sources have been quoted, then:
 - Their words have been re-written but the general information attributed to them has been referenced.
 - Where their exact words have been used. then their writing has been placed in italics and inside quotation marks, and referenced.
5. This project does not contain text, graphics or tables copied and pasted from the Internet, unless specifically acknowledged, and the source being detailed the thesis and in the references sections.

Signed in Pietermaritzburg, KwaZulu-Natal:  _____

Date: 28 July 2022

Declaration of Publications

Declaration of publications that form part of this thesis:

Chapter 4 M. W. Dlamini and G. T. Mola, 2019. Near-field enhanced performance of organic photovoltaic cells. *Physica B: Condensed Matter*, 552, pp.78-83.

I am the main contributor to this manuscript, I conducted the experiments, analysed the results and drafted the manuscript under the supervision of Professor G. T. Mola,

Chapter 5 M. W. Dlamini, M. S. Hamed, X. G. Mbuyise and G. T. Mola, 2020. Improved energy harvesting using well-aligned ZnS nanoparticles in bulk-heterojunction organic solar cell. *Journal of Materials Science: Materials in Electronics*, 31(12), pp.9415-9422.

I am the main contributor to this manuscript, I conducted the experiments, analysed the results and drafted the manuscript with the assistance of the co-contributors, Dr M. S. Hamed and Dr X. G. Mbuyise, under the supervision of Professor G. T. Mola,

Chapter 6 M. W. Dlamini, X. G. Mbuyise and G. T. Mola, 2022. ZnO: Ag nano-particles decorated hole transport layer for improved photon harvesting. *Applied Physics A*, 128(2), pp.1-10.

I am the main contributor to this manuscript, I conducted the experiments, analysed the results and drafted the manuscript with the assistance of the co-contributor, Dr X. G. Mbuyise, under the supervision of Professor G. T. Mola,

Declaration of publications that do not form part of this thesis:

1. Tessema G. Mola, Xolani G. Mbuyise, S. O. Oseni, W. M. Dlamini, P. Tonui, E. A. Arbab, K. Kaviyarasu and M. Maaza, 2018. Nanocomposite for solar energy application. In *Nano Hybrids and Composites* (Vol. 20, pp. 90-107). Trans Tech Publications Ltd.

I contributed during the drafting of this manuscript.

2. X. G. Mbuyise, W. M. Dlamini and G. T. Mola, 2021. Metal nano-composite induced light trapping and enhanced solar cell performances. *Physica B: Condensed Matter*, 622, p.413321.

My contribution in this manuscript was with the X-ray analysis of the nanoparticles used in the study.

3. J. N. Ike, M. W. Dlamini, R. P. Dwivedia, Y. Zhang and G. T. Mola, 2022. Plasmon assisted optical absorption and reduced charge recombination for improved device performance in polymer solar cell. *Journal of Physics and Chemistry of Solids*, p.110662.

My contribution in this manuscript was with the X-ray analysis of the nanoparticles used in the study.

Signed in Pietermaritzburg, KwaZulu-Natal: _____

Date: 28 July 2022

Dedication

For my family, whose belief in me to succeed has kept me going.

For my son, Lwandile.

Acknowledgements

I would like to express my deepest appreciation to my supervisor Prof. Genene Tessema Mola, without whom I would have not been able to conduct and complete this research. I would like to thank him for his support through this project, for his advices, encouragement, guidance and patience.

I would also like to thank my family for their unconditional love and support, starting with my parents Mr Thulani Dlamini and Bagezile Dlamini, my siblings Amanda, Nosisa, Namhla, Fundile, Mendy and Lunga Dlamini, and my fiancée Dr Nondumiso Sosibo.

I would also like to thank my friends and colleagues at the University of KwaZulu-Natal, especially at the Microscopy and Microanalysis Unit for their support with TEM and SEM analysis, my colleagues in the School of Physics for their support and collaboration throughout this project, Dr Xolani Mbuyise, Dr Elhadi Arbab, Dr Mohammed Hamed, Mr Mzungezi Mthembu and Mr Jude Ike to name just a few.

To conclude, I would like to thank my employer, the National Metrology Institute of South Africa (NMISA), for their financial support for the study through their Human Capital Development. I would also like to thank Dr Clive Oliphant of the Materials Characterisation at NMISA for his unconditional support with surface and X-ray diffraction analysis.

Abstract

Narrow optical absorption band of fullerene based organic photovoltaic (OPVs) is one of the challenges to produce efficient polymer based solar panel that compete with inorganic counter part. There have been efforts to mitigate the challenges in the past but not enough to overcome all the problems. Plasmon light trapping using metal nano-particles (NPs) incorporated into the organic films is one of the mechanisms being investigated intensively in recent years. Excited plasmon meta nano-particles can dephase in number of ways that could assist in improving photon harvesting as well as charge transport processes in thin film organic solar cells without compromising the optimum thickness of the photoactive medium. The most investigated metal NPs are gold (Au) and silver (Ag) NPs due to their excellent plasmonic and light scattering properties. However, due to their scarcity and cost, several other metallic NPs have also been considered alternative options. Furthermore, mono metal NPs tend to possess high scattering coefficients but low absorption coefficients or vice versa. As a result, several nano-composites of NPs with differing scattering and absorption coefficients have been synthesized and studied.

In this study, we have investigated the effect of inexpensive, solution processed and environmentally friendly metal NPs in organic solar cell based poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) blend solar absorber. Metal nano-composites using metals such as zinc (Zn), copper (Cu), Ag, manganese (Mn) and sulphur (S) were synthesized via simple low temperature colloidal chemistry. These nano-composites were bimetallic (copper coated with silver, Cu@Ag), zinc sulphide (ZnS), zinc oxide (ZnO) coated with Ag (ZnO:Ag) and zinc sulphide doped with manganese (ZnS:Mn). The size, chemical composition and morphology of the synthesized NPs were studied using high resolution scanning electron microscopy (HRSEM), high resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS/EDX). X-ray diffraction (XRD) was used to study their crystalline structure. The optical properties of the NPs in deionized water were studied using UV spectroscopy (UV-Vis). SEM analysis of the NPs showed various structures which mainly consisted of core shell type particles agglomerated together to form large clusters of nano-composites. EDX chemical composition analysis showed no significant impurities. This was consistent with the XRD which showed no diffraction peaks corresponding to impurity. HRTEM analysis confirmed the formation of a core-shell type structure for Cu@Ag with Cu core. Inter-planar (d-spacing) obtained via HRTEM

compared very well with those obtained via XRD analysis.

The NPs were incorporated either within the photoactive layer or the hole transport layer (HTL) of the solar structure. Significant enhancements on the optical and electrical properties of the OPV devices with NPs were observed when compared to pristine devices. Different NP concentrations were investigated ranging between (1 - 10)wt% relative to the absorber blend molecules. In some cases, the effect of solvent additives such as dimethyl sulfoxide (DMSO) at 5 wt% was used together with NPs in the HTL to boost the charge transport processes. The enhanced optical absorption, and electrical properties observed as increased current-densities (J), fill-factors and charge carrier mobilities resulted to improved power conversion efficiencies (PCEs) with increases exceeding 100 % when compared to pristine devices. The open-circuit voltages for all devices remained relatively unchanged. The enhancements in the optical and electrical properties which resulted to improved PCEs were attributed to strong light trapping through scattering by NPs and local surface plasmon resonance (LSPR) excitation on the metal-semiconductor interface. Light scattering at different angles into or within the photo-active layer increases its effective optical path length and hence more photons are absorbed. The thesis presents a series of experimental investigations on recently fabricated thin film organic solar cells with/without metal NPs at various concentration.

Contents

1	General Introduction	1
1.1	Introduction	1
1.2	Problem Statement and Research Motivation	2
1.3	Study objectives	3
1.4	Thesis Outline	3
2	The effect metal nano-particles on improving solar energy conversion using bulk-heterojunction organic solar cell	9
2.1	Abstract	9
2.2	Fundamental Properties of Plasmons	9
2.3	Plasmon Induced Resonance Energy Transfer	10
2.3.1	Dipole-dipole Coupling Energy Transfer	11
2.3.2	Near-field Enhancement Energy Transfer	11
2.4	Light Scattering	12
2.5	The Physics and Characterisation of Organic Solar Cells	13
2.5.1	The Physics of Organic Solar Cells	13
2.5.2	J-V Characterisation of Solar Cells	14
2.5.3	Charge Transport Properties	16
2.6	Controlling size and shape of metal NPs	17
2.7	The effect of metal nano-particles in OPV	18
2.7.1	Nano-particles in the hole transport buffer layer	18
2.7.2	The influence of metal nano-particles in the photoactive Layer	23
2.7.3	Metal nano-particles at the interface between charge transport buffer layer/Photoactive Layer	24
2.8	Bimetallic/core-shell nanoparticles	24
2.9	Conclusion	26
3	Materials and Methods	33
3.1	Synthesis of Ag@Cu Nanoparticles	33
3.2	Synthesis of Zinc Sulphide Nanoparticles	35
3.3	Synthesis of ZnO:Ag Nanoparticles	35
3.4	Synthesis of ZnS:Mn Nanoparticles	36

3.5	Device Fabrication	36
3.6	Device Characterisation	38
3.7	Characterisation of the Nanoparticles	38
4	Near-field enhanced performance of organic photovoltaic cells	42
4.1	Abstract	42
4.2	Introduction	43
4.3	Materials and Methods	44
4.3.1	Materials:	44
4.3.2	Synthesis and characterization of silver @ copper core-shell nanoparticles (Ag@Cu NPs):	44
4.3.3	Device Preparation	45
4.4	Results and Discussion	46
4.4.1	Electrical Properties	46
4.4.2	Charge Transport	48
4.4.3	Optical absorption	49
4.4.4	Morphology of Ag@Cu core-shell NPs	50
4.5	Conclusion	52
5	Improved energy harvesting using well-aligned ZnS nanoparticles in bulk-heterojunction organic solar cell	58
5.1	Abstract	58
5.2	Introduction	59
5.3	Materials and Methods	60
5.3.1	Materials:	60
5.3.2	Synthesis and characterization of ZnS nanoparticles:	60
5.3.3	Device Fabrication	60
5.4	Results and Discussion	61
5.4.1	XRD Analysis of ZnS NPs	61
5.4.2	SEM and TEM electron microscopy	64
5.4.3	Electrical Properties	64
5.4.4	Optical absorption of the photoactive film	66
5.4.5	Charge Transport	68
5.5	Conclusion	69
6	ZnO:Ag nano-particles decorated hole transport layer for improved photon harvesting	73
6.1	Abstract	73
6.2	Introduction	74
6.3	Experimental	77
6.3.1	Synthesis of ZnO:Ag nanoparticles	77

6.3.2	Device Fabrication and Characterisation	77
6.4	Results and Discussion	78
6.4.1	Morphological and Optical properties of ZnO:Ag NPs	78
6.4.2	Optical absorption	81
6.4.3	Device characterization	83
6.4.4	Charge Transport	85
6.5	Conclusion	86
7	Manganese doped zinc sulphide nanoparticles as scattering centres in P3HT PCBM based solar cells	93
7.1	Abstract	93
7.2	Introduction	93
7.3	Materials and Methods	94
7.3.1	Materials:	94
7.3.2	Synthesis and characterization of ZnS nanoparticles:	95
7.3.3	Device Fabrication	95
7.4	Results and Discussion	96
7.4.1	Structural and Morphological Analysis of ZnS:Mn NPs	96
7.4.2	Optical absorption of the photoactive film	99
7.4.3	Electrical Properties	100
7.4.4	Charge Transport	102
7.5	Conclusion	103
8	Conclusion	106

List of Abbreviation

Ag	Silver
Au	Gold
Al	Aluminum
BHJ	Bulk heterojunction
Cu	Copper
EDX	Energy dispersive X-ray
ETL	Electron transport layer
FF	Fill-factor
FWHM	Full width at half maximum
HTL	Hole transport layer
HOMO	Highest occupied molecular orbital
ITO	Indium tin oxide
J_{max}	Maximum current density
J_{SC}	Short-circuit current density
J-V	Current density-voltage Characteristics
LiF	Lithium fluoride
LUMO	Lowest unoccupied molecular orbital
LSPR	Localized surface plasmon resonance
MNPs	Metallic nanoparticles
NC	Nanocomposite
Ni	Nickel
NPs	Nanoparticles

OPVs	Organic photovoltaics
OSCs	Organic solar cells
P3HT	Poly(3-hexylthiophene)
PCE	Power conversion efficiency
PCBM	[6,6]-phenyl-C ₆₁ -butyric acid methyl ester
PEDOT:PSS	Poly(ethylene-3-4-dioxy thiophene):poly styrene sulphonate
PL	Photoluminiscence
PSCs	Polymer solar cells
PV	Photovoltaic
PVP	Polyvinyl pyrrolidone
SCLC	Space charge limited current
SEM	Scanning electron microscope
R_s	Series resistance
R_{sh}	Shunt resistance
TEM	Transmission electron microscope
UV-Vis	Ultra violet-visible
V_a	Applied voltage
V_{bi}	Built-in voltage
V_{max}	Maximum voltage
V_{oc}	Open circuit voltage
XRD	X-ray diffractometer
ZnO	Zinc oxide
ZnS	Zinc sulphide
ZnS:Mn	Zinc sulphide:manganese

List of Figures

2.1	Illustration of (a) localized surface plasmon resonance of a nanoparticle, figure from Ref. [1], (b) radiative decay and non-radiative decay of a localized surface plasmon resonance, figure from Ref. [2], respectively.	10
2.2	A schematic energy diagram of a donor/acceptor interface. The energy band gap is given by the difference between the energy of the HOMO and LUMO. The open-circuit voltage can be derived from the difference between the HOMO (IP) of the donor and LUMO (EA) of the acceptor.	14
2.3	J-V characteristics of an OPV cell under illumination, where MPP refers to maximum power point. V_{MPP} and J_{MPP} are V_{max} and J_{max} , respectively. Figure taken from Ref. [25].	15
2.4	(a) shows tuning of Ag NPs LSPR by varying the NP size from 30 nm to 40 nm and 60 nm, (b) shows the SEM images of the Ag NPs synthesized via polyol process. (a) and (b) were obtained from [32].	18
2.5	Nanoparticle size plotted against reaction temperature. Figure taken from Ref. [33].	19
2.6	Far-field effect caused by MNPs placed on the surface of the photoactive layer	20
3.1	Schematic representation of the reduction reaction equation for the formation of Cu nanoparticles [1].	34
3.2	Schematic representation of the (a) device structure, (b) P3HT polymer, (c) PCBM fullerene and (d) the fabricated organic solar cells.	37
3.3	(a) shows the spin coating machine used to deposit PEDOT:PSS and active layer, (b) shows the Edwards Auto 306 vacuum deposition chamber used to deposit the LiF and Al layers.	37
3.4	Shows a Keithley source meter, a PET Solar Simular and a sample holder used during the characterisation of the OPV devices.	39
4.1	Schematic diagram for bulk heterojunction organic solar cell based on Ag@Cu plasmonic nanoparticles incorporated into P3HT:PCBM active layer.	45
4.2	The current-voltage characteristic of P3HT:PCBM based solar cells prepared with (a) 5 % wt% Ag@Cu and (b) 10 % wt% Ag@Cu plasmonic nanoparticles under AM 1.5G illumination at 100 mW/cm ²	47

4.3	The space-charge limited current measurements of P3HT:PCBM based solar cells prepared with (a) 5 % wt% Ag@Cu and (b) 10 % wt% Ag@Cu plasmonic nanoparticles.	48
4.4	Optical absorption spectra of the P3HT:PCBM BHJ active layers containing Ag@Cu nanoparticles at 0%, 5 % and 10 % by weight.	50
4.5	Optical absorption of the Ag@Cu nanoparticles thin film.	51
4.6	Scanning electron microscopy images and EDX of Ag@Cu nanoparticles prepared with solution processing.	52
4.7	Transmission electron microscopy images of Ag@Cu nanoparticles prepared with solution processing.	53
5.1	X-ray diffraction pattern for ZnS nanoparticles.	62
5.2	(a) & (b)HRTEM images (c) & (d) HRSEM, (e) SAED pattern images of ZnS nanoparticles and (f) the EDX of the ZnS NPs.	63
5.3	Schematic diagram (a) of the OPV devices, (b) - (d) current-voltage characteristics of P3HT:PCBM based organic solar cells.	65
5.4	(a) Optical absorption spectra of the P3HT:PCBM blend films. (b)–(d) are the charge transport properties obtained from space charge limited current data which are compared with Mott–Gurney Law	67
6.1	Schematic diagrams of localized surface plasmon resonance in spherical metallic NPs and possible resonance absorption [22].	75
6.2	Schematic diagram for bulk heterojunction organic solar cell based on P3HT:PCBM with ZnO:Ag NPs nanoparticles incorporated into the anode buffer layer PEDOT:PSS.	76
6.3	(a) X-ray diffraction pattern for ZnO:Ag nanoparticles. (b) Shows FIBSEM images of the synthesized ZnO:Ag NPs.	79
6.4	Optical absorption of (a) ZnO:Ag NPs in deionized water and (b) device films w/o ZnO:Ag NPs in PEDOT:PSS.	82
6.5	The current-voltage characteristic under AM 1.5G illumination at 100 mW/cm ² of P3HT:PCBM based solar cells prepared with pristine PEDOT:PSS and PEDOT:PSS doped with 5 wt% and 1 mg or 1.5 mg ZnO:Ag NPs.	84
7.1	Schematic device structure for P3HT:PCBM OPV incorporated with ZnS:Mn NPs.	96
7.2	X-ray diffraction pattern for (a) ZnS and (b) ZnS:Mn nanoparticles.	97
7.3	Transmission electron microscopy analysis of the ZnS:Mn nanoparticles showing d-spacing for the (111) plane.	98
7.4	Scanning electron microscopy and energy dispersive spectra analysis of the ZnS:Mn nanoparticles.	99

7.5	Optical absorption spectra of the (a) ZnS:Mn NPs in deionized water and (b) P3HT:PCBM films w/o ZnS:Mn NPs.	100
7.6	The J-V characteristics of P3HT:PCBM devices w/o ZnS:Mn NPs	101
7.7	Charge transport property curves obtained by fitting the experimental data to the Mott-Gurney Law at Space-Charge-Limited Current region.	103

List of Tables

2.1	Performance parameters of different photoactive layers	22
4.1	Summary of solar cell parameters of BHJ devices based on P3HT:PCBM mixed with Ag@Cu plasmonic nanoparticles under AM 1.5G illumination at 100 mW/cm ²	46
4.2	Summary of charge transport properties obtained from the SCLC measurements under dark current density.	49
5.1	Inter-planner spacing (d_{hkl}) from XRD data card with corresponding (hkl) and lattice parameter values for ZnS.	62
5.2	Summary of the best device performance of solar cells based on P3HT:PCBM blend at different concentrations of ZnS.	66
6.1	Peak position, FWHM, d-spacing, crystallite size (D) and hkl values for the ZnO:Ag NPs annealed at 350 °C for 3 h under ambient	80
6.2	Summary of performance parameters of BHJ devices based on P3HT:PCBM mixed with Ag@Cu plasmonic nanoparticles under AM 1.5G illumination at 100 mW/cm ²	85
7.1	Inter-planner spacing (d_{hkl}) from XRD data card with corresponding (hkl) and lattice parameter values for ZnS.	98
7.2	Summary of best performed solar cell devices based on P3HT:PCBM blend at different concentrations of ZnS:Mn NPs.	102

Chapter 1

General Introduction

1.1 Introduction

Due to the rising cost of energy production from the scarce fossil fuel, researchers embarked on finding alternative sources of energy production. Solar energy is one of the possible renewable energy sources that can ease the scarcity of energy and prevent environmental pollution. In recent years, bulk heterojunction organic photovoltaic cells emerged to be of great interest due numerous advantages such as easy process-ability, light weight, mechanical flexibility, eco-friendliness, and low fabrication cost through roll-to-roll printing. It is to be noted that polymer blend film possesses high optical absorption coefficient as high as 10^5 L mol^{-1} [1–6]. Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl- C_{60} -butyric acid methyl ester (PCBM) blend film has become the most studied and promising electron donor and acceptor blend, and have demonstrated power conversion efficiencies (PCE) in excess of 6 % [2, 5–8, 10]. However, the organic photovoltaic still face several challenges such as low photon absorption, generation and dissociation of electron-hole pairs, charge carrier transport and extraction of the generated charge carriers at the respective electrodes.

Because of short diffusion length ($\approx 10 \text{ nm}$) of exciton and low charge carrier mobilities in polymer medium, the photoactive layer thickness of the polymer absorber is restricted to the range 140 - 250 nm, which is very thin to capture all the incident photons [4, 11, 12]. Therefore, a need to improve the light trapping and absorption mechanisms in thin film OPVs has become an important issue in research. Conventional methods of light trapping use textures that have features incomparable or even larger than the thickness of the actual thin film solar cells [13]. These would create undesirable morphology resulting to significant surface recombination losses. Therefore, different light trapping mechanisms, e.g., metal nano-grating, surface texturing and photonic crystals, have been suggested, however, these methods require sophisticated fabrication equipment and techniques [14–19].

In recent years, metallic nano-particles (NPs) have been introduced into solar cells to enhance photon harvesting by utilizing the localized surface plasmonic resonance (LSPR) of

metallic NPs [20] while keeping the active layer thin. Metallic nanoparticles (MNPs) may be easier and cheaper to fabricate, or exhibit a higher performance compared to dielectric light scattering approaches [16]. When incorporated close to the interface between the photo-active area and transport layers, the NPs lead to concentrated optical electric fields near the junction [16, 22], which enhances exciton creation within an exciton diffusion length away from the photo-active medium [16]. This phenomenon is associated with comparatively small nanoparticles, much smaller than the wavelength of the incident light. Though promising, the near-field light concentration is always accompanied by strong ohmic loss from the NPs, which is dissipated as heat [23]. Incorporation of MNPs in photovoltaic is aimed at improving the photons absorption either by local surface plasmon resonance or by way of near and far-field scattering, which increases the optical path length within a photo-active medium [19]. Recent studies have shown that the incorporation of plasmonic metallic nano-structures into solar cells can significantly improve the PCE of solar cells by multiple folds due to photons trapping via scattering and near-field effects [13, 18, 26–30]. Plasmonics is an emerging field that makes use of the nanoscale properties of metals [13], which are defined to be the collective oscillation of conduction electrons upon irradiation with light of certain wavelength [31]. The excitation of the localized surface plasmon resonance (LSPR) can be achieved when the frequency of the incident light matches with oscillation frequency of metal surface electron plasma, resulting in a strong near-field around the interface between the dielectric and metallic nanoparticles [28, 32, 33]. The resonance frequency of LSPR depends strongly on the size, shape of the NP and the dielectric environment around the metallic nano-particles (NPs) [13, 28, 34]. Therefore, by manipulating the size, shape and dielectric environment of the metallic NPs, the surface plasmon resonance and associated properties can be tuned depending on the applications [13].

1.2 Problem Statement and Research Motivation

The increasing demand for more energy due to growing world population and urbanization resulted in more consumption of fossil fuels, which causes the depletion of the natural resources and severe global warming because of CO₂ emission. These call for alternative clean and environmentally friendly energy sources. Solar energy is one of the abundant renewable energy sources that has been utilised to supplement and potentially reduce the reliance on fossil fuel. There has been a number of solar cell technologies developed to harvest solar energy. The most widely used technology due to its high power conversion efficiency and durability is based on inorganic materials such as silicon. However, some of these inorganic materials are not easy to find and they are expensive to process due to heat requirement. Recently, organic photovoltaic solar cells have gained tremendous research interest due to their low fabrication cost, environmental friendliness, flexibility, light weight and potential for roll-to-roll fabrication. However, polymer based photovoltaic suffer from low carrier mobilities and short exciton diffusion length thus limiting their photo-active layer thickness

to less than 200 nm. This leads to low photon absorption and thus low power conversion efficiencies. Therefore, there is a need to improve photon absorption in polymer solar cells while keeping their photoactive layer thickness thin (< 200 nm). As a potential solution to this photoactive layer thickness limitation is the use of plasmonic photo-catalytic nano-composites that can scatter or absorb incident photons and improve optical absorption of organic thin film solar cells. These nano-composites can scatter incident photons in different directions inside the photo-active layer thus increasing its optical path length. Hence, more light could be absorbed and converted to electrical energy. The nano-composites can also be tuned to absorb incident photons through localized surface plasmon resonance and convert it to energetic electrons and holes. Thus improving charge carrier generation in organic photovoltaic. These nano-composites could be solution-processable, cheap and environmentally friendly.

1.3 Study objectives

- i. Synthesize solution-processable and environmentally friendly metal nano-particles (NPs) that possess good optical and electrical properties. The NPs are expected to possess plasmonic features and/or light scattering features.
- ii. Characterize the morphology, structural and optical properties of the solution-processed metal NPs.
- iii. Fabricate organic photovoltaic doped with metal NPs (and/or solvent additive) at different functional layers of the solar cell. Which is either in the photo-active layer or/and the charge transport buffer layer (PEDOT:PSS) to enhance their optical and electrical properties, thus improving their power conversion efficiency.
- iv. Investigate current-voltage properties of the fabricated OPVs, and determine the effect of NPs on photons harvesting and the charge transport processes.

1.4 Thesis Outline

In this thesis, we presented and discussed the performance of newly fabricated organic photovoltaic (OPV) devices doped with metal NPs either in the photo-active layer (P3HT:PCBM) or the buffer layer (PEDOT:PSS). In chapter 2, a literature review is presented on the application of metal NPs in OPV using NPs such as gold and silicon. This chapter also discussed the fundamental principles about interaction of light with plasmonic NPs in polymer medium (LSPR and forward light scattering) and how the NPs can contribute to solar energy harvesting and charge transport processes in OPV. Chapter 3 briefly presents the materials and methods used to synthesize and fabricate the NPs and OPV devices used in the experimental chapters. Chapter 4 reports on the synthesis and characterization of Ag@Cu NPs and their enhancements effects on P3HT:PCBM OPVs. The optical and electrical properties

of OPV devices doped with Ag@Cu in the photo-active layer are presented and discussed. Chapter 5 presents and discusses an improved energy harvesting in OPV devices doped with ZnS in the photoactive layer. The morphology and structural properties of the solution-processed ZnS NPs are presented. This chapter presents and discussed the improvements on the optical and electrical properties of the devices upon the addition of ZnS NPs. Chapter 6 reports on the device enhancements as a result of doping PEDOT:PSS film with ZnO:Ag and dimethyl sulfoxide. The electrical and optical properties of the devices are presented and discussed. The morphology, optical and structure of the ZnO:Ag NPs are also presented. Chapter 7 reports on the device enhancements as a result of doping the photoactive layer film with ZnS:Mn NPs. The electrical and optical properties of the devices are presented and discussed. The morphology, optical and structure of the ZnS:Mn NPs are also presented. Finally, chapter 8 gives a summary of our results and draw conclusions based on the findings of the investigations.

Bibliography

References

- [1] B. Hailegnaw, G. Adam and T Yohannes, 2015. Effect of short chain iodoalkane solvent additives on photovoltaic performance of poly (3-hexylthiophene) and phenyl-c61-butyric acid methyl ester based bulk heterojunction solar cells. *Thin Solid Films*, 589, pp.272-277.
- [2] S. Yan, L. Lv, Y. Ning, L. Qin, C. Li, X. Liu, Y. Hu, Z. Lou, F. Teng and Y. Hou, 2015. Effects of solvent additives on trap-assisted recombination in P3HT: ICBA based polymer solar cells. *physica status solidi (a)*, 212(10), pp.2169-2173.
- [3] M. N. Yusli, T. W. Yun, K. Sulaiman, 2009. Solvent effect on the thin film formation of polymeric solar cells. *Materials Letters*, 63(30), pp.2691-2694.
- [4] S. R. Gollu, R. Sharma, G. Srinivas, S Kundu and D Gupta, 2016. Incorporation of silver and gold nanostructures for performance improvement in P3HT: PCBM inverted solar cell with rGO/ZnO nanocomposite as an electron transport layer. *Organic Electronics*, 29, pp.79-87.
- [5] G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, 1995. Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor-acceptor heterojunctions. *Science*, 270(5243), pp.1789-1791.
- [6] F. C. Krebs, J. Alstrup, H. Spanggaard, K. Larsen and E. Kold, 2004. Production of large-area polymer solar cells by industrial silk screen printing, lifetime considerations and lamination with polyethyleneterephthalate. *Solar energy materials and solar cells*, 83(2-3), pp.293-300.
- [7] A. De Sio, T. Madena, R. Huber, J. Parisi, S. Neyshadt, F. Deschler, E. Da Como, S. Esposito and E. Von Hauff, 2011. Solvent additives for tuning the photovoltaic properties of polymer–fullerene solar cells. *Solar Energy Materials and Solar Cells*, 95(12), pp.3536-3542.
- [8] F. Reisdorffer and O. Haas and P. Le Rendu and T. P Nguyen, 2012. Co-solvent effects

- on the morphology of P3HT: PCBM thin films. *Synthetic Metals*, 161(23-24), pp.2544-2548.
- [9] S. K. Jang, S. C. Gong and H. J. Chang, 2012. Effects of various solvent addition on crystal and electrical properties of organic solar cells with P3HT: PCBM active layer. *Synthetic metals*, 162(5-6), pp.426-430.
- [10] M. T. Dang, L. Hirsch and G. Wantz, 2011. P3HT: PCBM, best seller in polymer photovoltaic research. *Advanced Materials*, 23(31), pp.3597-3602.
- [11] V. Shrotriya, E. H. Wu, G. Li, Y. Yao and Y. Yang, 2006. Efficient light harvesting in multiple-device stacked structure for polymer solar cells. *Applied physics letters*, 88(6),
- [12] P. W. M. Blom, V. D. Mihailetschi, L. J. A. Koster and D. E. Markov, 2007. Device physics of polymer: fullerene bulk heterojunction solar cells. *Advanced Materials*, 19(12), pp.1551-1566.
- [13] S. Pillai and M. A. Green, 2010. Plasmonics for photovoltaic applications. *Solar Energy Materials and Solar Cells*, 94(9), pp.1481-1486.
- [14] Y. H. Lee, D. H. Kim, T. W. and Kim, 2017. Enhanced power conversion efficiency of organic photovoltaic devices due to the surface plasmonic resonance effect generated utilizing Au-WO₃ nanocomposites. *Organic Electronics*, 45, pp.256-262.
- [15] W. Yu, L. Shen, Y. Long, P. Shen, W. Guo, W. Chen and S. Ruan, 2014. Highly efficient and high transmittance semitransparent polymer solar cells with one-dimensional photonic crystals as distributed Bragg reflectors. *Organic Electronics*, 15(2), pp.470-477.
- [16] M. Song, H. Kim, C. S. Kim, J. Jeong, C. Cho, J. Lee, S. Jin, D. Choi and D. Kim, 2015. ITO-free highly bendable and efficient organic solar cells with Ag nanomesh/ZnO hybrid electrodes. *Journal of Materials Chemistry A*, 3(1), pp.65-70.
- [17] X. Yu, X. Yu, J. Zhang, Z. Hu, G. Zhao and Y. Zhao, 2014. Effective light trapping enhanced near-UV/blue light absorption in inverted polymer solar cells via sol-gel textured Al-doped ZnO buffer layer. *Solar energy materials and solar cells*, 121, pp.28-34.
- [18] L. Müller-Meskamp, Y. H. Kim, T. Roch, S. Hofmann, R. Scholz, S. Eckardt, K. Leo and A. F. Lasagni, 2012. Efficiency enhancement of organic solar cells by fabricating periodic surface textures using direct laser interference patterning. *Advanced Materials*, 24(7), pp.906-910.
- [19] J. Zhu, X. Zhu, R. Hoekstra, L. Li, F. Xiu, M. Xue, B. Zeng and K. L. Wang, 2012. Metallic nanomesh electrodes with controllable optical properties for organic solar cells. *Applied Physics Letters*, 100(14), p.143109.

- [20] L. Lu, Z. Luo, T. Xu and L. Yu, 2013. Cooperative plasmonic effect of Ag and Au nanoparticles on enhancing performance of polymer solar cells. *Nano letters*, 13(1), pp.59-64.
- [21] J. Y. Lee and P. Peumans, 2010. The origin of enhanced optical absorption in solar cells with metal nanoparticles embedded in the active layer. *Optics Express*, 18(10), pp.10078-10087.
- [22] S. Fujimori, R. Dinyari, J. Y. Lee and P. Peumans, 2009. Plasmonic light concentration in organic solar cells. *Nano Letters*.
- [23] B. Cai, B. Jia, Z. Shi and M. Gu, 2013. Near-field light concentration of ultra-small metallic nanoparticles for absorption enhancement in a-Si solar cells. *Applied Physics Letters*, 102(9), p.093107.
- [24] A. Paris, A. Vaccari, A.C. Lesina, E. Serra and L. Calliari, 2012. Plasmonic scattering by metal nanoparticles for solar cells. *plasmonics*, 7(3), pp.525-534.
- [25] S. W. Baek, G. Park, J. Noh, C. Cho, C. H. Lee, M. K. Seo, H. Song and J Y Lee, 2014. Au@ Ag core-shell nanocubes for efficient plasmonic light scattering effect in low bandgap organic solar cells. *Acs Nano*, 8(4), pp.3302-3312.
- [26] Z. Tang, W. Tress and O. Inganäs, 2014. Light trapping in thin film organic solar cells. *Materials today*, 17(8), pp.389-396.
- [27] S. W. Baek, J. Noh, C. H. Lee, B. Kim, M. K. Seo and J. Y. Lee, 2013. Plasmonic forward scattering effect in organic solar cells: a powerful optical engineering method. *Scientific reports*, 3, p.1726.
- [28] X. H. Liu, L. X. Hou, J. F. Wang, B. Liu, Z. S. Yu, L. Q. Ma, S. P. Yang and G. S. Fu, 2014. Plasmonic-enhanced polymer solar cells with high efficiency by addition of silver nanoparticles of different sizes in different layers. *Solar energy*, 110, pp.627-635.
- [29] J. G. Smith, J. A. Fauchaux and P. K. Jain, 2015. Plasmon resonances for solar energy harvesting: a mechanistic outlook. *Nano Today*, 10(1), pp.67-80.
- [30] H. Shen, P. Bienstman and B. Maes, 2009. Plasmonic absorption enhancement in organic solar cells with thin active layers. *Journal of Applied Physics*, 106(7), p.073109.
- [31] H. Shen, P. Bienstman and B. Maes, 2017. Solid-state plasmonic solar cells. *Chemical reviews*, 118(6), pp.2955-2993.
- [32] D. H. Wang, K. H. Park, J.H. Seo, J. Seifter, J. H. Jeon, J. K. Kim, J. H. Park, O. O. Park and A. J. Heeger, 2011. Enhanced power conversion efficiency in PCDTBT/PC70BM bulk heterojunction photovoltaic devices with embedded silver nanoparticle clusters. *Advanced Energy Materials*, 1(5), pp.766-770.

-
- [33] H. Choi, J. P. Lee, S. J. Ko, J. W. Jung., H. Park, S. Yoo, O. Park, J. R. Jeong, S. Park and J. Y. Kim, 2013. Multipositional silica-coated silver nanoparticles for high-performance polymer solar cells. *Nano letters*, 13(5), pp.2204-2208.
- [34] J. A. Schuller, E.S Barnard., W. Cai, Y. C. Jun, J. S. White and M. L. Brongersma, 2010. Plasmonics for extreme light concentration and manipulation. *Nature materials*, 9(3), pp.193-204.

Chapter 2

The effect metal nano-particles on improving solar energy conversion using bulk-heterojunction organic solar cell

2.1 Abstract

Solution processed organic photovoltaic cell are under intense investigation by both industrial and academic institutions due to their potential for the fabrication of low cost, flexible and light weight solar panel. To enhance film morphology, photons harvesting, charge carrier transport properties researchers have developed several processing techniques such as the use of solvent additives, plasmonic nano-particle doping and thermal annealing, to name a few. This chapter focuses on the review of several investigations that have been reported in recent years on the role of plasmonic effect on enhancing the optoelectronic properties of organic photovoltaic. Particular emphasis is given to the nano-particles such as gold (Au), copper (Cu) and silver (Ag). Incorporation of plasmon nano-particles in photovoltaic shows tremendous improvement in their electrical properties and power conversion efficiency of the devices. These nano-particles were incorporated in a number of functional layers of the device such as charge transport buffer layer, buffer layer/photo-active layer interface or within the photo-active layer.

2.2 Fundamental Properties of Plasmons

In recent years, plasmons have been used to trap light and enhance the performance of photovoltaic. Plasmons are the collective oscillation of free/conduction electrons in noble metal surfaces in response to incident light. These plasmons can propagate along metal surface as electron density waves or oscillate locally as electron clouds on metal nano-particles, see

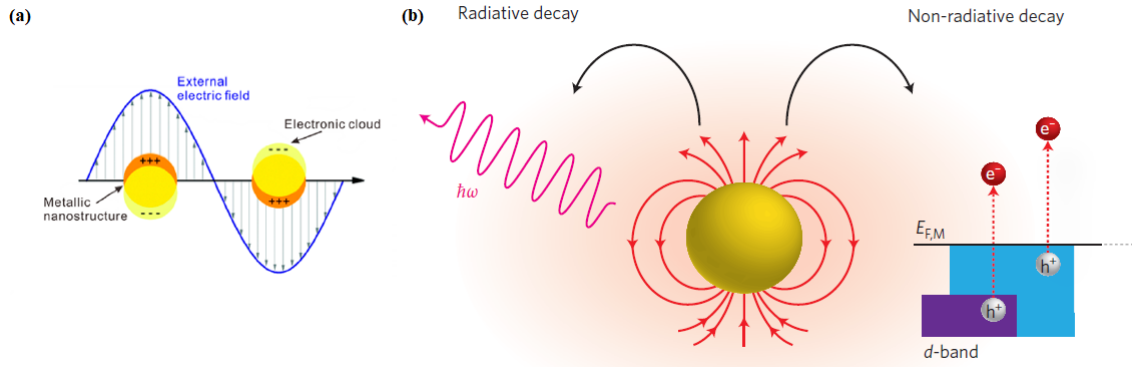


Figure 2.1: Illustration of (a) localized surface plasmon resonance of a nanoparticle, figure from Ref. [1], (b) radiative decay and non-radiative decay of a localized surface plasmon resonance, figure from Ref. [2], respectively.

Fig. 2.1.

A phenomenon known as surface plasmon resonance or local surface plasmon resonance (LSPR) occurs when the oscillation frequency of the electron plasma on the metal surface matches with that of the incident light. LSPR occurs when a surface plasmon is confined to a particle whose size is less than the wavelength of the incident wave, and the free electrons on metal surface collectively oscillate around the nuclei [3]. This resonant frequency differs from metal to metal and can be tuned by the size, shape and morphology of the NP. At resonance, there is a possibility of creating hot electrons that jump to conduction band and a significantly enhanced electric fields around the NPs surfaces [4]. Resonance is usually achieved in the visible and near infrared wavelength region for noble metal NPs [4]. The enhanced electric field as a result of surface plasmon resonance may cause strong light scattering and generate huge charge carriers [5]. Due to these SPR properties, SPR have been researched tremendously as a mechanism to improve the performance of photovoltaic. Plasmon NPs can significantly enhance light trapping mechanisms by using spectral modification techniques to move unabsorbed frequencies of the solar system into the area of maximum cell absorption, by scattering and focusing the electromagnetic field into the active region of devices [6]. This is achieved by tuning the size, shape, morphology and the dielectric environment around a plasmon NP. Therefore, enhancement of solar cells using NPs is very beneficial because it ensures light absorption is enhanced while the photoactive layer thickness remains in nano-scale for OPV.

2.3 Plasmon Induced Resonance Energy Transfer

The phenomenon of LSPR has wide range of applications such as photo-catalysis and energy harvesting through photovoltaic processes. When plasmon NPs are irradiated with light of wavelength, λ , much larger than the NP sizes, the conduction electrons of the MNPs are displaced with respect to the nuclei (creating a large electric dipole) due to the electric field of

the incident light. Due to Coulomb attraction between the displaced electrons and the nuclei, a restoring force is then created which causes the electrons to oscillate with the frequency of the incident wave and resonant occurs [25]. An intense electric field near the MNP could result from this electric dipole with its intensity tens to thousands of times greater than that of the incident light [25, 26]. This electric field enhancement around plasmonic NPs is called near-field enhancement [25]. There are two mechanisms generally understood to describe energy from the plasmon metal to the semiconductor, via dipole-dipole coupling and near-field enhancement.

2.3.1 Dipole-dipole Coupling Energy Transfer

The dipole-dipole coupling generates exciton below and near the semiconductor band edge [27]. Li et al. showed, in 2012, that electron-hole pairs can be created in a semiconductor via resonant energy transfer from plasmonic metal, which in the near-field is similar to Förster resonance energy transfer [27]. That is, energy is transferred by coupling the large plasmon dipole to the electron-hole pair dipole in the semiconductor [25, 28]. The dipole-dipole energy transfer mechanism was shown by Xiang-Chao et al as follows. The interaction Hamiltonian between a dipole $\vec{\mu}$ and an electric field $\vec{E}$ can be expressed as [25]

$$H' = -\vec{\mu} \cdot \vec{E} \quad (2.1)$$

Substituting $\vec{E}$ with the plasmon dipole induced electric field, the perturbation Hamiltonian H' becomes the dipole-dipole interaction term $\hat{\mu}_A$

$$H_{AB} = \frac{\mu_A \mu_B}{r^3} (3(\hat{\mu}_A \cdot \hat{r})(\hat{\mu}_B \cdot \hat{r}) - (\hat{\mu}_A \cdot \hat{\mu}_B)) \quad (2.2)$$

where μ_A and μ_B are the plasmon dipole and electron-hole dipole, respectively. The plasmon dipole moment μ_A can be calculated from Mie theory as [11]

$$\mu_A = \frac{\epsilon_{metal} - \epsilon_{dielectric}}{\epsilon_{metal} + 2\epsilon_{dielectric}} a^3 E_0 \quad (2.3)$$

where ϵ is the dielectric constant, a is the NP radius and E_0 is the incident electric field.

2.3.2 Near-field Enhancement Energy Transfer

The enhanced near-field is strongest at the surface of the NP and decays exponentially with distance from the surface of the NP. Since the rate of electron-hole pair formation in a semiconductor is proportional to the local intensity of the electric field, the rate of electron-hole formation in some regions of the semiconductor increases by a few orders of magnitude [26] due to the near-field enhancement. The enhanced near-field can enhance the inter-band or other optical transitions in the nearby semiconductor if the LSPR spectra overlap with

them [25]. When the overlap is significant, the enhanced electric fields at and near the NP surfaces are suggested to enhance exciton generation within the semiconductor [12]. Near field enhancement could be play as an additional mechanism for exciton disassociation and light scattering.

2.4 Light Scattering

According to laws of optics, when light encounters an object it will either propagate in the forward direction giving rise to refraction and absorption, or propagate in the reverse direction giving rise to reflection [13]. Among theories that have been developed to describe this process are the Rayleigh scattering theory [13] and the Mie scattering theory [13–16] for spherical scatterers such as particles. Rayleigh scattering theory is applicable to scattering by small particles in the "Rayleigh regime" where $x \ll 1$, with $x = \frac{2\pi r}{\lambda}$ being the ratio of particle circumference to the wavelength λ for a spherical particle [13, 17]. That is, the Rayleigh scattering theory applies to scattering by particles whose radii are much smaller than the wavelength of the incident light. For a dielectric (non-absorbing) single particle, the intensity of the light scattered is given by [13, 18]

$$I = I_0 \frac{1 + \cos(\theta)^2}{2d^2} \left(\frac{2\pi}{\lambda} \right)^4 \left| \frac{m^2 - 1}{m^2 + 2} \right|^2 r^6 \quad (2.4)$$

where I_0 is the incident intensity, d is the distance to the particle, θ is the scattering angle and m is the refractive index of the particle. Integrating over the sphere surrounding the particle gives the Rayleigh scattering cross-section as [13]

$$\theta_{scat, Rayleigh} = \frac{2}{3} \pi^5 \frac{(2r)^6}{\lambda^4} \left| \frac{m^2 - 1}{m^2 + 2} \right|^2 \quad (2.5)$$

where m is the refractive index of the scatterer. Equation 2.5 shows that the Rayleigh scattering is proportional to the square of the particle volume, 6^{th} power of the particle size (r) and inversely proportional to the incident wavelength. The Mie scattering theory is applicable to particle sizes beyond the "Rayleigh regime" and regardless of whether the particles are of a light absorbing or non-absorbing material [13]. The Mie theory gives the extinction coefficient (C_{ext}), scattering (C_{sca}) and absorption (C_{abs}) cross-sections as follows [13, 19]

$$C_{ext} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1) Re(a_n + b_n) \quad (2.6)$$

$$C_{sca} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1) Re(|a_n|^2 + |b_n|^2) \quad (2.7)$$

$$C_{abs} = C_{ext} - C_{sca} \quad (2.8)$$

where $k = \frac{2\pi N}{\lambda}$, N is the refractive index of the surrounding medium, a_n and b_n are defined as

$$a_n = \frac{m\phi_n(mka)\phi'_n(ka) - \phi_n(ka)\phi'_n(mka)}{m\phi_n(mka)\chi'_n(ka) - \chi_n(ka)\phi'_n(mka)} \quad (2.9)$$

$$b_n = \frac{\phi_n(mka)\phi'_n(ka) - m\phi_n(ka)\phi'_n(mka)}{\phi_n(mka)\chi'_n(ka) - m\chi_n(ka)\phi'_n(mka)} \quad (2.10)$$

where ϕ and χ are the Riccati-Bessel functions of the first and third order kind, respectively. $a = r$ is the particle radius, and here $m = \frac{N_p}{N}$, N_p is the complex refractive index of the particle [19].

2.5 The Physics and Characterisation of Organic Solar Cells

2.5.1 The Physics of Organic Solar Cells

Bulk heterojunction solar cells utilize two materials (donor and acceptor) with different electron affinities and ionization potentials. At the donor/acceptor interface, the resulting potentials are strong and may favor exciton dissociation [20]. The material with larger electron affinity accepts (acceptor material) the electron and the material with lower ionization potential (acceptor material) accepts the hole. This will occur if the difference in potential energy is greater than the binding energy. Figure 2.2 schematically shows the physical processes in a bulk heterojunction organic solar cell. Both the donor and acceptor materials have the highest occupied molecular orbital (HOMO), or ionization potential (IP), and lowest unoccupied molecular orbital (LUMO), or electron affinity (EA) [21]. The difference in EA and IP of the donor and acceptor materials set up electrostatic forces at the donor/acceptor interface. With properly chosen donor and acceptor combination, the EA and IP differences can generate strong electric fields that may break up the excitons into free electrons and holes more efficiently [21].

In inorganic solar cells, the absorption of photon energy creates free charge carriers (free electron-hole pairs) while it creates excitons (electron-hole pairs bound together by electrostatic) [20, 21]. In OPVs however, the incident photon energy is absorbed to excite the donor, creating excitons in the donor material (electrons in the LUMO and holes in the HOMO) and diffuse towards the donor/acceptor interface. At the interface, the excitons dissociate leading to charge separation. The electrons are accepted by the acceptor material and the holes by remain in the donor material as schematically depicted in Fig. 2.2. The charge carriers are then transported through the selective buffer layer to their respective electrode for collection.

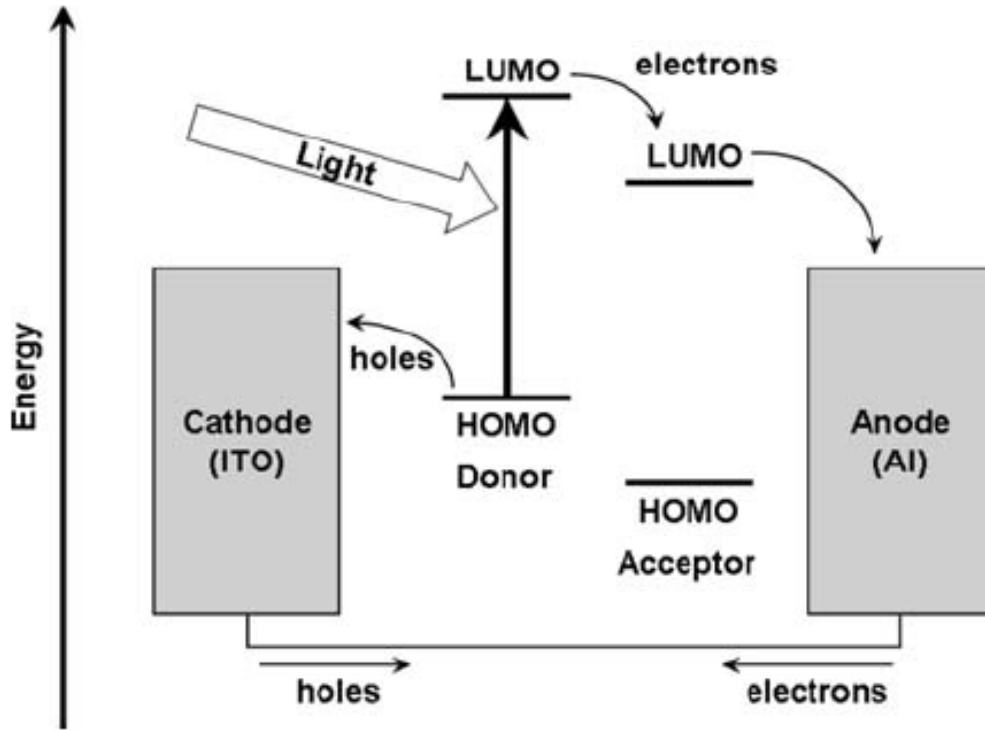


Figure 2.2: A schematic energy diagram of a donor/acceptor interface. The energy band gap is given by the difference between the energy of the HOMO and LUMO. The open-circuit voltage can be derived from the difference between the HOMO (IP) of the donor and LUMO (EA) of the acceptor.

2.5.2 J-V Characterisation of Solar Cells

The current density (J) obeys a simple diode current equation given by the Shockley's theory as [22, 23]

$$J = J_s \left(\exp\left(\frac{qV}{k_B T}\right) - 1 \right) - J_{ph}(V) \quad (2.11)$$

where J_s is the reverse saturation current density, q is the electron charge, V is the applied voltage, J_{ph} is the photo-generated current density, k_B is the Boltzmann's constant and T is temperature. The first term of Eq. 2.11 expresses the junction current density of the diode or thermally generated current density typically dominated by recombination at donor/acceptor interface [22, 23]. For an ideal solar cell, J_{ph} is equal to the current density, J_{sc} , at short-circuit conditions. Solar cell performance parameters can then be derived from Eq. 2.11 after employing certain boundary conditions [22] such as open-or short-circuit conditions. The voltage across the devices at open-circuit conditions ($J=0$) can be expressed in terms of the photo-generated and reverse saturation current densities as follows [23]

$$V_{oc} = \frac{nk_B T}{q} \ln \left[\frac{J_{ph}}{J_s} + 1 \right] \approx \frac{nk_B T}{q} \ln \left[\frac{J_{sc}}{J_s} \right] \quad (2.12)$$

where $J_{ph}=J_{sc} \gg J_s$ and n is the ideality factor of the diode. An ideality factor $n=1$ indicates that carrier recombination in the depletion region is negligible and diffusion current

is dominant in the cell. Under practical conditions, the devices exhibit both recombination and diffusion currents and the ideality factor ranges between 1 and 2 [23]. The open-circuit voltage, V_{oc} , is one of the important limitations inhibiting the performance of OPVs to date, it is typically half of the incident photon energy [23]. It is mainly related to the cathode work function, morphology, energy band gaps of the absorber layer, and reverse saturation current density [23, 24].

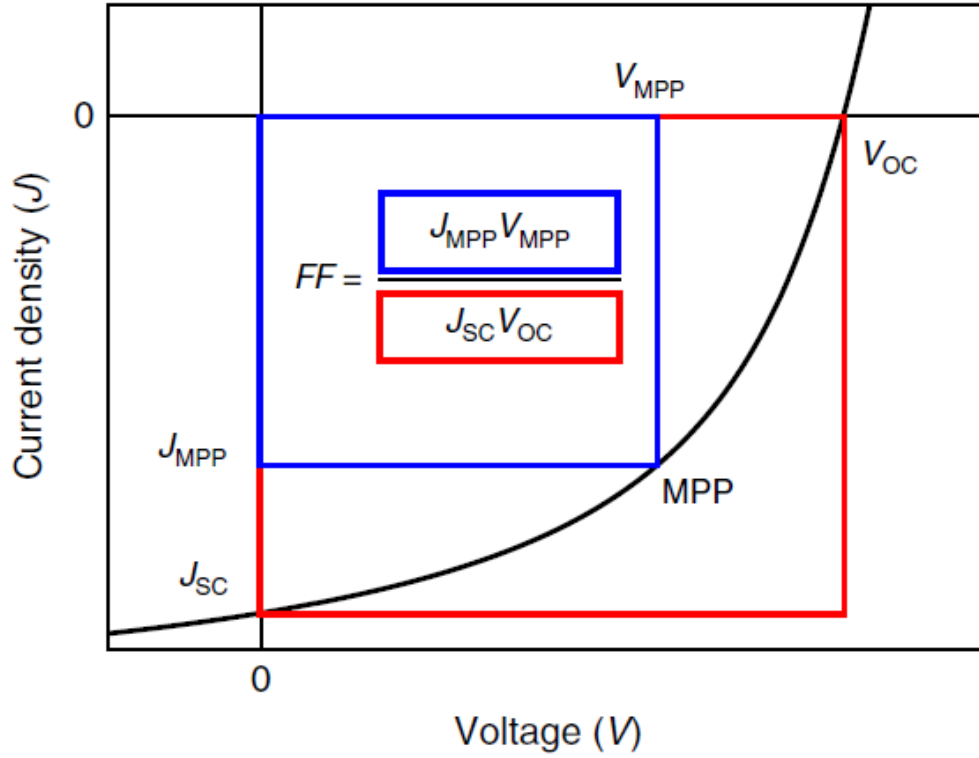


Figure 2.3: J-V characteristics of an OPV cell under illumination, where MPP refers to maximum power point. V_{MPP} and J_{MPP} are V_{max} and J_{max} , respectively. Figure taken from Ref. [25].

There exist a point (maximum power point, MPP - see Fig. 2.3) in the J-V curve where power produced is maximum and is denoted by $V = V_{max}$ and $J = J_{max}$. The product of J_{max} and V_{max} gives an area of the largest for any point on the J-V curve. The ratio of the rectangles given by V_{oc} and J_{sc} , and by J_{max} and V_{max} gives the device fill-factor (FF), which is a measure of the squareness of the J-V characteristic curve [26].

$$FF = \frac{J_{max} V_{max}}{J_{sc} V_{oc}} \quad (2.13)$$

An empirical formula for the fill-factor is given by [26]

$$FF = \frac{V_{oc} - \frac{k_B T}{q} \ln \left[\frac{q V_{oc}}{k_B T} + 0.72 \right]}{V_{oc} + \frac{k_B T}{q}} \quad (2.14)$$

The FF is a sensitive cell parameter which depends on the mobility-lifetime product of the bulk properties of the material, active layer thickness and the morphology of the cathode-

polymer interface [27]. The most important parameter of a solar cell is its power conversion efficiency (PCE), η , given by [28]

$$\eta = \frac{V_{oc}J_{sc}FF}{P_{in}} \quad (2.15)$$

where P_{in} is the incident solar power. Low PCE for OPVs has been a critical hindrance for their commercialisation. However, it has received tremendous attention from researchers in recent years. Researchers have investigated many different strategies to improve the OPV device properties to enhance their PCE such as creating low/narrow bandgap polymers, film morphology optimisation, and different device architectures [24, 28]. Narrow-bandgap polymers can maximize J_{sc} and lowered highest occupied molecular orbital (HOMO) increases V_{oc} . However, lowering HOMO will also increase the energy bandgap negatively affecting the J_{sc} . Therefore, there is a need to improve J_{sc} while not negatively affecting V_{oc} and vice-versa. As can be seen from Eq. 2.13, an increase in J_{sc} and/or V_{oc} without an increase in J_{max} and V_{max} may negatively affect the FF.

2.5.3 Charge Transport Properties

There are several ways to study the charge transport properties in the solar cell devices and the determination of various transport parameters such as charge mobility, (μ). These include the time-of-flight, field-effect transistor and space charge limited current methods. We discuss here the widely used method known as space charge limited current (SCLC). The SCLC method is easy to perform requiring no sophisticated device preparation and experimental set-up such as using pulsed lasers. The SCLC method assumes that charge transport in an organic layer sandwiched between two electrodes is bulk limited and not contact limited. The electrodes are chosen such that only electrons or holes are able to be injected at low voltages. When an external electric field is applied across the organic layer, charge is injected into the layer resulting to space-charge build up [50]. At steady-state conditions, charge inside the device saturates, charge injection then only occurs to replace charge extracted on the opposite electrode [50]. The SCLC region current density is given by the Mott-Gurney law [30, 50, 51]

$$J_{sclc} = \frac{9}{8}\epsilon_o\epsilon_r\mu\frac{V^2}{L^3} \quad (2.16)$$

where ϵ_o is the permittivity of free-space, ϵ_r is the dielectric constant of the medium and L is the layer thickness. Where charge changes with the applied electric field, μ is then given by

$$\mu = \mu_o \exp(\gamma\sqrt{E}) \quad (2.17)$$

where μ_o is the zero-field mobility, γ is the field-dependence effect factor, and $E=V/L$ is the applied electric field. Eq.6.7 then takes the form

$$J_{sclc} = \frac{9}{8} \epsilon_o \epsilon_r \mu_o \exp(0.89\gamma\sqrt{V/L}) \frac{V^2}{L^3} \quad (2.18)$$

taking into account that the field is not uniform across the semiconductor layer. The charge mobility, μ_o , and field-dependence factor, γ , can then be obtained in practical by fitting the Mott-Gurney law in Eq.6.9 to the J-V experimental data obtained under dark condition where the $J \propto V^2$. The SCLC method for obtaining charge mobility is very prone to misinterpretation [51] and mobility values can vary by more than one order of magnitude on nominally identical devices [50].

2.6 Controlling size and shape of metal NPs

MNPs can be synthesized to well-controlled sizes and well-defined shapes using effectively simple solution chemistry. Controlling the size and shape of the MNPs helps tune their LSPR as it strongly depends on these two properties. Wang et al. [32] synthesized Ag NPs with uniformly controlled shapes and sizes. The NPs had average diameters of 30 nm, 40 nm and 60 nm. The NPs were synthesized using polyol chemistry where silver nitrate (AgNO_3) was used as the precursor, PVP as the stabilizer. The size was controlled by the use of three kinds of polyols: 1,2-propanediol (60 nm NPs), 1,4-butanediol (40 nm NPs) and 1,5-pentanediol (30 nm NPs) [32].

Figure 1 shows the UV-vis spectra of the synthesized NPs and their scanning electron microscopy (SEM) images. The SEM images shows uniform size distribution for the 30 nm, 40 nm and 60 nm NPs. The NPs showed maximum absorption at 390 nm for the 30 nm NPs, which then shifted to 420 nm and 450 nm for the 40 nm and 60 nm NPs, respectively. Derrick et al. [33] synthesized copper (Cu) NPs with sizes ranging between 5 - 25 nm by varying the reaction temperature from 150 °C to 210 °C. The NP sizes showed an increasing trend as the reaction temperature was increased.

Figure 2.5 shows the NPs diameters plotted against the reaction temperature. NPs synthesized at 150 °C showed an average diameter of 5 nm and increased to 25 nm as the reaction temperature was increased to 190 °C. For temperatures above 210 °C, the NPs started showing different shapes such as rods, cubes and tetrahedrons with rods being the common shapes [33]. Stabilizers such as PVP and PVA, which have polyvinyl skeletons with polar groups, are used during synthesis of NPs to control the size and inhibit agglomeration of the NPs. In a PVP/PVA stabilised synthesis process of Ag NPs, the *sp* orbital of Ag^+ can accept lone pairs of nitrogen and oxygen atoms of PVA/PVP to form coordination bond [34, 35] thus protecting the NPs from agglomeration. In addition, several reports have reported post synthesis stability of PVP stabilized Ag NPs remaining stable for long periods exceeding one month [36, 37]. Chen et al. [38] studied, among other effects, the effect of PVP concentration in the synthesis of uniform Ag NPs. It was observed that the absorption intensity in the 420 nm absorption band gradually intensified as the PVP concentration was

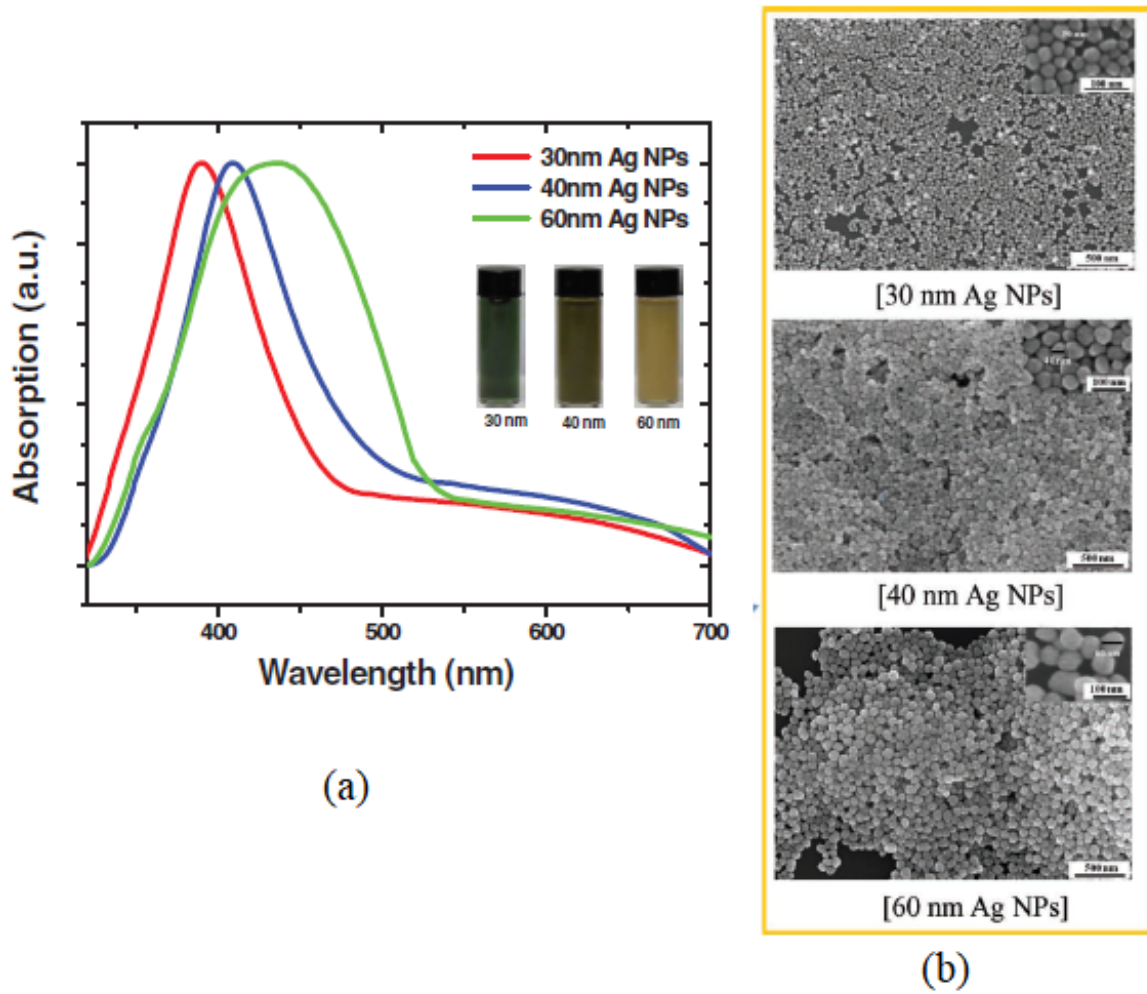


Figure 2.4: (a) shows tuning of Ag NPs LSPR by varying the NP size from 30 nm to 40 nm and 60 nm, (b) shows the SEM images of the Ag NPs synthesized via polyol process. (a) and (b) were obtained from [32].

increased from 0.075 M to 0.35 M. In addition, the NP size got smaller as the concentration increased from 0.075 M to 0.15 M causing the absorption peak to shift slightly to shorter wavelengths. For concentrations higher than 0.15 M of PVP, there was no more particle size reduction observed. This demonstrates the sensitivity of NP size and shape to the reaction temperature and time, reducing agent, and stabilizer. Therefore, manipulating the size and shape of the NPs during synthesis can help to tune their LSPR.

2.7 The effect of metal nano-particles in OPV

2.7.1 Nano-particles in the hole transport buffer layer

The incorporation of a small quantity of metal nano-particles in either the hole transport layer (HTL), the interface between the hole transport layer/photo-active layer or the photo-active layer is expected to enhance the photovoltaic performance in OPVs. It has been shown that the strong near-field due to LSPR around NPs such as gold (Au) NPs mainly distribute

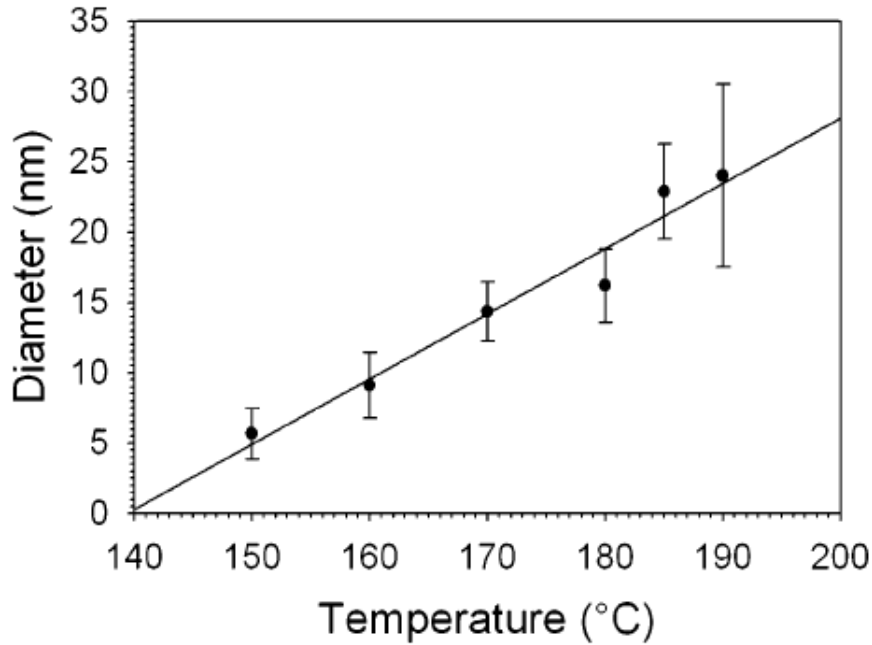


Figure 2.5: Nanoparticle size plotted against reaction temperature. Figure taken from Ref. [33].

laterally along the hole transport layer PEDOT:PSS rather than vertically into the adjacent layer, leading to minimal enhancement of light absorption in the active layer [11]. Furthermore, the LSPR around a NP decays exponentially with the increase in distance from the particle [40, 41]. This suggests that NPs incorporated into the HTL will be more beneficial for forward light scattering into the photo-active layer than enhancing light absorption via near-field. As smaller size NPs have larger absorption cross-section leading to LSPR and larger NPs have larger scattering cross-section leading, smaller size NPs are then better embedded in close proximity (interface) to or within the photo-active layer than in the HTL.

Hsiao et al. [42] embedded Au NPs with tunable LSPR peak positions of 520 nm, 530 nm, 540 nm, 660 nm, 780 nm and 850 nm into PEDOT:PSS buffer layer to enhance light trapping efficiency. The NPs included were nano-spheres of radii 15 nm, 35 nm and 55 nm, and nanorods of dimensions 54 nm by 20 nm, 46 nm by 13 nm and 49 nm by 12 nm. As the LSPR of a nano-particle strongly depends on its size and dimensions. The LSPR peaks red-shifted from 520 nm to 530 nm and 540 nm when the particle size was changed from 15 nm to 35 nm and 55 nm, respectively. The different aspect ratio nanorods possessed strong absorption bands along the long axis for the longitudinal modes at longer wavelengths of 650 nm, 780 nm and 850 nm as the aspect ratio changed from 2.7, 3.5 and 4.1, respectively [42]. Incorporation of the Au NPs ($d = 55$ nm) in PEDOT:PSS resulted to a highest increase of 8 % in the J_{sc} increasing from 9.28 mA cm^{-2} to 10.03 mA cm^{-2} and 17 % enhancement in the PCE increasing from 3.46 % to 4.07 % (see Table I). The nanorods also showed significant enhancement in the J_{sc} and PCE, which were increased to 10.71 mA cm^{-2} and 4.13 %, respectively.

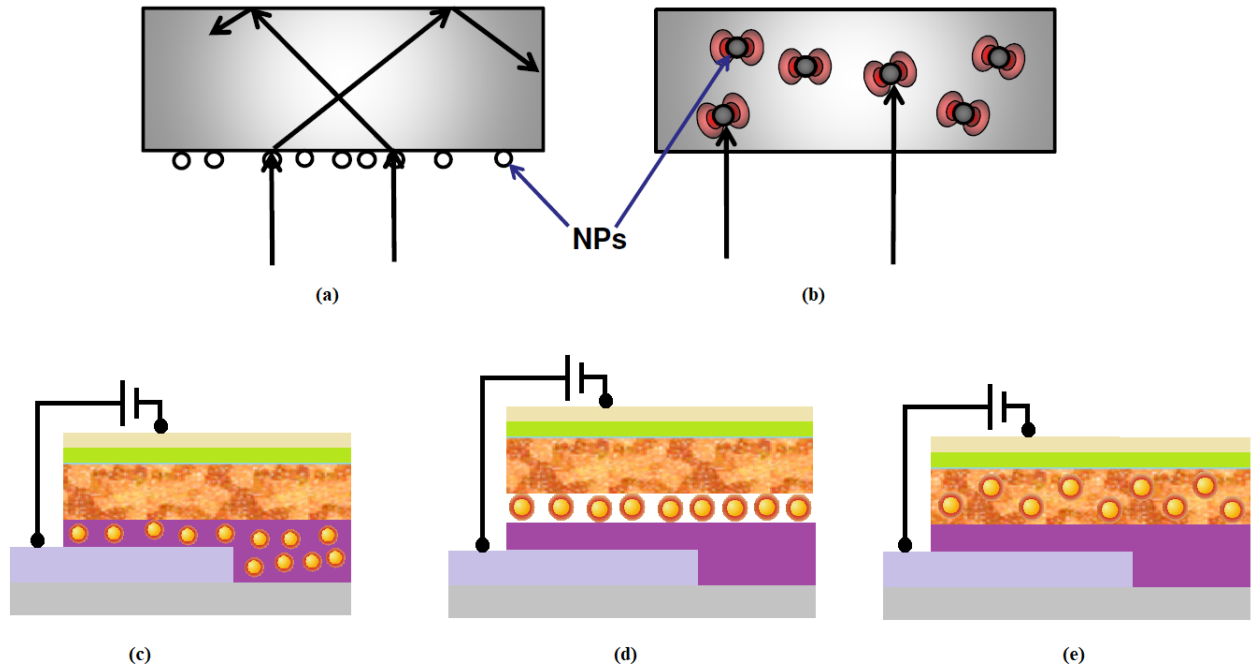


Figure 2.6: (a) shows far-field effect caused by MNPs placed on the surface of the photoactive layer, (b) near-field effect caused by MNPs embedded within the photoactive layer, (c) - (e) are schematics of photovoltaic cells with MNPs in the buffer layer, buffer/photoactive layer interface and in the photoactive layer, respectively. (a) and (b) were obtained from [16].

respectively, for nanorods with aspect ratio of 3.5. These enhancement could be attributed to light scattering effect with incident light scattered by the nano-particles into the photo-active layer thereby increasing the optical path length. The improvement could also be attributed to near-field enhancement, which could decrease the recombination level of geminate exciton and increase the probability of exciton dissociation in the photo-active layer [42–44] due to NPs close to the HTL/active layer interface. Li et al. [45] incorporated decahedral-shaped Au NPs in PEDOT:PSS of P3HT:PC₆₀BM and PBDT-TS1:PC₇₀BM based OPVs. The incorporation of these NPs resulted in a considerable improvement in the photon absorption which yielded a significant enhancement in the device PCEs for both P3HT and PBDT-TS1 based devices with 14 % and 28 % increases, respectively (see Table I). Reflectance spectra and absorption spectra measurements showed an improved absorption and reduced reflectivity of the devices as the Au NPs concentration in PEDOT:PSS was increased from 0 - 0.8 wt%. External quantum efficiency measurements showed good agreement with enhanced J_{sc} and covered a broadband wavelength range from 400 - 650 nm [45]. This verified the broadband plasmonic enhancement of the decahedral Au NPs and indicated that the J_{sc} enhancements in Au NPs doped devices originates from improved light absorption [45]. Electrical enhancement have also been reported for other NP shapes such as nanoprism and metals such as silver. Yao et al. [46] used Ag nanoprisms with average edge lengths of ca. 25 nm and ca. 40 nm exhibiting LSPR peaks at 450 nm and 535 nm, respectively. These were incorporated in PEDOT:PSS of polymerpoly(indacenodithieno[3,2-b]thiophene-

difluoro-benzothiadiazole) (PIDTT-DFBT) and PC₇₁BM based devices. Incorporation of Ag NPs prepared by thermal induction (TNP) in PEDOT:PSS at an optimised concentration of 1 wt% increased the average J_{sc} by 6.3 % and the PCE by 7.1 % (see Table I). When photo induction synthesized NPs (PNP) were used, the average J_{sc} was further increased to 13.72 mA cm⁻² and the PCE to 8.29 %. As would be expected, the V_{oc} and FF remained relatively unchanged. The authors noted that the PCE enhancement of 11 % for PNP is higher than those reported for devices incorporated with spherical Ag NPs [46, 47] or Au NPs [46, 48] with similar LSPR in PEDOT:PSS. The observed enhanced performances were attributed to increased carrier generation resulting from improved light harvesting [46].

BHJ Blend	NPs	Structure/location	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	Ref
P3HT:PC ₆₀ BM	Au Nanospheres	PEDOT:PSS:NPs	0.59(0.59)	10.03(9.28)	69(64)	4.07(3.46)	[42]
P3HT:PC ₆₀ BM	Au Nanorods	PEDOT:PSS:NPs	0.59(0.59)	10.71(9.28)	65(64)	4.13(3.46)	[42]
P3HT:PC ₆₀ BM	Au NRs+NPs	PEDOT:PSS:NPs:NPs	0.59(0.59)	11.49(9.28)	63(64)	4.28(3.46)	[42]
P3HT:PC ₆₀ BM	Au NPs (0.8 wt%)	PEDOT:PSS:NPs	0.58(0.58)	10.74(9.47)	66.1(65.3)	3.90(3.42)	[45]
PBDT-TS1:PC ₇₀ BM	Au NPs (0.8 wt%)	PEDOT:PSS:NPs	0.82(0.81)	18.72(14.72)	67.34(67.41)	9.99(7.81)	[45]
PIDTT-DFBT:PC ₇₁ BM	Ag (TNP) (1.0 wt%)	PEDOT:PSS:NPs	0.96(0.96)	13.5(12.70)	62(62)	8.35(7.66)	[46]
PIDTT-DFBT:PC ₇₁ BM	Ag (PNP) (1.0 wt%)	PEDOT:PSS:NPs	0.96(0.96)	13.72(12.70)	62(62)	8.50(7.66)	[46]
PCDTBT:PC ₇₀ BM	Au NPs (5 wt%)	Active layer	0.89	11.16	65(64)	6.45(5.77)	[49]
Si-PCDTBT:PC ₇₀ BM	Au NPs (5 wt%)	Active layer	0.57	13.13	64(63)	4.54(3.92)	[49]
P3HT:PC ₇₀ BM	Au NPs (5 wt%)	Active layer	0.63	11.18	61	4.36(3.54)	[49]
P3HT:PCBM	Au NPs (4 v/v)	Active layer	0.60(0.60)	8.90(8.27)	61.03(53.22)	3.26(2.64)	[50]
P3HT:PCBM	Au NPs (5 v/v)	Active layer	0.60(0.60)	9.77(8.29)	63.38(53.22)	3.71(2.64)	[50]
P3HT:PCBM	Au NPs (6 v/v)	Active layer	0.60(0.60)	9.60(8.27)	61.32(53.22)	3.53(2.64)	[50]
PCDTBT:PCBM	Ag NPs(0.4 wt%)	Active layer	0.74(0.67)	3.79(2.54)	44(38)	1.25(0.65)	[51]
PCDTBT:PCBM	Ag NPs (0.7 wt%)	Active layer	0.84(0.67)	4.64(2.54)	44(38)	1.72(0.65)	[51]
PCDTBT:PCBM ^a	Ag NPs (0.4 wt%)	Active layer	0.82(0.79)	0.96(0.71)	21(21)	0.18(0.12)	[51]
PCDTBT:PCBM ^a	Ag NPs (0.7 wt%)	Active layer	0.83(0.79)	0.31(0.71)	23(21)	0.24(0.12)	[51]
PCDTBT:PC ₇₀ BM	Ag NPs (20 vol %)	PEDOT:PSS:NPs	0.89(0.89)	12.41(11.22)	66(64)	7.29(6.39)	[18]
PCDTBT:PC ₇₀ BM	Au NPs (20 vol %)	PEDOT:PSS:NPs	0.87(0.87)	10.71(10.32)	63(58)	5.87(5.21)	[18]
PCDTBT:PC ₇₀ BM	Au@Ag NPs (20 vol %)	PEDOT:PSS:NPs	0.87(0.87)	11.10(10.32)	63(58)	6.08(5.21)	[18]
PTB7:PC ₇₀ BM	Au NPs (20 vol %)	PEDOT:PSS:NPs	0.73(0.74)	16.64(16.43)	67(64)	8.14(7.78)	[18]
PTB7:PC ₇₀ BM	Au@Ag NPs (20 vol %)	PEDOT:PSS:NPs	0.74(0.74)	17.38(16.43)	68(64)	8.74(8.14)	[18]
P3HT:PC ₆₁ BM	Cu-Au NPs (0.44 wt%)	PEDOT:PSS:NPs	0.64(0.64)	8.62(8.24)	60.4(61.1)	3.34(3.21)	[20]
P3HT:PC ₆₁ BM	Cu-Au NPs (0.88 wt%)	PEDOT:PSS:NPs	0.64(0.64)	10.91(8.24)	52.3(61.1)	3.63(3.21)	[20]
P3HT:PC ₆₁ BM	Cu-Au NPs (1.76 wt%)	PEDOT:PSS:NPs	0.64(0.64)	9.54(8.24)	55.9(61.1)	3.41(3.21)	[20]
PTB7:PC ₇₀ BM	Ag@SiO ₂	ITO/NPs/PEDOT:PSS	0.74(0.74)	16.10(14.64)	67(67)	8.20(7.51)	[54]
PTB7:PC ₇₀ BM	Ag@SiO ₂	PEDOT:PSS/NPs	0.74(0.74)	16.65(14.64)	67(67)	8.92(7.51)	[54]

Table 2.1: Performance parameters of different photoactive layers with different plasmonic NPs at different device locations reported in literature. The table shows a summary of literature results for devices with and without (values in brackets) plasmonic NPs.

2.7.2 The influence of metal nano-particles in the photoactive Layer

To enhance the efficiency of OPVs, researchers have incorporated metallic nanoparticles in the photoactive layer to yield an improved optical absorption and photocurrent generation over a broad range of visible wavelengths [55]. However, this is done albeit the concern of the photoactive layer sensitivity, exciton quenching and non-radiative recombination as a result of bare metallic NPs in close proximity to the active layer. Yang et al. [49] reported several positive effects when truncated octahedral Au NPs (ca. 70 nm) were embedded in photoactive layers of P3HT:PC₇₀BM, poly[N-9'-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)](PCDTBT):PC₇₀BM and poly[4,4'-bis(2-ethylhexyl)dithieno(3,2-b:2',3'-d)silole]-2,6-diyl-alt-[4,7-bis(2-thienyl)-2,1,3-benzothiadiazole]-5,5'-diyl (Si-PCPDTBT):PC₇₀BM blend based BHJs at 5 wt%. Incorporation of the Au NPs enhanced the fill-factors by 1 % for PCDTBT:PC₇₀BM and for Si-PCPDTBT:PC₇₀BM blend based BHJs devices. These enhancements were attributed to significantly reduced series resistances [49] which were reduced by 20 % and 36 % for PCDTBT:PC₇₀BM and Si-PCPDTBT:PC₇₀BM, respectively. The NP embedded BHJs devices showed enhanced PCEs increasing by 23 %, 12 % and 16 % for P3HT, PCDTBT and Si-PCPDTBT active layers (see Table I), respectively. These improvements were attributed to increased J_{sc} , FF and induced photocurrent-efficiency IPCE due to enhanced light absorption caused by light scattering [49]. There was no plasmon-induced light concentration [49] and this may be due to the large size of the Au NPs with high scattering cross-section and minimal absorption cross-section which could have led to LSPR enhancements. Spyropoulos et al. [50] also obtained significantly enhanced device performance when surfactant-free Au NPs were incorporated into P3HT:PCBM photoactive layer blend. The J_{sc} of the devices was increased by 18 % and FF increased by 19 %, yielding a 40.5 % increase in the PCE (see Table I) at 5 % Au NPs volume ration. UV-vis absorption spectra in the region 450 - 650 nm showed an increase in absorption proportional to the Au NPs concentration (3 - 6 % v/v) in the photo-active layer with a maximum peak at 610 nm, which fairly coincides with Au NP extinction peak [50]. The Au NPs also yielded an enhanced and broadened photoluminescence intensity, which can be attributed to the fact that the LSPR increases the degree of light collection and, thereby enhanced light excitation rate [50]. In overall, the enhanced device performances can be attributed to enhanced near-field around small diameter NPs and light scattering from large diameter NPs increasing optical path length in the photoactive layer. Parlak et al. [51] incorporated Ag NPs of average size 6 nm in PCDTBT:PCBM blend based devices with conventional and inverted structures. Devices with the conventional structure showed a highest improvement of 165 % and 83 % on the PCE and J_{sc} (see Table I), respectively. Similarly, the inverted structure devices showed improvements with the PCE and J_{sc} increasing by 100 % and 85 %, respectively. UV-vis absorption spectra of the PCDTBT:PCBM devices with/without Ag NPs showed increased intensity as the NP

concentration increased from 0 % to 0.4 % and 0.7 %. This absorption enhancement can be attributed to light scattering (increasing optical path length) and near-field enhancement due to the small size Ag NPs LSPR. The root mean square roughness (morphology) of the blend films was slightly increased from 13 nm to 15 nm and could also increase light absorption by means of photo-trapping effect [51].

2.7.3 Metal nano-particles at the interface between charge transport buffer layer/Photoactive Layer

Plasmonic NPs have also been incorporated into OPVs at the interface between the buffer layer and photoactive layer. At this location, the NPs can scatter incident light into the photoactive layer thus increasing the optical path length. Secondly, the plasmonic NPs in contact with the photoactive layer can improve photocurrent due to LSPR enhanced near-field. Yoon et al. [55] reported a 16 % enhancement of optical absorption in P3HT:PCBM blend based OPVs devices due to an increased electric field by excited LSPR around Ag NPs sandwiched between PEDOT:PSS and the P3HT:PCBM photoactive layer. They observed a 12.9 % enhancement in the IPCE from 45.7 % at 480 nm (reference device) to 51.6 % at 500 nm (with Ag NPs). However, the Ag NPs in contact with the photoactive layer resulted in highly elevated reverse saturation suggesting surface recombination on the Ag NPs, leading to a higher leakage current density for $V < 0.5$ V [55]. Furthermore, the FF and V_{oc} of the Ag NPs incorporated devices decreased from 64 % to 35 % and 0.56 V to 0.42 V, respectively. This was attributed to the increased series resistance ($13.3 \Omega \text{ cm}^2$ to $48.1 \Omega \text{ cm}^2$) and lowered shunt resistance for the FF, and higher surface recombination for V_{oc} [55].

2.8 Bimetallic/core-shell nanoparticles

The most studied metallic NPs have been mono atomic Au and Ag NPs because of their outstanding LSPR effects and light scattering properties [56]. However, mono-metallic NPs may possess high scattering cross section with low absorption cross section or vice-versa, thus limiting their effectiveness over the UV-vis spectral range. For instance, Au NPs possess long-range plasmonic effect but low light scattering while Ag NPs exhibit high light scattering effect with short range LSPR effect [18, 56]. To improve on this drawback, researchers have studied bimetallic nano-composites involving metals such as Au, Ag, Zn and Cu [57]. These bimetallic NPs can offer superior magnetic, catalytic and optical properties over a broadened spectral range compared to their mono-metallic constituencies [57]. Baek et al. [18] observed a stronger scattering efficiency when core-shell nanocubes of Au@Ag were embedded into the anodic buffer layer PEDOT:PSS. This was due to a thin Ag shell layer on the Au NPs acting as scattering enhancer, thus solving the above-mentioned drawback. The overall performance of PCDTBT:PC₇₀BM based devices saw an increase of 16.7 % in the PCE and 7.6 % in J_{sc} (see Table I). PTB7:PC₇₀BM devices also showed a 12.3 % and 5.8 % increase in the PCE and

J_{sc} , respectively. This performance supersedes those of mono-metallic Au [49] or Ag [18] NPs. Near-field scanning microscopy measurements proved that light scattering was enhanced further by the improved forward light scattering effects of core-shell Au@Ag NCs compared to Au NPs [18]. Furthermore, Raman spectroscopy measurements were used to verify that photons scattered by the NCs improved light absorption in the photoactive material [18]. Bimetallic NPs can be synthesized to coat a more unstable metal such as Cu with a more stable metal such as Au or Ag. Tang et al. [20] synthesized oxidation resistant Cu-Au with a copper-rich core and Cu-Au bimetallic nanoshell. UV-vis spectroscopy measurements showed that the Cu-Au bimetallic NPs LSPR broadened and red-shifted to long wavelengths of 650 -700 nm compared to those of mono-metallic Cu NPs at 590 nm and Au NPs at 530 nm [20]. UV-vis spectra of PEDOT:PSS/NPs/P3HT:PC₆₁BM films showed a significantly enhanced absorption in a wide range (300 - 650 nm) beyond the plasmonic band of Cu-Au NPs suggesting that light scattering also played a role in the improvement of light harvesting [20]. As a result, the incorporation of Cu-Au NPs into the devices significantly enhanced the PCE by 13.4 %, 9.5 % and 12.6 % for P3HT:PCBM, PTB7:PC₆₁BM and PTB7:PC₇₁BM, respectively (see Table I). However, for all the OPV devices with Cu-Au NPs, the FF values were reduced in response to the increased PCE while V_{oc} remained relatively unchanged. The increased PCE values could be attributed to the increased J_{sc} of all the devices with Cu-Au NPs [20]. Though there has been reports of successful improvement on device performance by the incorporation of MNPs in OPVs, there are still concerns about exciton quenching by non-radiative energy transfer on the surface of bare MNPs. To overcome such drawback, researchers have investigated the effect of coating MNPs with a thin layer of insulators such as silica (SiO₂) [54, 58]. This silica shell does not only enhance the colloidal and chemical stability, it also controls the the minimum distance between core particles through shell thickness [59, 60]. This occurs while the LSPR of the core MNPs is preserved. This insulator coating may also prevent shorting between the active layer and the electrodes. Choi et al. [54] prepared Ag NPs ($\approx$ 50 nm) coated with a thin ($\approx$ 10 nm) insulating layer of SiO₂ and incorporated them in PTB7:PC₇₀BM blend based OPVs. UV-vis spectroscopy measurements of the Ag@SiO₂ NPs showed a red-shifted SPR at 450 nm when compared to that of bare Ag NPs of similar size [54]. This red-shift could be due to the change in the refractive index surrounding the NPs. Incorporation of the NPs between indium tin oxide (ITO) and PEDOT:PSS films (Type I), and between PEDOT:PSS and PTB7:PC₇₀BM films (Type II) resulted to a $\approx$ 10 % and $\approx$ 14 % increase of the J_{sc} for Type I and Type II OPV structures (see Table I), respectively. This resulted to a significant increase in the PCE by $\approx$ 10 % and $\approx$ 17 % for Type I and Type II OPV structures (see Table I), respectively. These improvements could be attributed to originate from the enhanced light absorption due to the light scattering and LSPR of the NPs. Both device types exhibited enhanced light absorption in the range 400 - 700 nm with a noticeable LSPR peak at 450 nm when compared to reference devices [54]. Type II devices possessed a strong light absorption and scattering via enhanced electric field compared to Type I devices [54].

As a result, Type II devices achieved the highest PCE due to a stronger coupling effect due to the close proximity of the NPs to the photoactive layer [54].

2.9 Conclusion

The local surface plasmon resonance of metal NPs has become a very useful mechanism to enhance light absorption in solar cells. The LSPR effect is dependent on size and shape of NPs and the refractive index of the environment surrounding the NPs. This review work have discussed on how size and shape of NPs can be controlled by changing the NP synthesis process conditions, reagents and reagents concentration. The optical properties and photocurrent generation of solar cells is enhanced via plasmon induced energy transfer. The metal NPs scatter incident light that increases optical path length and successfully trap light in the absorber medium. This way more light absorption can then be absorbed in the photoactive layer.

This review discussed the basic principle of LSPR energy transfer processes, light scattering and related optical parameters such as absorption cross section. Several plasmonic NPs have played important role in improving solar cell performances. The full understanding of the field still need additional effort on how mono-and bi-metallic nano-particles behave in the polymer medium in terms of balance light scattering; absorption; quenching etc.

Bibliography

References

- [1] J. Liu, H. He, D. Xiao, S. Yin, W. Ji, S. Jiang, D. Luo, B. Wang and Y. Liu, 2018. Recent advances of plasmonic nanoparticles and their applications. *Materials*, 11(10), p.1833.
- [2] C. Clavero, 2014. Plasmon-induced hot-electron generation at nanoparticle/metal-oxide interfaces for photovoltaic and photocatalytic devices. *Nature Photonics*, 8(2), pp.95-103.
- [3] K. M. Mayer and J. H. Hafner, 2011. Localized surface plasmon resonance sensors. *Chemical reviews*, 111(6), pp.3828-3857.
- [4] L. Feng, M. Niu, Z. Wen and X. Hao, 2018. Recent advances of plasmonic organic solar cells: Photophysical investigations. *Polymers*, 10(2), p.123.
- [5] P. Mandal and S. Sharma, 2016. Progress in plasmonic solar cell efficiency improvement: A status review. *Renewable and sustainable energy reviews*, 65, pp.537-552.
- [6] M. A. Alkhalayfeh, A. A. Aziz and M. Z. Pakhuruddin, 2021. An overview of enhanced polymer solar cells with embedded plasmonic nanoparticles. *Renewable and Sustainable Energy Reviews*, 141, p.110726.
- [7] X. C. Ma, Y. Dai, L. Yu and B. B. Huang, 2016. Energy transfer in plasmonic photocatalytic composites. *Light: Science & Applications*, 5(2), pp.e16017-e16017.
- [8] S. Linic, P. Christopher and D. B. Ingram, 2011. Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy. *Nature materials*, 10(12), pp.911-921.
- [9] J. Li, S. K. Cushing, F. Meng, T. R. Senty, A. D. Bristow and N. Wu, 2015. Plasmon-induced resonance energy transfer for solar energy conversion. *Nature Photonics*, 9(9), pp.601-607.
- [10] N. Kholmicheva, L. R. Romero, J. Cassidy and M. Zamkov, 2018. Prospects and applications of plasmon-exciton interactions in the near-field regime. *Nanophotonics*, 8(4), pp.613-628.

- [11] S. K. Cushing, J. Li, F. Meng, T. R. Senty, S. Suri, M. Zhi, M. Li, A. D. Bristow and N. Wu, 2012. Photocatalytic activity enhanced by plasmonic resonant energy transfer from metal to semiconductor. *Journal of the American Chemical Society*, 134(36), pp.15033-15041.
- [12] J. G. Smith, J. A. Fauchaux and P. K. Jain., 2015. Plasmon resonances for solar energy harvesting: a mechanistic outlook. *Nano Today*, 10(1), pp.67-80.
- [13] Q. Zhang, D. Myers, J. Lan, S. A. Jenekhe and G. Cao, 2012. Applications of light scattering in dye-sensitized solar cells. *Physical Chemistry Chemical Physics*, 14(43), pp.14982-14998.
- [14] Q. Fu and W. Sun, 2001. Mie theory for light scattering by a spherical particle in an absorbing medium. *Applied Optics*, 40(9), pp.1354-1361.
- [15] I. W. Sudiarta and P. Chylek, 2001. Mie-scattering formalism for spherical particles embedded in an absorbing medium. *JOSA A*, 18(6), pp.1275-1278.
- [16] J. Y. Lee and P. Peumans, 2010. The origin of enhanced optical absorption in solar cells with metal nanoparticles embedded in the active layer. *Optics Express*, 18(10), pp.10078-10087.
- [17] H. Moosmüller and W. P. Arnott, 2009. Particle optics in the Rayleigh regime. *Journal of the Air & Waste Management Association*, 59(9), pp.1028-1031.
- [18] C. F. Bohren and D. R. Huffman, 2008. Absorption and scattering of light by small particles. John Wiley & Sons.
- [19] A. Paris, A. Vaccari, A.C. Lesina, E. Serra and L. Calliari, 2012. Plasmonic scattering by metal nanoparticles for solar cells. *plasmonics*, 7(3), pp.525-534.
- [20] P. W. Blom, V. D. Mihailetschi, L. J. A. Koster and D. E. Markov, 2007. Device physics of polymer: fullerene bulk heterojunction solar cells. *Advanced Materials*, 19(12), pp.1551-1566.
- [21] N. Yeh and P. Yeh, 2013. Organic solar cells: Their developments and potentials. *Renewable and Sustainable Energy Reviews*, 21, pp.421-431.
- [22] G. T. Mola, W. E. Dlamini and S. O. Oseni., 2016. Improving optical absorption bandwidth using bi-layer bulk heterojunction organic photoactive medium. *Journal of Materials Science: Materials in Electronics*, 27(11), pp.11628-11633.
- [23] N. K. Elumalai and A. Uddin, 2016. Open circuit voltage of organic solar cells: an in-depth review. *Energy & Environmental Science*, 9(2), pp.391-410.

- [24] J. Li, X. Zhang, C. Liu, Z. Li, Y. He, Z. Zhang, L. Shen, W. Guo and S. Ruan, 2017. The role of polymer dots on efficiency enhancement of organic solar cells: Improving charge transport property. *Optics Communications*, 395, pp.127-132.
- [25] D. Bartesaghi, I. del Carmen Pérez, J. Kniepert, S. Roland, M. Turbiez, D. Neher and L. J. A. Koster, 2015. Competition between recombination and extraction of free charges determines the fill factor of organic solar cells. *Nature communications*, 6(1), pp.1-10.
- [26] A. Luque and S. Hegedus, 2003. *Photovoltaic science and engineering*. Chichester: John Wiley & Sons Ltd, pp.92-99.
- [27] D. Gupta, S. Mukhopadhyay and K. S. Narayan, 2010. Fill factor in organic solar cells. *Solar Energy Materials and solar cells*, 94(8), pp.1309-1313.
- [28] X. Guo, N. Zhou, S. J. Lou, J. Smith, D. B. Tice, J. W. Hennek, R. P. Ortiz, J. T. L. Navarrete, S. Li, J. Strzalka and L. X. Chen, 2013. Polymer solar cells with enhanced fill factors. *Nature Photonics*, 7(10), pp.825-833.
- [29] J. C. Blakesley, F. A. Castro, W. Kylberg, G. F. Dibb, C. Arantes, R. Valaski, M. Cremona, J. S. Kim and J. S. Kim, 2014. Towards reliable charge-mobility benchmark measurements for organic semiconductors. *Organic Electronics*, 15(6), pp.1263-1272.
- [30] V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey and J. L. Brédas, 2007. Charge transport in organic semiconductors. *Chemical reviews*, 107(4), pp.926-952.
- [31] J. A. Röhr, D. Moia, S. A. Haque, T. Kirchartz and J. Nelson, 2018. Exploring the validity and limitations of the Mott–Gurney law for charge-carrier mobility determination of semiconducting thin-films. *Journal of Physics: Condensed Matter*, 30(10), p.105901.
- [32] D. H. Wang, K. H. Park, J. H. Seo, J. Seifter, J. H. Jeon, J. K. Kim, J. H. Park, O. O. Park and A. J. Heeger, 2011. Enhanced power conversion efficiency in PCDTBT/PC70BM bulk heterojunction photovoltaic devices with embedded silver nanoparticle clusters. *Advanced Energy Materials*, 1(5), pp.766-770.
- [33] D. Mott, J. Galkowski, L. Wang, J. Luo and C. J. Zhong, 2007. Synthesis of size-controlled and shaped copper nanoparticles. *Langmuir*, 23(10), pp.5740-5745.
- [34] G. Guo, W. Gan, J. Luo, F. Xiang, J. Zhang, H. Zhou and H. Liu, 2010. Preparation and dispersive mechanism of highly dispersive ultrafine silver powder. *Applied Surface Science*, 256(22), pp.6683-6687.
- [35] Z. Zhang, B. Zhao and L. Hu, 1996. PVP protective mechanism of ultrafine silver powder synthesized by chemical reduction processes. *Journal of Solid State Chemistry*, 121(1), pp.105-110.

- [36] D. Wang, C. Song, Z. Hu and X. Zhou, 2005. Synthesis of silver nanoparticles with flake-like shapes. *Materials Letters*, 59(14-15), pp.1760-1763.
- [37] A. Mirzaei, K. Janghorban, B. Hashemi, M. Bonyani, S. G. Leonardi and G. Neri, 2017. Characterization and optical studies of PVP-capped silver nanoparticles. *Journal of Nanostructure in Chemistry*, 7(1), pp.37-46.
- [38] D. Chen, X. Qiao, X. Qiu and J. Chen, 2009. Synthesis and electrical properties of uniform silver nanoparticles for electronic applications. *Journal of materials science*, 44(4), pp.1076-1081.
- [39] D. D. Fung, L. Qiao, W. C. Choy, C. Wang, E. I. Wei, F. Xie and S. He, 2011. Optical and electrical properties of efficiency enhanced polymer solar cells with Au nanoparticles in a PEDOT–PSS layer. *Journal of Materials Chemistry*, 21(41), pp.16349-16356.
- [40] M. Salvador, B. A. MacLeod, A. Hess, A. P. Kulkarni, K. Munechika, J. I. Chen and D. S. Ginger, 2012. Electron accumulation on metal nanoparticles in plasmon-enhanced organic solar cells. *ACS nano*, 6(11), pp.10024-10032.
- [41] K. Jung, H. J. Song, G. Lee, Y. Ko, K. Ahn, H. Choi, J. Y. Kim, K. Ha, J. Song J. K. Lee and C. Lee, 2014. Plasmonic organic solar cells employing nanobump assembly via aerosol-derived nanoparticles. *ACS nano*, 8(3), pp.2590-2601.
- [42] Y. S. Hsiao, S. Charan, F. Y. Wu, F. C. Chien, C. W. Chu, P. Chen and F. C. Chen, 2012. Improving the light trapping efficiency of plasmonic polymer solar cells through photon management. *The Journal of Physical Chemistry C*, 116(39), pp.20731-20737.
- [43] F. C. Chen, J. L. Wu, C. L. Lee, Y. Hong, C. H. Kuo and M. H. Huang, 2009. Plasmonic-enhanced polymer photovoltaic devices incorporating solution-processable metal nanoparticles. *Applied Physics Letters*, 95(1), p.182.
- [44] J. L. Wu, F. C. Chen, Y. S. Hsiao, F. C. Chien, P. Chen, C. H. Kuo, M. H. Huang and C. S. Hsu, 2011. Surface plasmonic effects of metallic nanoparticles on the performance of polymer bulk heterojunction solar cells. *ACS nano*, 5(2), pp.959-967.
- [45] Q. Li, F. Wang, Y. Bai, L. Xu, Y. Yang, L. Yan, S. Hu, B. Zhang, S. Dai and Z. A. Tan, 2017. Decahedral-shaped Au nanoparticles as plasmonic centers for high performance polymer solar cells. *Organic Electronics*, 43, pp.33-40.
- [46] K. Yao, M. Salvador, C. C. Chueh, X. K. Xin, Y. X. Xu, D. W. Dequillettes, T. Hu, Y. Chen, D. S. Ginger and A. K. Y. Jen, 2014. A general route to enhance polymer solar cell performance using plasmonic nanoprisms. *Advanced Energy Materials*, 4(9), p.1400206.

- [47] S. W. Baek, J. H. Kim, J. Kang, H. Lee, J. Y. Park and J. Y. Lee, 2015. Enhancing the internal quantum efficiency and stability of organic solar cells via metallic nanofunnels. *Advanced Energy Materials*, 5(24), p.1501393.
- [48] L. Lu, Z. Luo, T. Xu and L. Yu, 2013. Cooperative plasmonic effect of Ag and Au nanoparticles on enhancing performance of polymer solar cells. *Nano letters*, 13(1), pp.59-64.
- [49] D. H. Wang, D. Y. Kim, K. W. Choi, J. H. Seo, S. H. Im, J. H. Park O. O. Park and A. J. Heeger, 2011. Enhancement of donor-acceptor polymer bulk heterojunction solar cell power conversion efficiencies by addition of Au nanoparticles. *Angewandte Chemie*, 123(24), pp.5633-5637.
- [50] G. D. Spyropoulos, M. M. Stylianakis, E. Stratakis and E. Kymakis, 2012. Organic bulk heterojunction photovoltaic devices with surfactant-free Au nanoparticles embedded in the active layer. *Applied Physics Letters*, 100(21), p.213904.
- [51] E.A. Parlak, T. A. Tumay, N. Tore, Ş. Sarioğlu, P. Kavak and F. Türksoy, 2013. Efficiency improvement of PCDTBT solar cells with silver nanoparticles. *Solar energy materials and solar cells*, 110, pp.58-62.
- [52] S. W. Baek, G. Park, J. Noh, C. Cho, C. H. Lee, M. K. Seo, H. Song and J Y Lee, 2014. Au@ Ag core-shell nanocubes for efficient plasmonic light scattering effect in low bandgap organic solar cells. *Acs Nano*, 8(4), pp.3302-3312.
- [53] M. Tang, B. Sun, D. Zhou, Z. Gu, K. Chen, J. Guo, L. Feng and Y. Zhou, 2016. Broad-band plasmonic Cu-Au bimetallic nanoparticles for organic bulk heterojunction solar cells. *Organic Electronics*, 38, pp.213-221.
- [54] H. Choi, J. P. Lee, S. J. Ko, J. W. Jung, H. Park, S. Yoo, O. Park, J. R. Jeong, S. Park and J. Y. Kim, 2013. Multipositional silica-coated silver nanoparticles for high-performance polymer solar cells. *Nano letters*, 13(5), pp.2204-2208.
- [55] W. J. Yoon, K. Y. Jung, J. Liu, T. Duraisamy, R. Revur, F. L. Teixeira, S. Sengupta and P. R. Berger, 2010. Plasmon-enhanced optical absorption and photocurrent in organic bulk heterojunction photovoltaic devices using self-assembled layer of silver nanoparticles. *Solar Energy Materials and Solar Cells*, 94(2), pp.128-132.
- [56] S. O. Oseni and G. T. Mola, 2019. Bimetallic nanocomposites and the performance of inverted organic solar cell. *Composites Part B: Engineering*, 172, pp.660-665.
- [57] G. T. Mola and E. A. Arbab, 2017. Bimetallic nanocomposite as hole transport co-buffer layer in organic solar cell. *Applied Physics A*, 123(12), p.772.

-
- [58] B. Chen, W. Zhang, X. Zhou, X. Huang, X. Zhao, H. Wang, M. Liu, Y. Lu and S. Yang, 2013. Surface plasmon enhancement of polymer solar cells by penetrating Au/SiO₂ core/shell nanoparticles into all organic layers. *Nano Energy*, 2(5), pp.906-915.
- [59] J. C. Flores, V. Torres, M. Popa, D. Crespo and J. M. Calderón-Moreno, 2008. Preparation of core-shell nanospheres of silica-silver: SiO₂@ Ag. *Journal of Non-Crystalline Solids*, 354(52-54), pp.5435-5439.
- [60] L. M. Liz-Marzán and P. Mulvaney, 2003. The assembly of coated nanocrystals. *The Journal of Physical Chemistry B*, 107(30), pp.7312-7326.

Chapter 3

Materials and Methods

3.1 Synthesis of Ag@Cu Nanoparticles

The Ag@Cu NPs were synthesized using solution chemistry. These NPs were obtained by converting Ag@Cu₂O core-shell metal-semiconductor using ascorbic acid as the reducing agent and polyvinylpyrrolidone (PVP) as the stabilising agent. The Ag@Cu₂O core-shell was obtained by mixing a colloidal solution of Ag with a solution containing Cu²⁺ and PVP. The Cu₂O shell was further reduced to Cu with excess amounts of ascorbic acid.

The synthesis started by dissolving ascorbic acid in 80 mL of deionized water to form an ascorbic acid solution of 0.5 mM concentration. To this solution, 0.8 g PVP capping agent was added and stirred homogeneously until all the PVP dissolved. Then 1.4 mL of NaOH (0.1 M) was added to the above solution and stirred for 5 min. Then, 0.8 mL AgNO₃ (0.1 M) in deionized water was added into the above mixture with stirring for 15 min under dark conditions and on a hot plate at 30 °C. The solution was then aged at 80 °C for 30 min to produce silver colloid. A second 50 mL solution consisting of PVP (192 mg), Cu(NO₃)₂ · 3H₂O (45.8 mg) and NH₄NO₃ was prepared. Subsequently, 70 mL of the silver colloid solution was added to the second copper containing solution. A NaOH (3.2 mL) solution of 0.2 M concentration was added drop wise to the above solution and stirred for 5 min under room temperature. Ag@Cu₂O core-shell metal-semiconductor NPs thus formed. To further reduce the Cu₂O shell to Cu, 5.6 mL of ascorbic acid (0.1 M) was added drop wise and the solution was stirred for 5 min. The Ag@Cu core-shell NPs were then recovered by centrifuging at 5 000 rpm for 30 min and then washed with deionized water and ethanol. This procedure was obtained from [2]. This procedure was preferred because it uses environmentally friendly ascorbic acid as opposed to the toxic NaBH₄ reducing agent. Ascorbic acid can reduce both Ag⁺ and Cu²⁺ to Ag⁰ and Cu⁰, respectively. The reaction of Ag⁺ with ascorbic acid is as follows



This reaction produces Ag NPs in the range 20 - 100 nm [3] and 36 - 82 nm when PVP is

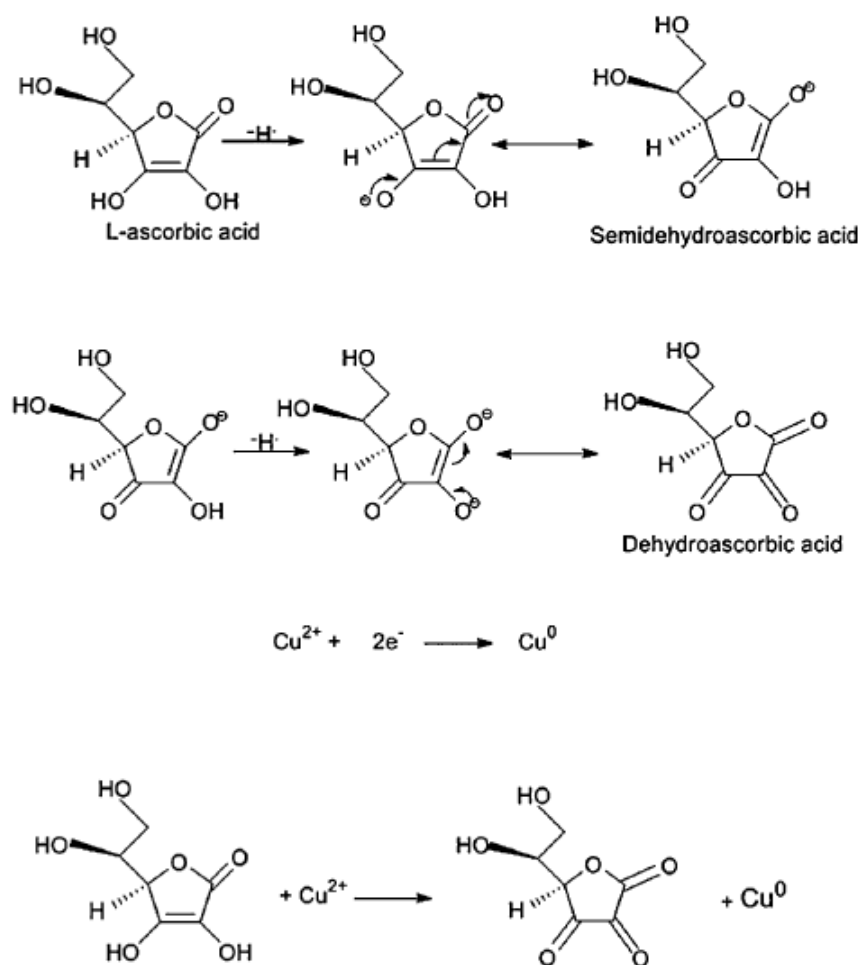
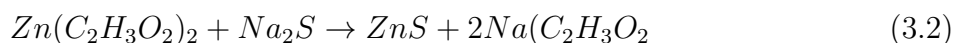


Figure 3.1: Schematic representation of the reduction reaction equation for the formation of Cu nanoparticles [1].

used as a capping agent [4]. Synthesis of the Cu NPs is a bit challenging due to its oxidative tendency. As mentioned above, the Cu precursor is first reduced to Cu_2O and even $\text{Cu}(\text{OH})_2$ or CuO at low reducing agent concentration. Only when excess ascorbic acid was added were Cu_2 reduced to Cu NPs. In the presence of capping agent, these Cu NPs can be much finer ranging between 2 - 20 nm [5].

3.2 Synthesis of Zinc Sulphide Nanoparticles

Zinc sulphide (ZnS) is a very attractive candidate for use in novel photonic crystal devices operating in the region from visible to near-infra red [6]. ZnS synthesized at low temperature ($< 1296 \text{ K}$) by colloidal chemistry has been found to possess the cubic zinc blende structure which is a stable phase at low temperature [6]. In this study, ZnS NPs were synthesized via colloidal chemistry at room temperature. A 0.5 M zinc acetate solution was prepared by dissolving the required amount of zinc acetate in 50 mL of deionized water. A second solution of 0.5 M sodium sulphide (100 mL) with 3 g PVP was prepared separately. The two solutions were then mixed together drop wise with vigorous stirring at room temperature. The ZnS NPs then formed and were recovered by filtering. The NPs were then with deionized water and twice with absolute ethanol to remove unreacted sodium. The NPs were then dried in oven at 100°C for 3 hours. The reaction follows this equation



3.3 Synthesis of $\text{ZnO}:\text{Ag}$ Nanoparticles

Zinc oxide is a wide-direct band gap (3.37 eV) semiconductor with a large free exciton binding energy (60 meV) [29, 35] It has attained great attention for its potential use in several fields such as gas sensors, field emitters and solar cells [29]. Various processes to synthesize ZnO NPs have been studied, these include thermal decomposition, electrodeposition, ultrasonic, microwave-assisted techniques, chemical vapour deposition, hydrothermal and precipitation methods [9]. In this present study, the ZnO used were purchased from Sigma Aldrich, Co. The ZnO nanopowder used was made up of $< 50 \text{ nm}$ ZnO NPs with 6 % aluminium doping. The $\text{ZnO}:\text{Ag}$ NPs were synthesized by dispersing 1.25 g of ZnO NPs in 20 mL aqueous solution of 0.25 M AgNO_3 under stirring at $50 - 60^\circ\text{C}$ under dark dark. The resulting solution was stirred for 25 min. The resulting precipitate was recovered by decanting out the excess AgNO_3 followed by washing with hot distilled water several times and then dried at $300 - 350^\circ$ for 3 hours. Coating ZnO NPs with noble metals such as Ag could significantly enhance its photocatalytic properties [29]. The metallic silver shell can enhance the photocatalytic properties of ZnO NPs by creating a local electric field and enhance electrical properties by the optical vibration of surface plasmon [29].

3.4 Synthesis of ZnS:Mn Nanoparticles

Zinc sulphide doped with transition metals such as manganese is known to have efficient light emitting properties [10]. These properties can be observed even at room temperature [10]. At low metal concentration, $\leq 10\%$, the ZnS:Metal exhibits a zinc blende structure. The lattice parameter, crystalline structure, and optical band gap of ZnS:Metal can be varied by varying the mole fraction of Zn [10]. In this study, ZnS:Mn NPs were synthesized following the procedure as explained in [11] with some modifications. In this study, 2.5 g of sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) was dissolved in 12.5 mL deionized water and stirred for 1 hour at room temperature. On separate beakers, 2 g of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 0.5 g of manganous chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) were each dissolved in 12.5 mL deionized water and stirred. The zinc nitrate and manganous chloride solutions were then mixed together and then poured into the sodium sulphide solution and stirred for 4 hours at room temperature. The resulting precipitate was centrifuged and separated from the solution. It was then washed with methanol repeatedly to remove impurities. The precipitate was then dried overnight at 150°C in a convection oven.

3.5 Device Fabrication

The OPV devices were fabricated on unpatterned ITO coated glass substrates. The glass substrates ($2\text{ cm} \times 2\text{ cm}$) were first etched with an acid solution ($\text{HCL}:\text{H}_2\text{O}:\text{HNO}_3$ at 48%:48%:4%) to remove half part of the ITO. Half part of a glass substrate was covered with a insulation tape and the uncovered part was then immersed in the acid solution to remove ITO. After etching, the substrates were successively cleaned in an ultrasonic water bath with detergent, distilled water, acetone and isopropanol, respectively, for 10 min holding time. The substrates were then dried in an oven at 120°C for 30 min.

A thin layer of PEDOT:PSS was then spin coated onto the substrates at 3 500 rpm using a spin coating machine (see Fig. 3.3). For some devices, see Chapter 6, the PEDOT:PSS was incorporated with ZnO:Ag and also doped with DMSO. The PEDOT:PSS was then dried in oven for 30 min at $100 - 120^\circ$. Several polymer:fullerene blends with a 1:1 ratio were prepared. The blends were based on P3HT and PCBM with no NPs (pristine blend, Chapter 6) or incorporated with Ag@Cu NPs (Chapter 4), ZnSNPs (Chapter 5) or ZnS:MnNPs (Chapter 7). The P3HT:PCBM blend solutions were sonicated for 3 hours at 40°C to ensure good NP dispersion and good polymer:fullerene miscibility. The P3HT:PCBM blend solutions were spin coated on top of the dried PEDOT:PSS layer at 1 300 rpm.

The samples were dried again in oven under nitrogen atmosphere for 10 min before being transferred into a vacuum deposition chamber for the deposition of lithium fluoride (LiF) and aluminium (Al) electrode. Thin layers of LiF (0.5 nm) and Al (80 nm) were deposited on the samples at a base pressure of 10^{-6} mBar. Edwards Auto 306 vacuum thermal deposition chamber was used for deposition of LiF and Al. A deposition mask was used to make six

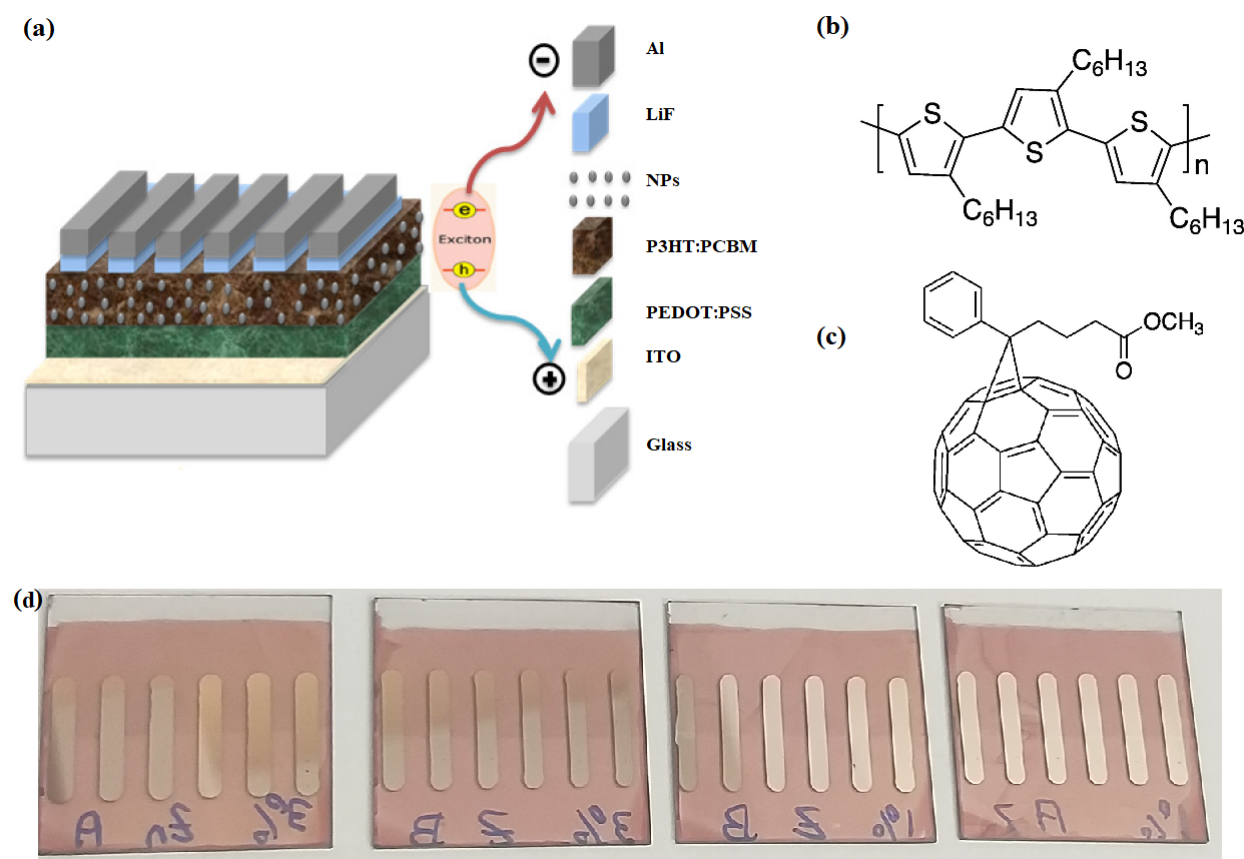


Figure 3.2: Schematic representation of the (a) device structure, (b) P3HT polymer, (c) PCBM fullerene and (d) the fabricated organic solar cells.



(a)



(b)

Figure 3.3: (a) shows the spin coating machine used to deposit PEDOT:PSS and active layer, (b) shows the Edwards Auto 306 vacuum deposition chamber used to deposit the LiF and Al layers.

diodes per glass sample. The deposition chamber is installed with a digital film thickness monitor connected to a quartz crystal sensor. During deposition, the deposition rate is controlled by adjusting the electrical current through the evaporation filament. Film thickness is then monitored through the digital film thickness monitor. Current is switched off and a barrier is positioned above the evaporating material once the desired film thickness is attained. The resulting device structures were (i) Glass/ITO/PEDOT:PSS:/P3HT:PCBM/LiF/Al; (ii) Glass/ITO/PEDOT:PSS:NP_s/P3HT:PCBM/LiF/Al and (iii) Glass/ITO/PEDOT:PSS/P3HT:PCBM:NP_s/LiF/Al.

3.6 Device Characterisation

The fabricated devices were characterized for their optical and electrical properties to study the effects of incorporating the NPs. The current-voltage (J-V) characteristics of the devices were measured using a computer-interfaced Keithley 2420 source meter under standard light illumination using solar simulator (PET, Photo Emission Tech Inc., SS50AAA) at AM1.5 operating at an integrated power intensity of 100 mW cm^{-2} shown in Fig. 3.4. The J-V data was then plotted using an OriginLab software. The maximum current density (J_{max}) and maximum voltage (V_{max}) were then determined as illustrated in Fig. 2.2. The FF and PCE were then determined using Eq. 2.10 and Eq. 2.12, respectively.

The J-V characteristics of the OPVs under dark conditions were also used to determine the charge transport properties of the OPV devices. The measured dark current data at the space charge limited region was fitted to the Mott-Gurney law shown in Eq. 2.15 to obtain charge mobilities of the devices. Optical absorption of the devices was also measured by measuring UV-vis absorption of the thin film with or without NPs.

3.7 Characterisation of the Nanoparticles

The surface and structural morphology of the NPs were studied using scanning electron microscope (SEM), transmission electron microscope (TEM) and X-ray diffraction. The X-ray diffraction (XRD) pattern of the synthesized NPs was measured using a PANalytical Empyrean diffractometer operated at 40 mA and 45 kV. The XRD pattern was collected at 2θ values ranging from 20 - 90 degrees. The XRD data was used to determine the lattice parameter and d-spacing of the NPs. The d-spacing results were then compared with d-spacings obtained using the TEM. TEM measurements were performed using a JEOL 400CX HRTEM or JEM 1400 TEM. Surface morphology of the NPs was performed using a Zeiss EVO LS 15 variable pressure SEM.



(b)



Figure 3.4: Shows a Keithley source meter, a PET Solar Simulator and a sample holder used during the characterisation of the OPV devices.

Bibliography

References

- [1] J. Xiong, Y. Wang, Q. Xue and X. Wu, 2011. Synthesis of highly stable dispersions of nanosized copper particles using L-ascorbic acid. *Green Chemistry*, 13(4), pp.900-904.
- [2] A. Yang, S. Li, Y. Wang, L. Wang, X. Bao and R. Yang, 2015. Synthesis of Ag@ Cu₂O core-shell metal-semiconductor nanoparticles and conversion to Ag@ Cu core-shell bimetallic nanoparticles. *Science China Technological Sciences*, 58(5), pp.881-888.
- [3] L. Suber, I. Sondi, E. Matijević and D. V. Goia, 2005. Preparation and the mechanisms of formation of silver particles of different morphologies in homogeneous solutions. *Journal of Colloid and Interface Science*, 288(2), pp.489-495.
- [4] A. Zielińska, E. Skwarek, A. Zaleska, M. Gazda and J. Hupka, 2009. Preparation of silver nanoparticles with controlled particle size. *Procedia Chemistry*, 1(2), pp.1560-1566.
- [5] T. M. D. Dang, T. T. T. Le, E. Fribourg-Blanc and M. C. Dang, 2011. Synthesis and optical properties of copper nanoparticles prepared by a chemical reduction method. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, 2(1), p.015009.
- [6] Y. Zhao, Y. Zhang, H. Zhu, G. C. Hadjipanayis and J. Q. Xiao, 2004. Low-temperature synthesis of hexagonal (wurtzite) ZnS nanocrystals. *Journal of the American Chemical Society*, 126(22), pp.6874-6875.
- [7] J. Jadhav and S. Biswas, 2016. Surface plasmon enhanced near-UV emission in monodispersed ZnO: Ag core-shell type nanoparticles synthesized by a wet chemical method. *Superlattices and Microstructures*, 91, pp.8-21.
- [8] Yildirim, Ö. A., Unalan, H. E. and Durucan, C., 2013. Highly efficient room temperature synthesis of silver-doped zinc oxide (ZnO: Ag) nanoparticles: structural, optical, and photocatalytic properties. *Journal of the American Ceramic Society*, 96(3), pp.766-773.
- [9] S. Talam, S. R. Karumuri and N. Gunnam, 2012. Synthesis, characterization, and spectroscopic properties of ZnO nanoparticles. *International Scholarly Research Notices*, 2012.

-
- [10] N. Karar, F. Singh and B. R. Mehta, 2004. Structure and photoluminescence studies on ZnS: Mn nanoparticles. *Journal of Applied Physics*, 95(2), pp.656-660.
 - [11] G. Murugadoss, 2012. Luminescence properties of co-doped ZnS: Ni, Mn and ZnS: Cu, Cd nanoparticles. *Journal of Luminescence*, 132(8), pp.2043-2048.

Chapter 4

Near-field enhanced performance of organic photovoltaic cells

Physica B: Condensed Matter 552 (2019) 78–83



Contents lists available at ScienceDirect

Physica B: Condensed Matter

journal homepage: www.elsevier.com/locate/physb



Near-field enhanced performance of organic photovoltaic cells

Mpilo Wiseman Dlamini, Genene Tessema Mola*



School of Chemistry & Physics, University of KwaZulu-Natal, Pietermaritzburg Campus, Private Bag X01, Scottsville 3209, South Africa

ARTICLE INFO

Keywords:

Nano-particles
Plasmon resonance
Photovoltaic
Core-shell
Charge transport

ABSTRACT

Metal nano-particles (NPs) have been successfully synthesized by the reduction of Ag@Cu₂O with the aid of surfactant PVP and excessive reducer ascorbic acid in ambient conditions. The composition and structures of the NPs were characterized by scanning and tunnelling microscopies (SEM and TEM). The synthesized nano-particles were employed as solar absorber in thin film organic photovoltaic (OPV) with the view to exploit the effect of local surface plasmon resonance (LSPR) of the metals. As a consequence, substantial improvement on the major solar cell parameters were measured by the incorporation of Ag@Cu NPs in the P3HT:PCBM based photo-active medium. The power conversion efficiency of the solar cell increased by 103% compared to those devices fabricated without metal nano-particles. The observed balanced charge transport, in the current experiment, is attributed to presence of metal nano-particles in OPV devices which are responsible for near field enhanced photons scattering in the medium.

4.1 Abstract

Metal nanoparticles (NPs) have been successfully synthesized by the reduction of Ag@Cu₂O with the aid of surfactant PVP and excessive reducer ascorbic acid in ambient conditions. The composition and structures of the NPs were characterized by scanning and tunnelling microscopies (SEM and TEM). The synthesized nanoparticles were employed as solar absorber in thin film organic photovoltaic (OPV) with the view to exploit the effect of local surface plasmon resonance (LSPR) of the metals. As a consequence, substantial improve-

ment on the major solar cell parameters were measured by the incorporation of Ag@Cu NPs in the P3HT:PCBM based photoactive medium. The power conversion efficiency of the solar cell increased by 103 % compared to those devices fabricated without metal nanoparticles. The observed balanced charge transport, in the current experiment, is attributed to presence of metal nanoparticles in OPV devices which are responsible for near field enhanced photons scattering in the medium.

4.2 Introduction

Solution processed bulk heterojunction (BHJ) organic solar cells have received significant scientific interest due to their low cost device fabrication, light weight and flexibility [1–4]. However, improving the overall device performance, without compromising the low cost of device fabrication and sufficient life time, is one of the major challenges facing OPVs today [5]. Several mechanisms have been tested to improve photons harvesting in OPV by way of enhanced optical absorption and efficient mechanisms to collect photogenerated currents. These include but not limited to the use of suitable solvents, thermal annealing, solvent additives and incorporation of metal nanoparticles. The efficient harvesting of solar radiation is one of the fundamental requirements to realize high power conversion in a solar cells [6]. Ideally, an increasing the thickness of the photoactive layer would have been the easiest route to enhance absorption through increased optical path length to harvest more photons. However, the exciton diffusion length in polymer medium is very short (~ 10 nm) that limits the size of the solar absorber film thickness to the range of (120 - 250) nm [6–9]. As a consequence, most of the incident photon in OPV cell remain undetected. On the otherhand, the incorporation of metallic nanoparticles in the photoactive medium of OPV serves as a mechanism to trap electromagnetic radiation by way of light scattering that resulted in enhanced optical absorption and overall device performances [7, 10]. This would then assist in the realization of an efficient and thin film solar absorber in OPV.

Furthermore, the metal NPs in conjugated polymer medium are not only improve the conductivity of the composite layer but also expected to cause local surface plasmon resonance (LSPR) which would assist in the harvesting of photons. LSPR is the result of a collective oscillation of charges on the surface of metal nanoparticles due to the interaction with the incident electromagnetic fields [10]. The plasmon excitation is doubly beneficial for the solar cells which on one hand serve as strong scattering center of the incident photons, on the other, create strong local electric field in the vicinity of the particle that can assist in exciton dissociations [11]. In an effort to maximize the contribution of LSPR in OPV; a number of investigators employed the metal nanocomposites in the various layers of the device configurations, such as photoactive medium or/and in charge transport buffer layers between the active layer and electrodes [12–14]. In most cases, it was reported that metal nanoparticles have positively contributed to improve device performance in thin film organic solar cells. Similar observations have been reported on the use of metal nanoparticles in

the preparation of dye synthesised solar cell (DSSC) [13–15]. The optical absorptions of the nanocomposites resulted from LSPR effect are dependent on the size, shapes, concentration and uniformity [16–19]. The most investigated metals that exhibit plasmonic resonance modes are gold, silver and copper which have optical absorbance in the visible or near infrared region of the electromagnetic spectrum [10, 20]. For effective use of LSPR in OPV, the optical absorbance of the nanoparticles preferably be in region of visible and near infrared part of the spectrum where the emission intensity is high. Nonetheless, it is reported that the incorporation of plasmonic Au and Ag nanoparticles into OPVs has significantly increased optical absorption which yields enhanced power conversion efficiencies (PCE) of the solar cell [20–23]. However, the cost and abundance of gold and silver make them unrealistic for mass production of cheap solar cells. In the current investigations, we employed Cu coated silver nanoparticle to keep low material cost by avoiding the use of scarce elements. In fact, Cu nanoparticles also exhibit localized surface plasmon resonance typically at about 590 nm which somewhat overlap with the optical absorption of those of Au and Ag [20, 24, 25].

4.3 Materials and Methods

4.3.1 Materials:

All the chemicals used in the fabrication of BHJ-OPV devices were purchased and used as received without any further purification except the synthesis of Ag@Cu NPs. Poly (3,4-ethylene dioxythiophene):poly (styrenesulfonate) (PEDOT:PSS), Poly (3-hexylthiophene-2,5-diyl) (P3HT) and phenyl-C71-butyric acid methyl ester (PCBM) were purchased from Ossila Co. Ltd. Copper nitrate hydrate ($> 99.5\%$ $\text{Cu}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, sodium hydroxide (NaOH), ammonium nitrate (NH_4NO_3) and chloroform were provided from Sigma Aldrich. Silver nitrate ($> 99.5\%$ AgNO_3 , Merck), polyvinylpyrrolidone (PVP, $(\text{C}_6\text{H}_9\text{NO})_n$, MW of 25 000 - 30 000, LAB), ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, Merck).

4.3.2 Synthesis and characterization of silver @ copper core-shell nanoparticles (Ag@Cu NPs):

The Ag@Cu core-shell nanoparticles were synthesized using a simple chemical reduction method and much of the details have been reported in literature [26]. Briefly, silver NPs were synthesized by adding 0.8 g of PVP as a stabilizer into 80 mL of ascorbic acid aqueous (5×10^{-4} mol/L) as a reducer and stirred for 15 min. Then 1.4 mL of NaOH aqueous (0.1 mol/L) was added to the resultant solution above and stirred again for 5 min. After that, 0.8 mL of AgNO_3 (0.1 mol/L) was added into the solution under stirring in hot plate at 30°C for 15 min. The resulting solution was heated at 80°C for 30 min to produce silver colloid. A 192 mg of PVP was dissolved in 50 mL aqueous solution comprising of $\text{Cu}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ and NH_4NO_3 by weight of 45.8 mg and 111.9 mg, respectively. Subsequently, 70 mL of silver

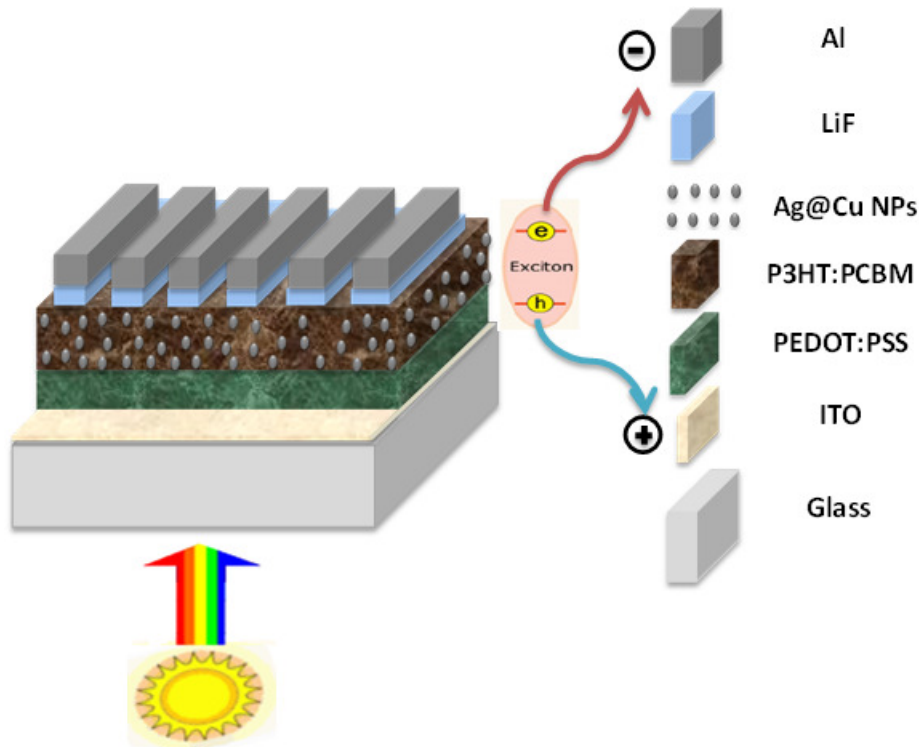


Figure 4.1: Schematic diagram for bulk heterojunction organic solar cell based on Ag@Cu plasmonic nanoparticles incorporated into P3HT:PCBM active layer.

colloid was added into the above solution. A 3.2 mL of NaOH aqueous solution (0.2 mol/L) was drop-wise added to the solution under stirring at room temperature for 5 min and then 5.6 mL of $C_6H_8O_6$ was added to complete the reaction under continuous stirring for 5 min. Finally, the Ag@Cu core-shell NPs powder was obtained by centrifuging the final solution at 5000 rpm for 30 min. Energy-dispersive X-ray spectroscopy was used to characterize the NP for the content of Ag and Cu. Furthermore, transmission electron microscopy was used to characterize the shape and size of the Ag@Cu nanoparticles. The morphology and elemental composition of the Ag@Cu core-shell NPs powder were investigated using JEM 1400 transmission electron microscope (TEM) and energy-dispersive analysis of X-ray (EDAX).

4.3.3 Device Preparation

Solution processed thin film organic solar cells based on P3HT:PCBM blend with Ag@Cu plasmonic nanoparticles were fabricated on unpatterned ITO coated glass substrates. The substrates were first partially etched with acid solution ($HCl:H_2O:HNO_3$ at 48%:48%:4%) to remove part of the ITO. They were then successively cleaned in ultrasonic bath with detergent, distilled water, acetone and isopropanol, respectively, for 10 min holding time. The samples were then dried in an oven at 120 °C for 30 min. A thin layer of PEDOT:PSS was spin coated onto the samples at 3500 rpm. The samples were dried again in the oven under nitrogen atmosphere. The solutions of the polymer blend P3HT:PCBM were prepared at 1:1 stoichiometric ratio by weight and then mixed with Ag@Cu NPs at 5 % or 10 % by weight

in chloroform solvent. The solutions were spin coated onto dried PEDOT:PSS film at 1300 rpm. The samples were dried again in the oven under nitrogen atmosphere for 10 min before being transferred into a vacuum deposition chamber for the deposition of LiF and aluminium. Thin layers of LiF (0.5 nm) and Al (60 nm) were deposited onto the samples resulting in devices with the following structure; ITO/PEDOT:PSS/P3HT:PCBM:NP/LiF/Al. Schematic diagram for device structure depicted in Fig. 4.1 shows the various layers of the organic solar cell based on Ag@Cu plasmonic nanoparticles incorporated into P3HT:PCBM active layer.

4.4 Results and Discussion

4.4.1 Electrical Properties

The performance of the newly fabricated thin film organic solar cells were derived from the measured current-voltage (J-V) characteristic curves. The J-V data provided in Fig. 4.2 are taken from the solar cells whose active layers contain the metal nanoparticles at the ratio of 5 % and 10 % of Ag@Cu NPs by weight. According to the result presented in the figure, notable differences on solar cell parameters were found at 10 % doping level compared to those devices prepared at 5% and 0%. The difference can be seen in terms of the measured high photocurrent, open-circuit voltage and fill factor. For example, the current density has increased to 12.20 mA cm^{-2} at 10 % from 7.5 mA cm^{-2} at 0 % content of the nanoparticles (see Table 4.1). Similarly, the open-circuit voltage slightly varies between 0.55 to 0.6 volts which is mainly attributed to the non-uniform distribution of the metal particles in the medium. Hence, there is a general increase in power conversion efficiency from 1.9 % to 3.87 % as the concentration of the metal nanoparticles increases from 0% to a 10 % by weight which corresponds to a 103 % growth in PCE (see Table 4.1). This is a significant development in improving the power conversion efficiency of thin film organic solar cell which are fabricated in ambient environment. The current results are comparable to the results re-

Table 4.1: Summary of solar cell parameters of BHJ devices based on P3HT:PCBM mixed with Ag@Cu plasmonic nanoparticles under AM 1.5G illumination at 100 mW/cm^2

Ag@Cu (%)	V_{oc} V	J_{sc} mA cm^{-2}	FF (%)	PCE (%)
0	0.56	7.50	45.00	1.90
5	0.58	9.80	54.10	3.04
5	0.56	10.40	53.10	3.10
5	0.57	10.10	57.00	3.29
10	0.55	11.40	58.50	3.65
10	0.55	12.20	57.66	3.84
10	0.60	11.90	54.40	3.87

ported by Notarianni et al., Woo et al., Spyropoulos et al. and Xie et al. who have employed nitrogen atmosphere and expensive Au nanoparticles [27, 28, 30–32] in device preparation.

The current experiment demonstrates the possibility of a novel and yet cost effective way of enhancing photovoltaic performance of OPV using metallic nanoparticles. The increase

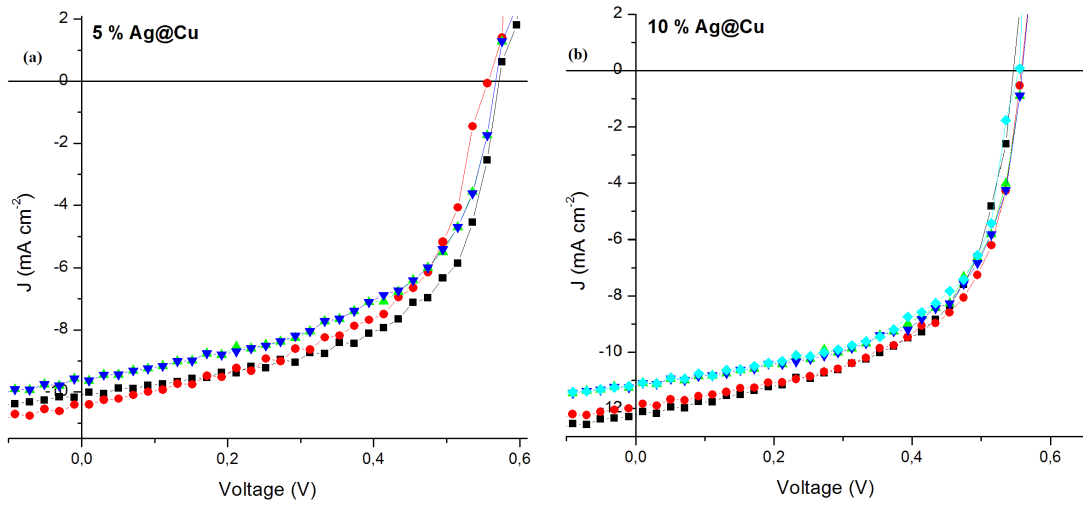


Figure 4.2: The current-voltage characteristic of P3HT:PCBM based solar cells prepared with (a) 5 % wt% Ag@Cu and (b) 10 % wt% Ag@Cu plasmonic nanoparticles under AM 1.5G illumination at 100 mW/cm^2 .

in the PCE is attributed to the measured high photocurrent from the devices due to the Ag@Cu nanoparticles. Shen et al. studied the effect of Ag nanoparticles in P3HT:PCBM based solar cells and found that the near-field enhancement is the main reason for improved optical absorption in the active layer [33]. A similar observation was also reported by Fu et al. on enhanced absorption efficiencies using Au NPs distributed inside the photoactive layer [34]. Therefore, the improved performance of the solar cell parameters in this investigation is mainly attributed to the near-field enhancement due to the Ag@Cu nanoparticles incorporated inside the active layer. Meanwhile, a strong correlation between the solar cell performance and the concentrations of the nanoparticle in the medium is observed where device performance linearly increases with concentration from 0 to 10 % of Ag@Cu NPs by weight. It has been reported that P3HT:PCBM based solar cells often suffered from unbalanced charge transport because of higher electron mobility in the medium than holes. Such imbalance in carriers mobility would negatively affect the photovoltaic performances [32, 35]. Hence, the presence of the metal nanocomposite in the photoactive layer appeared to have curbed this problem as demonstrated by the measured high values of J_{sc} and FF which can be attributed to a more balanced charge transport in the medium. Zheng et al. explained the observed hole mobility increase in terms of the formation of metal hopping sites for the transport of holes [36]. Tang et al. has reported a similar increase in PCE (9.5 % - 13.4 %) when Cu-Au NPs were incorporated in PEDOT:PSS buffer layer in the preparations of P3HT:PCBM solar cells [20]. Several studies have reported performance enhanced photovoltaic devices due to the incorporation of core-shell nanostructures as compared to bare

NPs. Chen et al. also incorporated Au@SiO₂ NPs in P3HT:PCBM based solar cells [37] and found that a PCE growth as high as 16 % (from 3.29 % to 3.80 %) which is higher than the enhancement achieved with bare Au NPs (≈ 13 %) [37]. The incorporation of core-shell NPs instead of bare metallic NPs overcomes some of the shortcomings associated with the later such as charge recombination within the metal, thermal and chemical stability and control over metal NP/polymer chromophore separation to inhibit nonradiative quenching [38–40].

4.4.2 Charge Transport

Space Charge Limited Current (SCLC) taken under dark conditions were employed to explore the charge transport properties of the devices doped with Ag@Cu NPs. The SCLC is often described by the Mott-Gurney's law using the field dependent mobility equation shown in the following equation [41]:

$$J = \frac{9}{8} \epsilon \epsilon_o \mu_o \exp \left(0.89 \gamma \sqrt{\frac{V}{L}} \right) \frac{V^2}{L^3} \quad (4.1)$$

where ϵ is the relative dielectric permittivity of the material, ϵ_o is the permittivity of free space, μ_o is the zero-field mobility, L is the active layer thickness, γ is the field activation factor and V is the voltage drop across the sample corrected by the built-in voltage V_{bi} .

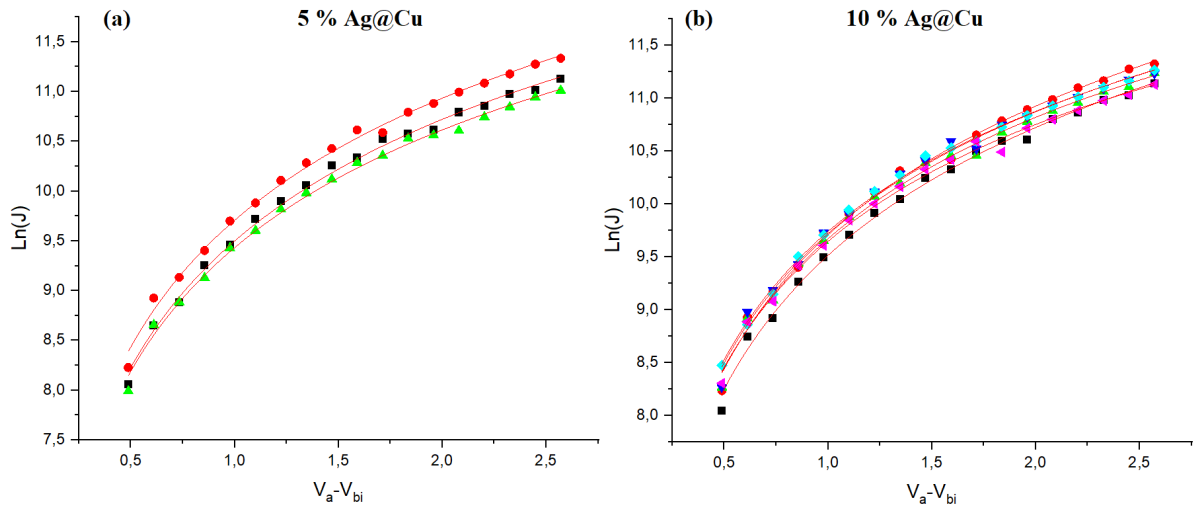


Figure 4.3: The space-charge limited current measurements of P3HT:PCBM based solar cells prepared with (a) 5 % wt% Ag@Cu and (b) 10 % wt% Ag@Cu plasmonic nanoparticles.

The experimental data were fitted to the theoretical Eq. 4.1 which are found to be in good agreement with the experimental data as shown in Fig. 4.3. The zero-field mobility (μ_o) and field activation factor derived from the analysis are comparable with the values found in literature (see Table 4.2). Furthermore, the zero-field mobility value derived from the fit indicated that the value found from 10 % doping level is 50 % higher than that of the 5 % concentration of Ag@Cu NPs. This suggests that germinate recombination in the devices

Table 4.2: Summary of charge transport properties obtained from the SCLC measurements under dark current density.

Concentration	μ_o	γ
%	($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	($\text{cm}^{\frac{1}{2}} \text{V}^{-\frac{1}{2}}$)
0	1.83×10^{-5}	-1.56×10^{-3}
5	3.45×10^{-2}	-1.5×10^{-3}
5	4.20×10^{-2}	-1.5×10^{-3}
5	3.54×10^{-2}	-1.9×10^{-3}
10	6.90×10^{-2}	-3.2×10^{-3}
10	7.21×10^{-2}	-2.8×10^{-3}
10	7.08×10^{-2}	-2.8×10^{-3}
10	6.32×10^{-2}	-2.7×10^{-3}

with 10 % NPs wt% has been reduced which is also evident in their enhanced FF. The observed μ_o values agree very well with the reduced series resistance which goes as low as $170 \Omega/\text{sq}$ for devices with 10 % NPs implying an improved charge transport in the devices.

4.4.3 Optical absorption

The effects of the local surface plasmon resonance of the nanocomposite on the optical properties of the photoactive film of the solar cells were investigated based on the measured UV-vis spectra provided in Fig. 4.4. The optical absorption given in Fig. 4.4 showed a typical P3HT:PCBM blend absorbance which has a pronounced absorbance in the range 450 nm to 650 nm with red shift especially for 10 % concentration. A broad absorption peak at 513 nm and two vibronic shoulder absorptions at 530 nm and 590 nm are distinctly visible. The two vibronic shoulder absorptions mentioned above are not as distinctly visible for the devices with 5 % as compared to devices with 10 % concentration of Ag@Cu NPs. This suggests that the crystalline structure of P3HT remains unchanged after the incorporation of the metal nanoparticles [20, 42]. Nevertheless, the absorption intensity is remarkably enhanced in devices with 10 % Ag@Cu NPs compared to devices with 5 % Ag@Cu NPs. NPs dispersed in the photoactive layer of OPV devices can significantly enhance the optical absorption, either via the formation of scattered waves at the large diameter NPs or due to the excitation of LSPR modes at the smaller diameter NPs [43, 44]. Fig. 4.5 shows the optical absorption spectra of metal nanoparticles thin film which were deposited by spin coating from the suspension of synthesized Ag@Cu core-shell NPs. The absorbance spectra shows two peaks at wavelength positions of 400 nm and 520 nm which are typical absorption peaks position for Ag NPs and Cu NPs, respectively. Interestingly, the characteristic surface plasmon resonance bands have been observed in the longer wavelength regions which is an indication of the effect of Ag@Cu core-shell NPs. The optical absorption of Ag@Cu core-shell NPs incorporated into the photoactive layer showed a red-shift to 750 nm because of an increase in the local dielectric constant correlated with increasing the thickness of Cu shell and plasmon absorption of Ag core.

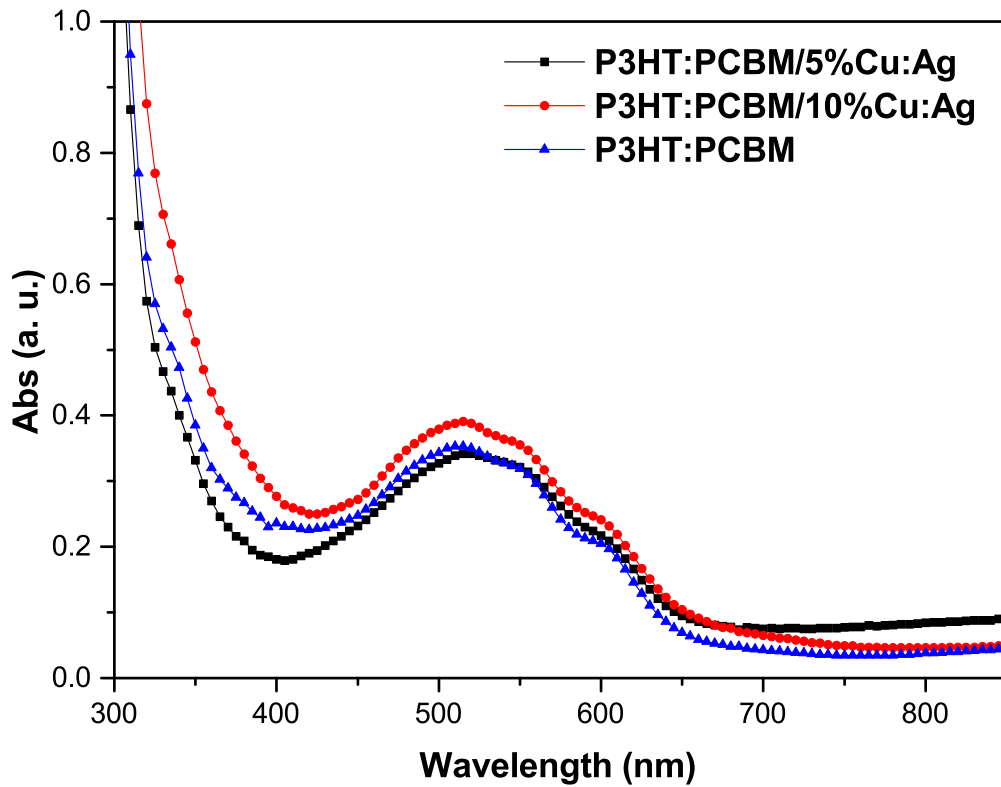


Figure 4.4: Optical absorption spectra of the P3HT:PCBM BHJ active layers containing Ag@Cu nanoparticles at 0%, 5 % and 10 % by weight.

4.4.4 Morphology of Ag@Cu core-shell NPs

The nanomorphology and particle sizes were investigated using SEM and TEM spectroscopes taken from Ag@Cu powder nanoparticles. The SEM image provided in Fig. 4.6(a) clearly showed various structures that mainly includes spherical shaped particles agglomerated to form a large block of nanocomposite. A detailed elemental analysis of Ag@Cu NPs was obtained by EDX measurements which exhibited characteristics peaks of Ag and Cu elements of the respective NPs sample with insignificant impurities (see Fig. 4.6(b)). In the selected region of the spectrum provided in Fig. 4.6(a), 52.8 % of the composition was Cu while silver takes 47.2 %. Furthermore, the TEM images given in Fig. 4.7 show the formation of core-shell type spherical structures where the shell distinctly visible as light colour from dark inner spherical core. The colour difference between the inner core and the outer shell is representing the various elemental composition of the nanoparticle which clearly showed the formation of bimetallic core-shell structure. Silver is the core of the structure of the nanoparticle, in this experiment, while copper forms the outer shell of the structure. According to the high resolution TEM images provided in Fig. 4.7(a) and (b), the diameter of Ag@Cu core-shell nanoparticles ranges from (30 - 55) nm. On the otherhand, the average thickness of the Cu shells is about 25 nm (Fig. 4.6(c)). Silver cores possess nearly smooth surface compared to

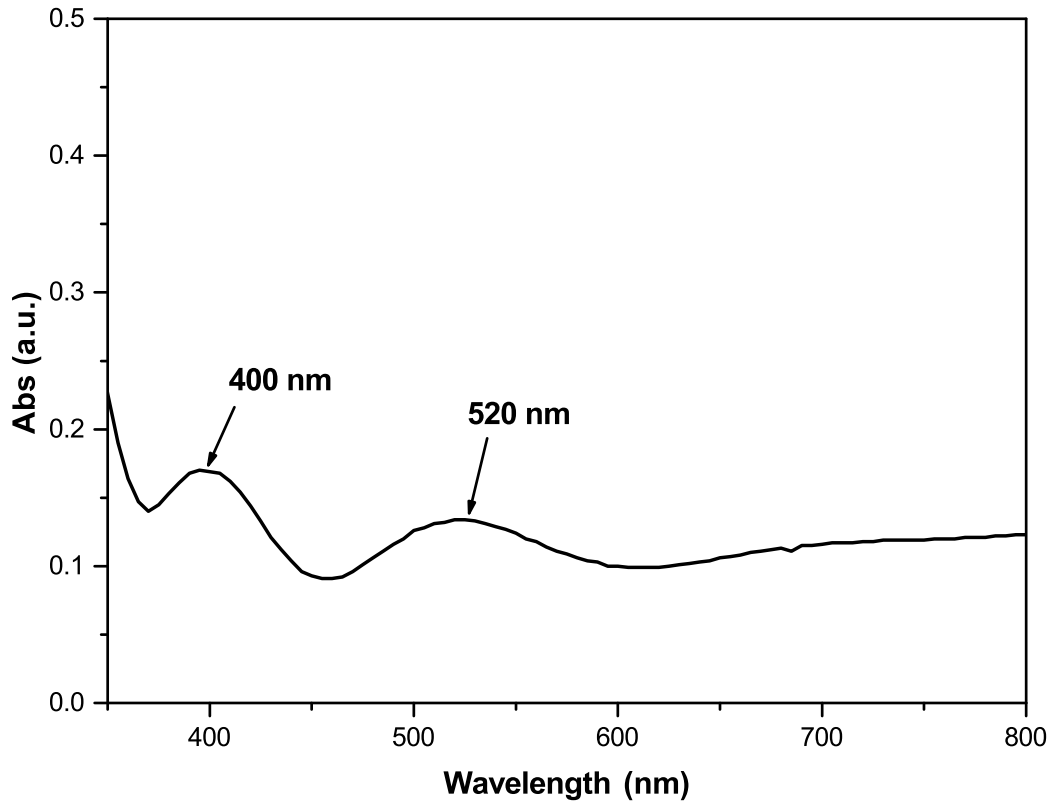


Figure 4.5: Optical absorption of the Ag@Cu nanoparticles thin film.

the Cu shells that contains various porous structure which are composed of single phases Cu nanocrystals with the various shapes and sizes (see Fig. 4.7(a) and 4.7(c)). Such single phase of Cu is expected to occur during the reduction of the Cu_2O to form Cu, thereby, the porous structure was created in the Cu shells.

The large nanoparticles (≥ 40 nm in diameter) can serve as effective sub-wavelength scattering elements that can significantly increase the optical path length of the light within the active layer [19, 25, 28]. The intermediate sizes between 20 nm to 40 nm in diameter can be an efficient photons scatter of the incident light which increases the optical path length in the polymer matrix, and therefore, enhance the optical absorption as observed in Fig. 4.4. Apart from local surface plasmon resonance of the Ag@Cu NPs in the polymer medium the metal nanoparticle would enhance the electrical conductivity of the medium that substantially improve the collection of the photogenerated current in OPV. Furthermore, the relatively small size of the nanoparticles (≤ 20 nm in diameter) can act as sub-wavelength antennas in which the enhanced near-field is coupled to the absorbing OPV layer [19, 25, 28]. Although the synthesis of core-shell metal nanoparticles seems relatively simple, it is however difficult to control the distribution of sizes, shapes and uniformity using solution processing method.

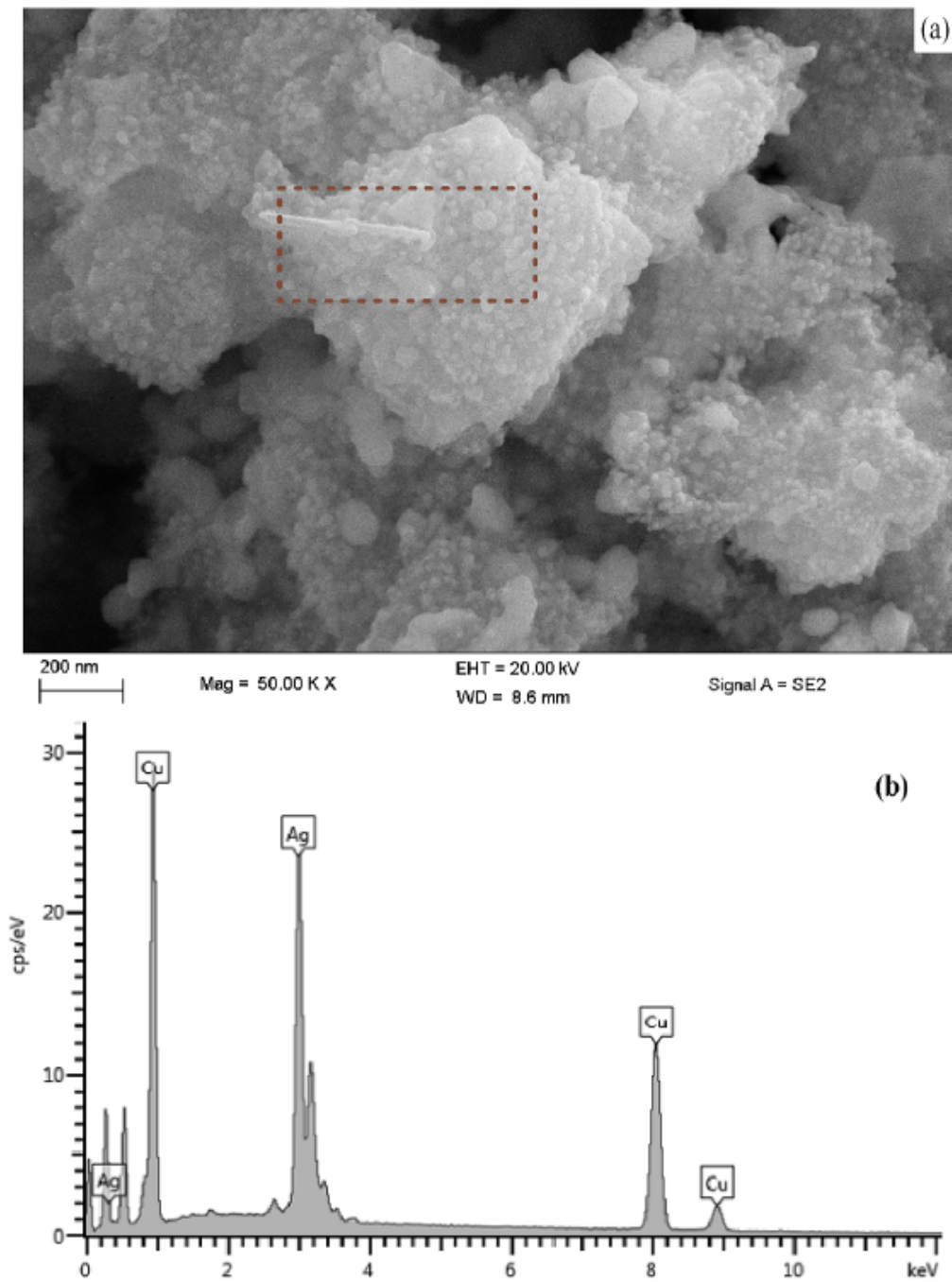


Figure 4.6: Scanning electron microscopy images and EDX of Ag@Cu nanoparticles prepared with solution processing.

4.5 Conclusion

The silver:copper (Ag@Cu) nanocomposite were successfully synthesized using solution phase strategy. The bimetallic nanoparticles of radius (40 - 55) nm were employed into a P3HT:PCBM photoactive medium in the preparation efficient and stable thin film organic solar cell. The performance of the solar cells were found to be dependent on the concentrations of the metal nanoparticles in the photoactive medium. The best device performance was found from the solar cell whose active layer contains 10 % Ag@Cu NPs by weight which resulted in 103 %

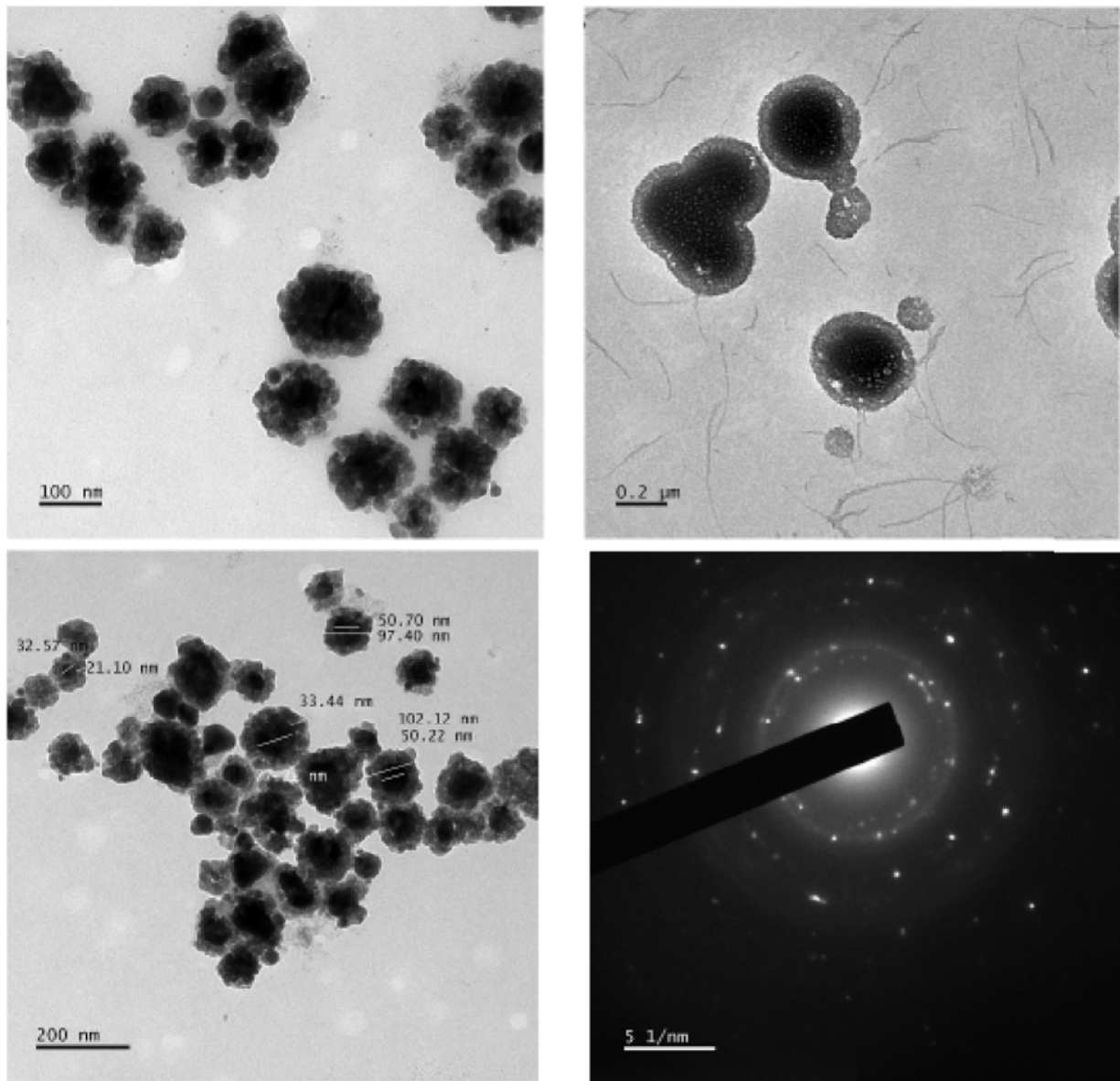


Figure 4.7: Transmission electron microscopy images of Ag@Cu nanoparticles prepared with solution processing.

increase in the power conversion efficiency compared to undoped (0%) photoactive medium. The improvements in both J_{sc} and FF could be due to an increased hole mobility resulting from a more balanced charge transport in the photoactive layer. Moreover, the occurrence of near field at the site of the metal nanoparticles not only facilitated exciton dissociation in the medium but also improved optical absorptions which enhanced the measured photocurrent. The incorporation of core-shell structured metal plasmonic particles within polymer medium enhanced the photovoltaic properties which are attributed to the formation of near-field and light scattering by the presence of both small and large diameter NPs. Finally, the use of core-shell type NPs is more effective than single phase metal NPs to reduce charge recombination, increase thermal and chemical stability and control of metallic NP/polymer chromophore separation to inhibit nonradiative quenching.

Bibliography

References

- [1] C. V. Hoven, X. Dang, R. C. Coffin, J. Peet, T. Nguyen and G. C. Bazan, 2010. Improved performance of polymer bulk heterojunction solar cells through the reduction of phase separation via solvent additives. *Advanced Materials*, 22(8), pp.E63-E66.
- [2] C. J. Brabec and J. R. Durrant, 2008, *Solution-Processed Organic Solar Cells*, vol 33(7), MRS Bulletin, Cambridge University Press, 670-675
- [3] K. M. Coakley, and M. D. McGehee, 2004, Conjugated polymer photovoltaic cells, *Chemistry of materials*, vol.16(23), 4533-4542
- [4] S. O. Oseni and G. T. Mola, 2017, The effect of uni-and binary solvent additives in PTB7: PC₆₁ BM based solar cells, *Solar Energy*, 150, 66-72.
- [5] T. Fleetham, J. Choi, H. W. Choi, T. Alford, D. S. Jeong, T. S. Lee, W. S. Lee, K. Lee, J. Li and I. Kim, 2015, Photocurrent enhancements of organic solar cells by altering dewetting of plasmonic Ag nanoparticles, *Scientific reports*, vol.5.
- [6] N. Kalfagiannis,, P. G. Karagiannidis, C. Pitsalidis, N. T. Panagiotopoulos, C. Gravalidis, S. Kassavetis, P. Patsalas, S. Logothetidis, 2012, Plasmonic silver nanoparticles for improved organic solar cells, *Solar Energy Materials and Solar Cells*, 104, 65-174.
- [7] P. Mandal and S. Sharma, 2016, Progress in plasmonic solar cell efficiency improvement: A status review, *Renewable and Sustainable Energy Reviews*, 65, 537-552.
- [8] F. Enrichi, A. Quandt and G. C. Righini, 2017, Plasmonic enhanced solar cells: Summary of possible strategies and recent results, *Renewable and Sustainable Energy Reviews*, 82, 2433-2439.
- [9] J. M. Lee and S. O. Kim, 2016, Enhancing organic solar cells with plasmonic nanomaterials, *Chem. Nano. Mat.*, vol. 2(1), 19-27.
- [10] M. Tang, B. Sun, D. Zhou, Z. Gu, K. Chen, J. Guo, L. Feng and Y. Zhou, 2016, Broad-band plasmonic Cu-Au bimetallic nanoparticles for organic bulk heterojunction solar cells, *Organic Electronics*, 38, 213-221.

- [11] X. G. Mbuyise, P. Tonui and G. T. Mola, 2016, The effect of interfacial layers on charge transport in organic solar cell, *Physica B: Condensed Matter*, 496, 34-37.
- [12] M. Notarianni, K. Vernon, A. Chou, M. Aljada, J. Liu and N. Motta, 2014, Plasmonic effect of gold nanoparticles in organic solar cells, *Solar Energy*, 106, 23-37.
- [13] O. Amiri, M. Salavati-Niasari, N. Mir, F. Beshkar, M. Saadat and F. Ansari, 2018, Plasmonic enhancement of dye-sensitized solar cells by using Au-decorated Ag dendrites as a morphology-engineered, *Renewable Energy* 125, 590-598.
- [14] O. Amiri, M. Salavati-Niasari, A. Rafiei, M. Farangi, 2017, 147% improved efficiency of dye synthesized solar cells by using CdS QDs, Au nanorods and Au nanoparticles, *RSC Advances*, 4 (107), 62356-62361.
- [15] O. Amiri, M. Salavati-Niasari, M. Farangi, M. Mazaheri, S. Bagheri, 2015, Stable plasmonic-improved dye sensitized solar cells by silver nanoparticles between titanium dioxide layers, *Electrochimica Acta*, 152, 101-107.
- [16] B. A. Taleatu, E. Omotoso, C. Lal, W. O. Makind, K. T. Ogundele, E. Ajenifuja, A. R. Lasisi, M. A. Eleruja, G. T. Mola, 2014, XPS and some surface characterizations of electrodeposited MgO nanostructure, *Surf. Interface Anal.*, Vol. 46, 372-377
- [17] M. V. Arularasu, M. Anbarasu, S. Poovaragan, R. Sundaram, K. Kanimozhi, C.M. Magdalane, K. Kaviyarasu, F. T. Thema, D. Letsholathebe, G. T. Mola and M. Maaza, 2018, Structural, optical, morphological and microbial studies on SnO₂ nanoparticles prepared by co-precipitation method. *Journal of nanoscience and nanotechnology*, 18(5), pp.3511-3517.
- [18] S. Woo, J. H. Jeong, H. K. Lyu, Y. S. Han and Y. Kim, 2012, In situ-prepared composite materials of PEDOT: PSS buffer layer-metal nanoparticles and their application to organic solar cells, *Nanoscale research letters*, vol. 7(1), 641.
- [19] G. D. Spyropoulos, M. M. Stylianakis, E. Stratakis and E. Kymakis, 2012, Organic bulk heterojunction photovoltaic devices with surfactant-free Au nanoparticles embedded in the active layer, *Applied Physics Letters*, vol. 100(21), 213904.
- [20] F. Xie, W. C. H. Choy, C. C. D. Wang, W. E. I. Sha and D. D. S. Fung, 2011, Improving the efficiency of polymer solar cells by incorporating gold nanoparticles into all polymer layers, *Applied Physics Letters*, vol. 99(15), 219.
- [21] B. H. Nguyen, V. H. Nguyen and D. L. Vu, 2015, Plasmonic enhancement of light trapping into organic solar cells, *Advances in Natural Sciences: Nanoscience and Nanotechnology*, vol. 6(4), 043002.

- [22] E. Stratakis and E. Kymakis, 2013, Nanoparticle-based plasmonic organic photovoltaic devices, *Materials Today*, vol. 16(4), 133-146.
- [23] G. Li, V. Shrotriya, Y. Yao and Y. Yang, 2005, Investigation of annealing effects and film thickness dependence of polymer solar cells based on poly (3-hexylthiophene), *Journal of Applied Physics*, vol. 98(4), 043704,
- [24] D. Chen, A. Nakahara, D. Wei, D. Nordlund and T. P. Russell, 2010, P3HT/PCBM bulk heterojunction organic photovoltaics: correlating efficiency and morphology, *Nano. letters*, vol. 11(2), 561-567.
- [25] D. H. Wang, D. Y. Kim, K. W. Choi, J. H. Seo, S. H. Im, J. H. Park, O. O. Park and A. J. Heeger, 2011, Enhancement of donor-acceptor polymer bulk heterojunction solar cell power conversion efficiencies by addition of Au nanoparticles, *Angewandte Chemie*, vol.123(24), 5633-5637.
- [26] C. J. Orendorff, T. K. Sau and C. J. Murphy, 2006, Shape-Dependent Plasmon-Resonant Gold Nanoparticles, *Small*, vol. 2(5), 636-639.
- [27] L. Lu, T. Zheng, Q. Wu, A. M Schneider., D. Zhao and L. Yu, 2015, Recent advances in bulk heterojunction polymer solar cells, *Chemical reviews*, vol. 115(23), 12666-12731.
- [28] Q. Gan, F. J. Bartoli and Z. H. Kafafi, 2013, Plasmonic-enhanced organic photovoltaics: Breaking the 10% efficiency barrier, *Advanced materials*, vol. 25(17), 2385-2396.
- [29] L. J. Sherry, S. Chang, G. C. Schatz, R. P. Van Duyne, B. J. Wiley and Y. Xia, 2005, Localized surface plasmon resonance spectroscopy of single silver nanocubes, *Nano letters*, vol.5(10), 2034–2038.
- [30] I. Pastoriza-Santos, A. Sánchez-Iglesias, B. Rodríguez-González and L. M. Liz-Marzán, 2009, Aerobic synthesis of Cu nanoplates with intense plasmon resonances, *Small*, vol. 5(4), 440-443.
- [31] H. Yang, S. He, H. Chen and H. Tuan, 2014, Monodisperse copper nanocubes: synthesis, self-assembly, and large-area dense-packed films, *Chemistry of Materials*, vol. 26(5), 1785-1793.
- [32] M. T. Dang, L. Hirsch and G. Wantz, 2011, P3HT: PCBM, best seller in polymer photovoltaic research, *Advanced Materials*, vol. 23(31), 3597-3602.
- [33] J. Lee and P. Peumans, 2010, The origin of enhanced optical absorption in solar cells with metal nanoparticles embedded in the active layer, *Optics Express*, vol. 18(10), 10078-10087.

- [34] A. Yang, S. Li, Y. Wang, L. Wang, X. Bao and R. Yang, 2015, Synthesis of Ag@Cu₂O core-shell metal-semiconductor nanoparticles and conversion to Ag@Cu core-shell bimetallic nanoparticles, *Science China Technological Sciences*, vol. 58(5), 881-888.
- [35] G. Li, V. Shrotriya, Y. Yao, J. Huang and Y. Yang, 2007, Manipulating regioregular poly (3-hexylthiophene):[6, 6]-phenyl-C 61-butyric acid methyl ester blends—route towards high efficiency polymer solar cells, *Journal of Materials Chemistry*, vol. 17(30), 3126-3140.
- [36] H. Shen, P. Bienstman and B. Maes, 2009, Plasmonic absorption enhancement in organic solar cells with thin active layers, *Journal of Applied Physics*, vol. 106(7), 073109.
- [37] W. Fu, X. Chen, X. Yang, L. Wang, Y. Shi, M. Shi, H. Li, A. K. Jen, J. Chen, Y. Cao and others, 2013, Optical and electrical effects of plasmonic nanoparticles in high-efficiency hybrid solar cells, *Physical Chemistry Chemical Physics*, vol. 15(40), 17105-17111.
- [38] S. O. Oseni and G. T. Mola, 2017, Properties of functional layers in inverted thin film organic solar cells, *Solar Energy Materials & Solar Cells*, Vol. 160, 241–256.
- [39] T. Zheng, W. C. Choy and Y. Sun, 2009, Hybrid nanoparticle/organic devices with strong resonant tunneling behaviors, *Advanced Functional Materials*, vol. 19(16), 2648-2653.
- [40] B. Chen, W. Zhang, X. Zhou, X. Huang, X. Zhao, H. Wang, M. Liu, Y. Lu and S. Yang, 2013, Surface plasmon enhancement of polymer solar cells by penetrating Au/SiO₂ core/shell nanoparticles into all organic layers, *Nano Energy*, vol. 2(5), 906-915.
- [41] X. G. Mbuyise, E. A. A. Arbab, K. Kaviyarasu, G. Pellicane, M. Maaza and G. T. Mola, 2017, Zinc oxide doped single wall carbon nanotubes in hole transport buffer layer, *Journal of Alloys and Compounds*, Vol. 706, 344-350
- [42] E. A. A. Arbab, G. T. Mola, 2016, V₂O₅ thin film deposition for application in organic solar cells, *Appl. Phys. A: Material Science & Processing*, Vol. 122:405, 1-8.
- [43] M. D. Brown, T. Suteewong, R. S. S. Kumar, V. D’Innocenzo, A. Petrozza, M. M. Lee, U. Wiesner and H. J. Snaith, 2010, Plasmonic dye-sensitized solar cells using core-shell metal-insulator nanoparticles, *Nano letters*, vol. 11(2), 438-445.
- [44] K. Ueno, T. Oshikiri, Q. Sun, X. Shi and H. Misawa, 2017, Solid-State Plasmonic Solar Cells, *Chemical reviews*.

Chapter 5

Improved energy harvesting using well-aligned ZnS nanoparticles in bulkheterojunction organic solar cell

Journal of Materials Science: Materials in Electronics
<https://doi.org/10.1007/s10854-020-03481-w>



Improved energy harvesting using well-aligned ZnS nanoparticles in bulk-heterojunction organic solar cell

Mpilo W. Dlamini¹ · Mohammed S. G. Hamed¹ · Xolani G. Mbuyise¹ · Genene T. Mola¹

Received: 17 February 2020 / Accepted: 25 April 2020
© Springer Science+Business Media, LLC, part of Springer Nature 2020

Abstract

Zinc sulphide (ZnS) nanoparticles (NPs) were synthesized by low temperature colloidal chemistry to produce stable zinc blend structure. The metallic ZnS NPs were incorporated into poly(3-hexylthiophene) (P3HT) and (6,6)-phenyl C₆₁-butyric acid methyl ester (PCBM) blend photoactive layer to improve the overall performance of organic solar cells (OSC). The newly fabricated devices have exhibited enhanced photocurrent which is likely to come from utilizing the near-field and light scattering effects due to the NPs. The short-circuit current density of the best solar cell was enhanced to as high as 15.65 mA cm⁻² followed by 51% and 4.0% maximum fill-factor (FF) and power conversion efficiency (PCE), respectively. This enhancement is very comparable to those obtained from the use of expensive plasmonic gold and silver nanoparticles. The current results are encouraging to improve the performance of OSC through a facile yet cost-effective and environmentally friendly approach of metal nanoparticles synthesis.

5.1 Abstract

Zinc sulphide (ZnS) nanoparticles (NPs) were synthesized by low temperature colloidal chemistry to produce stable zinc blend structure. The metallic ZnS NPs were incorporated into poly(3-hexylthiophene) (P3HT) and (6,6)-phenyl C₆₁-butyric acid methyl ester (PCBM) blend photo-active layer to improve the overall performance of organic solar cells (OSC).

The newly fabricated devices have exhibited enhanced photocurrent which is likely to come from utilising the near-field and light scattering effects due to the NPs. The short-circuit current density of the best solar cell was enhanced to as high as 15.65 mA cm^{-2} followed by 51 % and 4.0 % maximum fill-factor (FF) and power conversion efficiency (PCE), respectively. This enhancement is very comparable to those obtained from the use of expensive plasmonic gold and silver nanoparticles. The current results are encouraging to improve the performance of OSC through a facile yet cost-effective and environmentally friendly approach of metal nanoparticles synthesis.

5.2 Introduction

One of the most popular organic molecules blend, that served as a solar absorber medium in OSC, is the mixture of poly(3-hexylthiophene) (P3HT) and (6,6)-phenyl C₆₁-butyric acid methyl ester (PCBM). The power conversion efficiency of this polymer-fullerene combination has grown to as high as 5 % [1–5] through utilisation of several optimization techniques such as solvent additive, thermal and solvent annealing, and the utilisation of localized surface plasmon resonance (LSPR). However, limitations such as low charge carrier mobility, weak photon absorption in the visible spectrum, and low open-circuit voltage (V_{oc}) ($\sim 0.6 \text{ V}$ [6]) still exist in P3HT:PCBM blend based OSC due to the deep lying lowest unoccupied molecular orbital (LUMO) levels of PCBM [4, 7]. Different approaches have been taken to enhance performance of OPVs while keeping active layer thickness unchanged to avoid increasing charge recombination. Recently, metallic nanoparticles are increasingly being introduced into OSC devices for highly improved light harvesting by employing the LSPR effect of metallic nanoparticles [2, 7, 8].

The strong electromagnetic fields produced near metallic NPs can in principle be expected to enhance the optical absorption in OSCs [11]. We report here a power conversion efficiency increment of more than 50 % by the incorporation of plasmonic zinc sulphide (ZnS) NPs in the P3HT:PCBM blend photoactive layer. Zinc sulphide is an environmentally friendly and stable transition metal sulphide which can be synthesised easily and inexpensively [7] using low temperature colloidal chemistry. ZnS nanoparticles show special photoelectric properties, such as photoluminescence and electroluminescence [12]. It is a wide band gap semiconductor with high electron mobility ($600 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and has an electron affinity of about 3.9 eV making it an attractive material to use as an electron acceptor in hybrid photovoltaic devices [7]. Bredol et al. used ZnS NPs as electron acceptors and obtained a maximum V_{oc} of 1.2 V when hexagonal ZnS NPs were used in contact with P3HT at a ZnS NPs concentration of 50 wt% [13]. However, the PCE was rather low (0.2 %) compared to conventional BHJ P3HT:PCBM blend devices [7, 13]. The optical properties of ZnS NPs dramatically change due to their quantum confinement effect and improve as compared to their bulk counterparts [14]. Zinc sulphide exhibits polymorphism since it forms two main types of crystal phases, namely the most stable zincblende cubic structure ($< 1290 \text{ K}$) and

hexagonal phase with wurtzite symmetry at high-temperature above 1290 K [12, 14–16].

5.3 Materials and Methods

5.3.1 Materials:

Chemical materials used for the fabrication of OPVs were purchased and used as received without further processing except the synthesis of ZnS. Poly(3-hexylthiophene) (P3HT), phenyl-C₇₁-butyric acid methyl ester (PCBM) and PEDOT:PSS were purchased from Ossila Co. Ltd. Zinc acetate and sodium sulphide nonahydrate were purchased from Merck, Germany. Polyvinylpyrrolidone (PVP, (C₆H₉NO)_n, MW of 25 000 - 30 000) LAB.

5.3.2 Synthesis and characterization of ZnS nanoparticles:

The ZnS NPs were prepared as follows: 50 mL of 0.5 M zinc acetate solution was prepared with deionized water and stirred in a glass beaker to dissolve zinc acetate. In a separate beaker, 50 mL of 0.5 M of sodium sulphide was prepared and poured into 100 mL of deionized water with 3.0 g PVP and stirred until all solids were dissolved. The zinc acetate solution was then added to the sodium sulphide solution drop-wise while stirring at room temperature. The resulting precipitate was then filtered under reduced pressure and washed with distilled water and twice with ethanol to remove sodium ions. Finally, the resulting ZnS nanoparticles were then dried in oven at 100 °C for 3 hours. The morphology and elemental composition of the ZnS NPs powder were investigated using a scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDAX) analysis. X-ray diffraction data of ZnS was then acquired on a PANalytical Empyrean diffractometer operated at 45 kV and 40 mA. The pattern was collected from 2 θ values of 20 to 60 degrees, step size of 0.02 degrees and an acquisition time of 127 seconds per step.

5.3.3 Device Fabrication

P3HT:PCBM based organic solar cells mixed with ZnS plasmonic nanoparticles were fabricated on unpatterned ITO coated glass substrates. The substrates were first partially etched with acid solution (HCL:H₂O:HNO₃ at 48%:48%:4%) to remove part of the ITO. They were then successively cleaned in ultrasonic bath with detergent, distilled water, acetone and isopropanol, respectively, for 10 min waiting time. The samples were then dried in an oven at 120 °C for 30 min. A thin layer of PEDOT:PSS was spin coated onto the samples at 3500 rpm. The samples were dried again in the oven under ambient atmosphere. Three P3HT:PCBM (1:1) blend solutions with 3 wt%, 5 wt% or 8 wt% of ZnS NPs were prepared in chloroform and sonicated for 3 hours at 40 °C to ensure good dispersion of the NPs and miscibility of the polymer-fullerene blend. The P3HT:PCBM solutions incorporated with

ZnS NPs were then spin coated onto the PEDOT:PSS film at 1300 rpm for 40 sec. The samples were then dried in oven under nitrogen atmosphere for 10 min before being transferred into a vacuum deposition chamber (Edwards Auto 306) for deposition of lithium fluoride (LiF) and aluminium (Al). Thin layers of LiF (0.5 nm) and Al (80 nm) were deposited onto the samples at a base pressure of 10^{-6} mBar resulting in devices with the following structure: ITO/PEDOT:PSS/P3HT:PCBM:NP/LiF/Al. Schematic diagram for device structure depicted in Fig. 5.3(a) shows the various layers of the organic solar cell based on ZnS plasmonic nanoparticles incorporated into P3HT:PCBM active layer.

5.4 Results and Discussion

5.4.1 XRD Analysis of ZnS NPs

The newly synthesised zinc-sulphide powder was characterized in terms of its morphological and optical properties. The XRD pattern presented in Fig. 5.1 was taken from ZnS NPs powder which clearly showed well known diffraction peaks of the compound. The measured diffraction pattern matched very well with ICDD data card no.: 01-074-4985. Three prominent diffraction peaks are observed at 2θ values of 28.85° , 47.81° and 56.54° . These diffraction peaks correspond to the reflections of the beam from the (111), (220) and (311) planes of the cubic phase of ZnS. The inter-planar spacings (d_{hkl}) corresponding to these XRD peaks are given in Table 5.1.

The d-spacing obtained of the three prominent peaks match very well with the literature results of 3.07 Å, 1.89 Å and 1.59 Å from Saravanan et al. which matched very well with JCPDS data card no.: 79-0043 [14]. Kannappan et al. also observed similar diffraction peaks of solid state synthesized ZnS NPs at 2θ values of 28.51° , 47.91° and 56.56° [17]. The d-spacing of 3.07 Å obtained by calculation using the X-ray measurement data matches closely with the value of 3.10 Å obtained by TEM measurements (see red circle in Fig. 5.2(b)). The crystalline sizes (D_{size}) of the ZnS NPs were calculated using the Debye-Scherrer equation:

$$D_{size} = \frac{0.91\lambda}{\beta(2\theta)\cos(\theta)} \quad (5.1)$$

where λ (0.15406 nm) is the wavelength of the X-rays, β is the full width at half maximum in radians. The reflections from the (111), (220) and (311) planes, occurring at 2θ at 28.85° , 47.81° and 56.54° , respectively, were used for the crystalline size calculation and the results are shown in Table 5.1.

The D_{size} of 5.10 nm at $2\theta = 28.85^\circ$ matches very well with particle size determined using TEM (see circles A & B in Fig. 5.2(a)). The crystalline domain sizes obtained are not consistent suggesting that the sample contains non uniform particles. This is also supported by the TEM measurements with particle sizes close to 5.0 nm.

It has been reported that nano-sized ZnS mostly synthesized by colloid chemistry usually

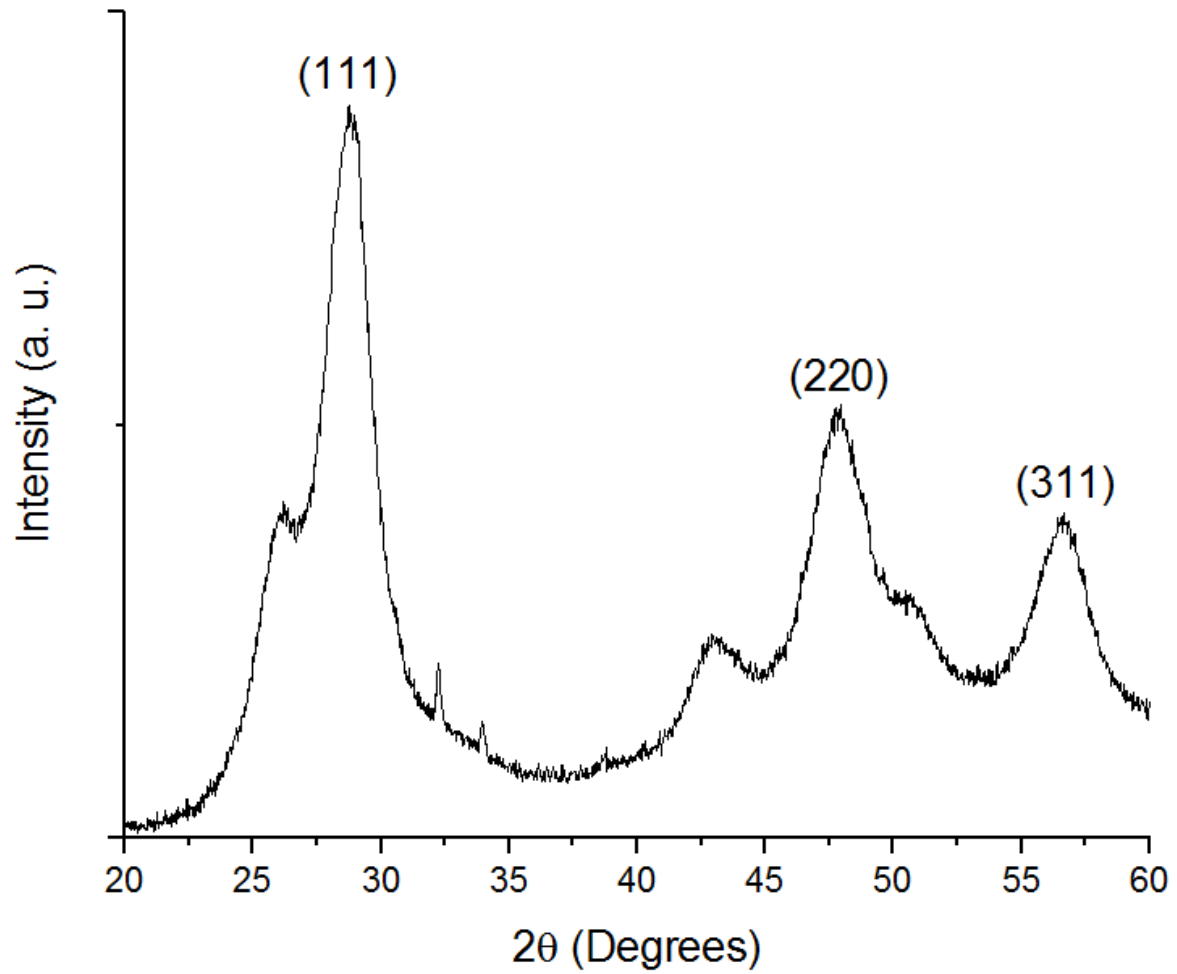


Figure 5.1: X-ray diffraction pattern for ZnS nanoparticles.

Table 5.1: Inter-planner spacing (d_{hkl}) from XRD data card with corresponding (hkl) and lattice parameter values for ZnS.

Pos. [2θ]	FWHM	hkl	d_{hkl} [Å]	a [Å]	D_{size} [nm]
28.85	1.6265	111	3.09	5.35	5.10
47.81	2.8259	220	1.90	5.37	3.11
56.54	2.6397	311	1.63	5.37	3.46

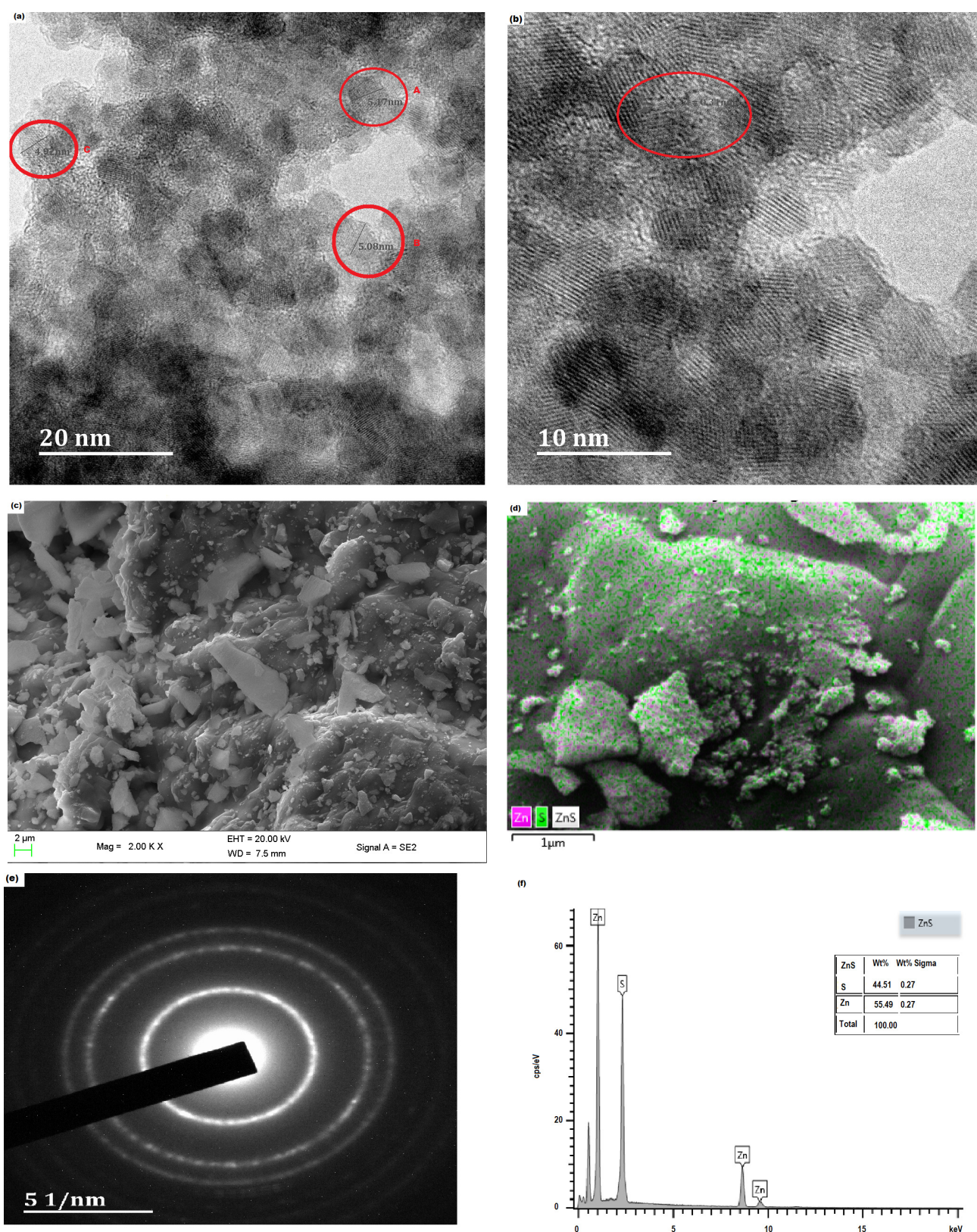


Figure 5.2: (a) & (b) HRTEM images (c) & (d) HRSEM, (e) SAED pattern images of ZnS nanoparticles and (f) the EDX of the ZnS NPs.

have the cubic zincblende structure which is a stable phase at low temperatures for ZnS [18]. We used the standard formula for a cubic structure to determine the average lattice constant a to be $a = 5.366$ Å. This value falls within the range of ZnS NPs lattice constants $a = 5.317$ Å [14] ($a = 5.318$ Å JCPDS card no.: 79-0043) and $a = 5.40$ Å [19] reported in literature.

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (5.2)$$

5.4.2 SEM and TEM electron microscopy

The microstructure and morphology of the synthesized zinc sulphide nanoparticles were investigated by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). The HRTEM image provided in Fig. 5.2(a), (b) show two dimensional disc like structures with well aligned crystal fringes as presented in (b). The crystallite size range of 5 - 8 nm which is consistent with the observation in XRD measurements. The SEM image provided in Fig. 5.2(c) indicated the formation of large clusters of the metal composite in extended space. The elemental mapping of the composite was also taken using EDX analysis suggesting a uniform distribution of the elements zinc and sulphur in the region (see Fig. 5.2(d)). Furthermore, the EDX data provided in Fig. 5.2(f) indicated that the elements zinc and sulphur existed in the synthesized powder with the proportion of 55.49 % zinc and 44.51 % sulphur. This confirms the absence of any impurity in the nanoparticles.

5.4.3 Electrical Properties

The current-voltage (J-V) characteristics of the devices were measured using a computer-interfaced Keithley 2420 source meter under standard light illumination using a solar simulator at AM1.5 operating at an integrated power intensity of 100 mW/cm² (see Fig. 5.3). The solar absorber layers of the devices were subject to high doping levels of ZnS at the concentration from 0 % to 8 % in P3HT:PCBM blend. The J-V characteristics of the solar cells showed a remarkable increase on the short-circuit current density and fill-factor (FF) compared to undoped solar absorber layer (see Table 5.2). This high FF is as a result of improved charge carrier mobilities and reduced recombination in the OPV devices. It has been reported that if charge generation changes significantly between open-circuit conditions and short-circuit conditions, then this would influence the device FF and such field-dependent charge carrier generation has been shown to be the main determinant in some donor/acceptor combinations [20–22]. Lakhwani et al. reported that for most high-efficiency OPV systems, geminate recombination is greatly reduced and bimolecular recombination is the main mechanism for charge recombination [23]. Therefore, it is the ratio of recombination and extraction of charge carriers that principally determines the dependence of the photocurrent on bias, and hence the FF [24].

The devices with 8 wt% ZnS NPs in its active layer showed very high photocurrent collection and witnessed reduction in the device fill factor. This could be attributed to the

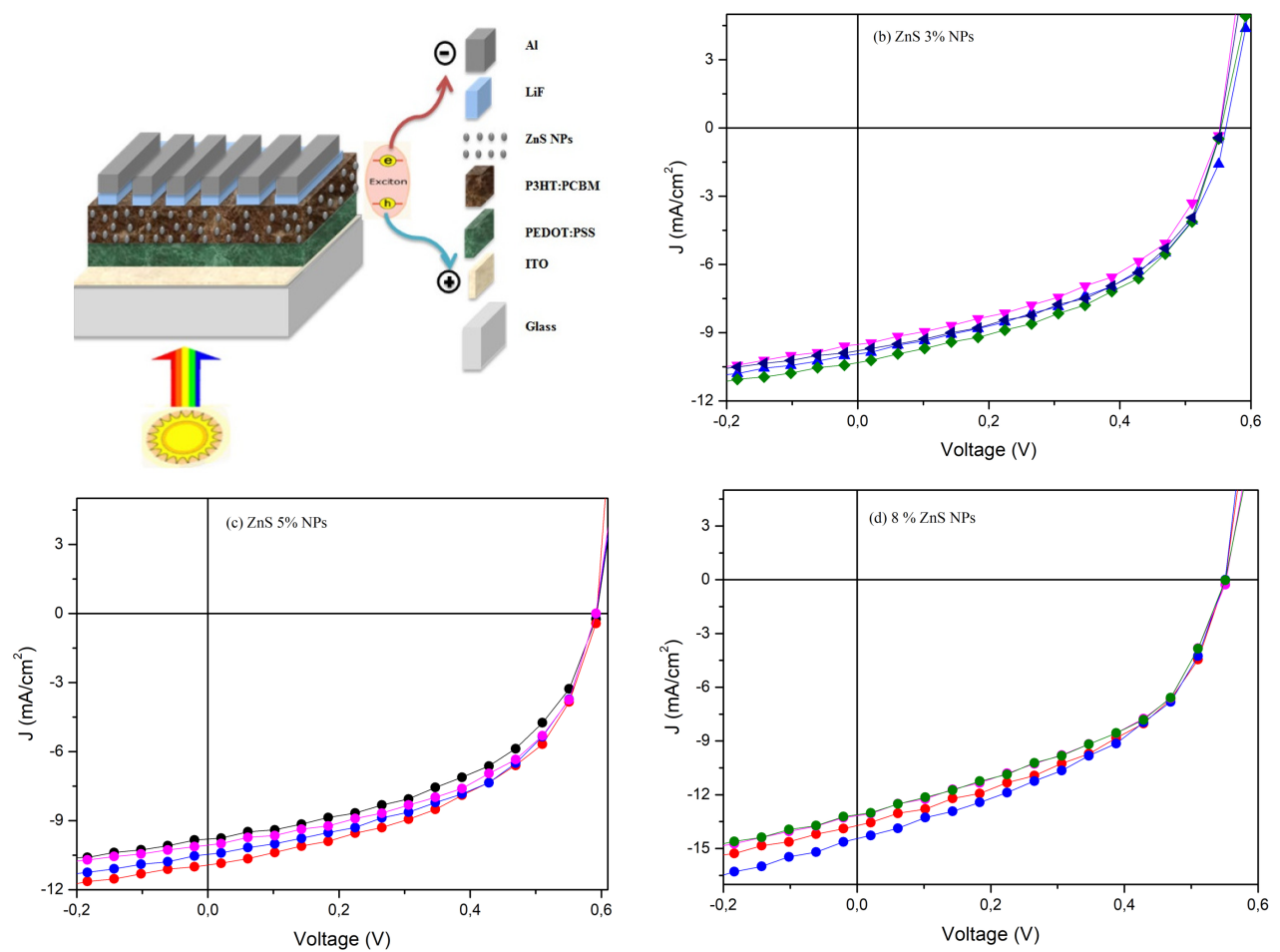


Figure 5.3: Schematic diagram (a) of the OPV devices, (b) - (d) current-voltage characteristics of P3HT:PCBM based organic solar cells.

loss of shunt resistance due to the presence of high concentrations of ZnS. The V_{oc} of all devices exhibited minor changes ranging between 0.55 - 0.59 V. The highest open-circuit voltage and fill-factor were recorded from the solar cells that contain 5 wt% concentration of ZnS. This suggests that the optimum amount of 8 wt% ZnS nanoparticles not only assisted charge generation but also improved the inter-facial conditions between the active layer and the electrodes which is responsible for high V_{oc} .

Table 5.2: Summary of the best device performance of solar cells based on P3HT:PCBM blend at different concentrations of ZnS.

Device (%)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	μ_o (cm ⁻² V ^{-$\frac{1}{2}$} s ⁻¹)
Pristine	0.56	7.50	45.00	1.90	1.83×10^{-5}
3 %	0.55	10.41	50.87	2.93	2.09×10^{-2}
5 %	0.59	10.89	48.91	3.16	6.00×10^{-2}
8 %	0.55	15.65	46.43	4.00	1.46×10^{-2}

In other words, the ZnS NPs did not introduce significant defect density (energy disorder) that negatively affected the HOMO and LUMO levels of the polymer blend. However, 5 wt% was not sufficient to warrant high short-circuit current and best efficiency as recorded in Table 5.2. The highest current-density measured from the solar cells was at the 8 wt% concentration of ZnS in the photo-active medium which is as high as 15.65 mA cm⁻² and PCE is 4 %. The electrical properties of the devices are shown in Fig. 5.3 (b) - (d). It is noted here that the dopant concentrations greater than 8 wt% were detrimental to the device performances. However, the enhanced device performance is attributed to the occurrence of near-field enhancement at the vicinity of the small diameter ZnS NPs as well as forward scattering from the larger diameter ZnS NPs, which improves optical path length and optical absorption in the photoactive layer. The performance data shown in Table 5.2 shows a strong correlation between the solar cell performance and the ZnS NPs concentration in the photoactive layer blend, where the NPs concentration is varied from 0 wt%(pristine devices) to 8 wt% that enhanced the overall device performance. It has been reported that charge carrier mobility imbalance in P3HT:PCBM OPVs negatively affects their performance [2]. The short-circuit current density (J_{sc}) and FF enhancements observed suggests that the incorporation of the plasmonic NPs helped improve the charge carrier mobility imbalance between the electron and hole mobilities. As a result of the enhancements on the J_{sc} and FF, the PCE of the OPV devices improved from 1.9 % to as high as 4.0 %. This is a remarkable enhancement considering the fact that the devices were fabricated under ambient conditions with no use of a glove box filled with inert gases.

5.4.4 Optical absorption of the photoactive film

The UV-Vis spectra of the photoactive films composed of P3HT:PCBM blend were taken with and without the inclusion of ZnS (see Fig. 5.4(a)). The absorption spectrum of the

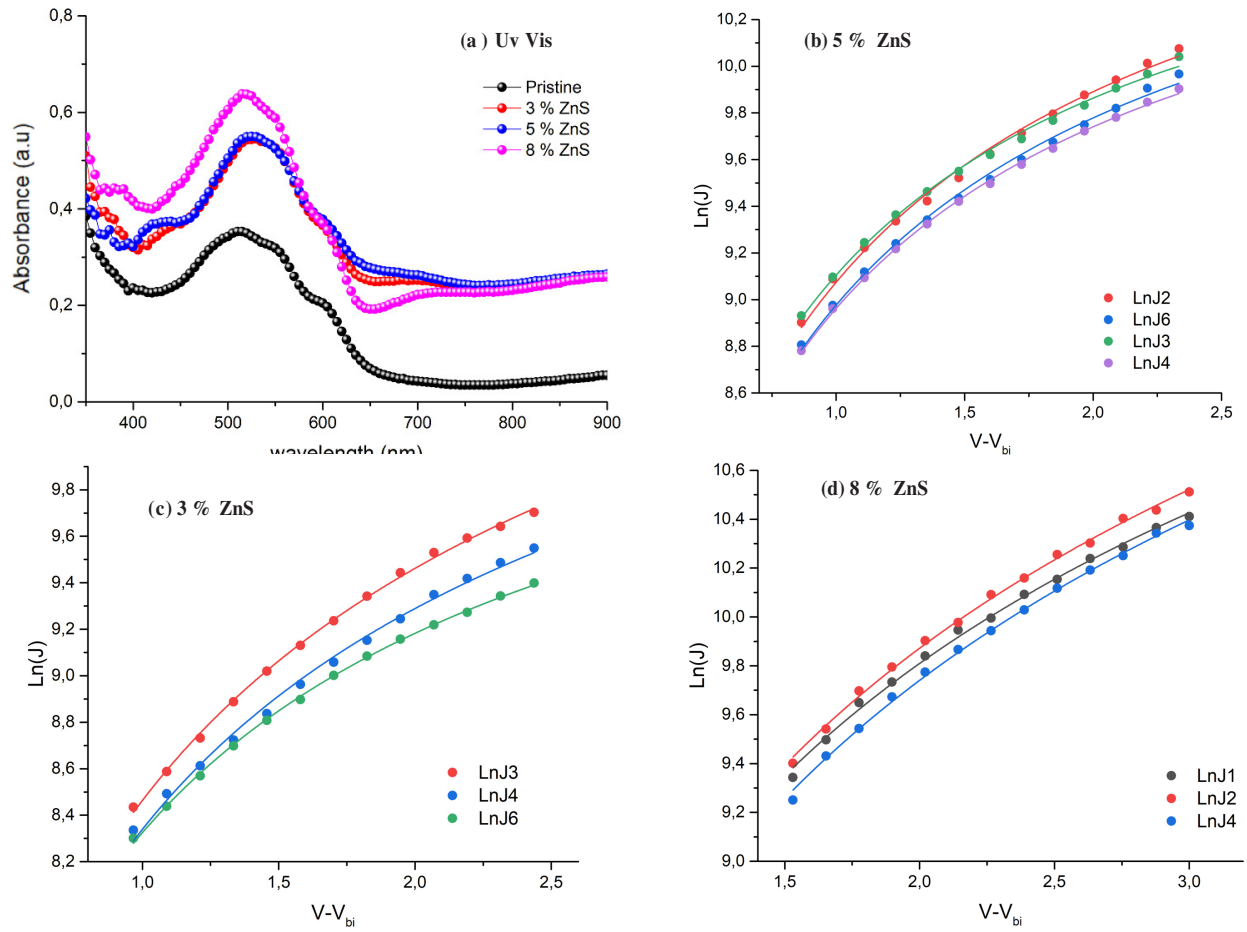


Figure 5.4: (a) Optical absorption spectra of the P3HT:PCBM blend films. (b)–(d) are the charge transport properties obtained from space charge limited current data which are compared with Mott–Gurney Law

pristine film shows the typical P3HT:PCBM blend absorption spectrum with broad absorption peak centred around 510 nm and two vibronic shoulders at 555 nm and 605 nm. The absorption spectra of the blend films containing ZnS NPs at different concentrations show two bumps located at 400 nm and above 700 nm. The peaks of the absorption spectra are generally red-shifted with respect to those of pristine film. The maximum absorption peaks are centred between 520 - 530 nm. The two vibronic shoulders are still distinctly visible even with those films containing ZnS. This suggests that the crystallinity of the P3HT:PCBM films was not disturbed by the incorporation of the ZnS NPs. The effect of red shift of the absorption spectra observed in the NPs-doped blend films is attributed to the interaction of ZnS with sulphur-rich back bone of the polymer chain. The red shift is in fact favourable since it repositions the absorption peak to an intense emission spectrum of the solar radiation. Furthermore, the ZnS NPs-doped films absorption observed, above 700 nm wavelength, is likely to come from the photons scattered at near-infrared regions. This is evident from the absorbance at the highest concentration of ZnS in the medium (8 wt%). Plasmonic NPs in the photoactive layer of OPVs can remarkably enhance optical absorption, either via the formation of scattered waves by the larger diameter NPs and/or due to the LSPR modes excitation at the smaller diameter NPs [2, 25, 26]. Therefore, the enhanced optical absorption observed in the blend films containing the nanoparticles can be attributed to the forward light scattering and LSPR effect from the ZnS NPs.

5.4.5 Charge Transport

The current-voltage characteristics of the OPV devices under dark illumination were used to study the charge transport properties of the devices. The measured space charge limited current (SCLC) was fitted to the Mott-Gurney law (Eq. 5.3) to determine the charge transport properties. The SCLC is often described by the Mott-Gurney law using the field-dependent mobility equation [2]:

$$J = \frac{9}{8} \epsilon \epsilon_o \mu_o \exp \left(0.89 \gamma \sqrt{\frac{V}{L}} \right) \frac{V^2}{L^3} \quad (5.3)$$

where ϵ is the relative dielectric permittivity of the material, ϵ_o is the permittivity of free space, L is the active layer thickness, γ is the field activation factor and V is the voltage drop across the sample corrected by the built-in voltage (V_{bi}). The experimental data were fitted with the natural logarithm of Eq. 5.3 to obtain charge mobilities of the device samples and the resultant mobilities are shown in Table 5.2. The experimental data agreed very well with the model as shown in Fig. 5.4 (b) - (d). The charge mobility values showed three orders of magnitude increase when plasmonic ZnS NPs were incorporated in the active layer of the devices. This observation suggests that geminate recombination in the devices was significantly reduced. It has been reported that a strong imbalance between the electron and hole charge carriers leads to space charge photocurrents, characterized by a square root dependence on applied voltage [27], which then limits the FF to about 40 % [28]. It was

observed in our experimental results for 3 wt% and 5 wt% ZnS NPs concentration that the enhanced charge carrier mobilities were accompanied by significant enhancements of the device FFs. However, the increase in charge carrier mobility in the devices with 8 wt% ZnS NPs concentration did not bring about significant increase in the device FFs compared to the pristine devices. Thermal annealing applied on the devices may have also contributed in the enhancement of the charge carrier mobility due to the self-organisation into crystalline structure of the regioregular polymer (P3HT).

5.5 Conclusion

Nano-structured ZnS NPs with average lattice parameter of $a = 5.3663 \text{ \AA}$ were successfully synthesized by colloidal chemistry. The nanoparticles were used in the solar absorber layer of thin film organic solar cell at various concentrations from (0-8) wt%. The evidence found from the experiment suggest that all devices fabricated with ZnS has shown improved performance compared to the undoped ones. Moreover, the incorporation of the NPs did not negatively affect the crystallinity of the polymers blend as evidenced from optical absorption of doped P3HT:PCBM films. The newly fabricated polymer solar cell exhibited remarkable enhancement in the measured photocurrent, fill-factor and open-circuit voltage. The best device performance was obtained at 8 wt% ZnS NPs concentration which resulted in a maximum J_{sc} of 15.65 mAcm^{-2} and highest PCE of 4.0 %. The occurrence of the near-field at the site of metal NPs facilitated fast exciton dissociation in the medium as well as enhanced photocurrent collection. It is to be noted here that the light scattering effect from metallic NPs increased path length thereby more photons were absorbed.

Bibliography

References

- [1] W. Ma, C. Yang, X. Gong, K. Lee and A. J. Heeger, 2005. Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology. *Advanced Functional Materials*, 15(10), pp.1617-1622.
- [2] A. Hayakawa, O. Yoshikawa, T. Fujieda, K. Uehara and S. Yoshikawa, 2007. High performance polythiophene/fullerene bulk-heterojunction solar cell with a TiO_x hole blocking layer. *Applied Physics Letters*, 90(16), p.163517.
- [3] G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, 2011. High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends. In *Materials For Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group* (pp. 80-84).
- [4] M. S. G. Hamed, S. O. Oseni, A. Kumar, G. Sharma and G. T. Mola, 2020, Nickel sulphide nano-composite assisted hole transport in thin film polymer solar cells, *Solar Energy*, 195, 310-317
- [5] S. K. Jang, S. C. Gong and H. J. Chang, 2012, Effects of various solvent addition on crystal and electrical properties of organic solar cells with P3HT: PCBM active layer. *Synthetic Metals*, 162(5-6), pp.426-430.
- [6] G. Zhao, Y. He and Y. Li, 2010, 6.5% Efficiency of polymer solar cells based on poly (3-hexylthiophene) and indene-C₆₀ bisadduct by device optimization. *Advanced Materials*, 22(39), pp.4355-4358.
- [7] T. A. Kareem and A. A. Kaliani, 2015, Fabrication and characterization of ZnSCubic: P3HT, ZnSHexa: P3HT and ZnSHexa: P3HT: PVA-Ag bulk heterojunction solar cells.
- [8] L. Lu, Z. Luo, T. Xu and L. Yu, 2012, Cooperative plasmonic effect of Ag and Au nanoparticles on enhancing performance of polymer solar cells. *Nano letters*, 13(1), pp.59-64.
- [9] M. W. Dlamini and G. T. Mola, 2019, Near-field enhanced performance of organic photovoltaic cells. *Physica B: Condensed Matter*, 552, pp.78-83.

- [10] E. A. A. Arbab and G. T. Mola, 2019, Metals decorated nanocomposite assisted charge transport in polymer solar cell. *Materials Science in Semiconductor Processing*, 91, pp.1-8.
- [11] D. D. Fung, L. Qiao, W. C. Choy, C. Wang, E.I. Wei, F. Xie and S. He, 2011, Optical and electrical properties of efficiency enhanced polymer solar cells with Au nanoparticles in a PEDOT–PSS layer. *Journal of Materials Chemistry*, 21(41), pp.16349-16356.
- [12] Y. Y. She, Y. A. N. G. Juan and K. Q. Qiu, 2010, Synthesis of ZnS nanoparticles by solid-liquid chemical reaction with ZnO and Na₂S under ultrasonic. *Transactions of Nonferrous Metals Society of China*, 20, pp.s211-s215.
- [13] M. Bredol, K. Matras, A. Szatkowski, J. Sanetra, and A. Prodi-Schwab, 2009, P3HT/ZnS: a new hybrid bulk heterojunction photovoltaic system with very high open circuit voltage. *Solar Energy Materials and Solar Cells*, 93(5), pp.662-666.
- [14] N. Saravanan, G. B. Teh, S. Y. P. Yap and K. M. Cheong,, 2008, Simple synthesis of ZnS nanoparticles in alkaline medium. *Journal of Materials Science: Materials in Electronics*, 19(12), pp.1206-1208.
- [15] P. D'Amico, A. Calzolari, A. Ruini and A. Catellani, 2017, New energy with ZnS: novel applications for a standard transparent compound. *Scientific reports*, 7(1), p.16805.
- [16] Y. Zhao, Y. Zhang, H. Zhu, G. C. Hadjipanayis and J. Q. Xiao, 2004, Low-temperature synthesis of hexagonal (wurtzite) ZnS nanocrystals. *Journal of the American Chemical Society*, 126(22), pp.6874-6875.
- [17] P. Kannappan and R. Dhanasekaran, 2018, Structural and optical characterization of ZnS nanoparticles Synthesized by low temperature. *International Journal of Recent Technology and Engineering (IJRTE)*, ISSN:2277-3878, 7(4S), pp.26-28.
- [18] Y. Zhao, Y. Zhang, H. Zhu, G. C. Hadjipanayis and J. Q. Xiao, 2004, Low-temperature synthesis of hexagonal (wurtzite) ZnS nanocrystals. *Journal of the American Chemical Society*, 126(22), pp.6874-6875.
- [19] C. S. Pathak, M. K. Mandal and V. Agarwala, 2013, Synthesis and characterization of zinc sulphide nanoparticles prepared by mechanochemical route. *Superlattices and Microstructures*, 58, pp.135-143.
- [20] D. Bartesaghi, I. del Carmen Pérez, J. Kniepert, S. Roland, M. Turbiez, D. Neher and L. J. A. Koster, 2015, Competition between recombination and extraction of free charges determines the fill factor of organic solar cells. *Nature communications*, 6, p.7083.
- [21] G. F. Dibb, F. C. Jamieson, A. Maurano, J. Nelson and J. R. Durrant, 2013, Limits on the fill factor in organic photovoltaics: distinguishing nongeminate and geminate recombination mechanisms. *The journal of physical chemistry letters*, 4(5), pp.803-808.

-
- [22] S. Albrecht, S. Janietz, W. Schindler, J. Frisch, J. Kurpiers, J. Kniepert, S. Inal, P. Pingel, K. Fostiropoulos, N. Koch and D. Neher, 2012, Fluorinated copolymer PCPDTBT with enhanced open-circuit voltage and reduced recombination for highly efficient polymer solar cells. *Journal of the American Chemical Society*, 134(36), pp.14932-14944.
- [23] G. Lakhwani, A. Rao, and R. H. Friend, 2014, Bimolecular recombination in organic photovoltaics. *Annual review of physical chemistry*, 65, pp.557-581.
- [24] R. Mauer, I. A. Howard and F. Laquai, 2010, Effect of nongeminate recombination on fill factor in polythiophene/methanofullerene organic solar cells. *J. Phys. Chem. Lett*, 1(24), pp.3500-3505.
- [25] M. D. Brown, T. Suteewong, R. S. S. Kumar, V. D’Innocenzo, A. Petrozza, M. M. Lee, U. Wiesner and H. J. Snaith, 2010, Plasmonic dye-sensitized solar cells using core-shell metal-insulator nanoparticles, *Nano letters*, vol. 11(2), 438-445.
- [26] K. Ueno, T. Oshikiri, Q. Sun, X. Shi and H. Misawa, 2017, Solid-State Plasmonic Solar Cells, *Chemical reviews*, DOI: 10.1021/acs.chemrev.7b00235.
- [27] V. D. Mihailetschi, J. Wildeman and P. W. M. Blom, 2005, Space-charge limited photocurrent. *Physical review letters*, 94(12), p.126602.
- [28] M. Lenes, M. Morana, C. J. Brabec and P. W. Blom, 2009, Recombination-limited photocurrents in low bandgap polymer/fullerene solar cells. *Advanced Functional Materials*, 19(7), pp.1106-1111.

Chapter 6

ZnO:Ag nano-particles decorated hole transport layer for improved photon harvesting

Applied Physics A (2022) 128:125
<https://doi.org/10.1007/s00339-021-05253-7>

Applied Physics A
Materials Science & Processing



ZnO:Ag nano-particles decorated hole transport layer for improved photon harvesting

Mpilo W. Dlamini¹ · Xolani G. Mbuyise¹ · Genene T. Mola¹

Received: 27 October 2021 / Accepted: 30 December 2021
© The Author(s), under exclusive licence to Springer-Verlag GmbH, DE part of Springer Nature 2022

Abstract

The effect of silver doped ZnO (ZnO:Ag) nano-particles in the hole transport buffer layer of thin film organic solar cell was studied in this article. Polymers molecules blend composed of poly(3-hexylthiophene-2,5-diyl):phenyl-C61-butyric-acid-methyl-ester (P3HT:PCBM) was used as a medium of solar absorber to investigate the effect of metal nano-particles in the transport layer. Furthermore, an additional improvement on the charge transport processes were expected by co-doping of dimethyl sulfoxide solvent additive on the absorber layer of the solar cells. Optical properties of the solar absorber films of the devices showed significant enhancement of absorbency from the use of metal nano-particles. As a result, device performances have been boosted as determined from improved device parameters such as the fill-factor and short-circuit current density were increased by 16% and 58%, respectively. The power conversion efficiency has increased from 2.56% (pristine devices) to a maximum of 4.88% for devices doped with 5 wt% dimethyl sulfoxide and 1.5 mg ZnO:Ag nano-particles.

Keywords Organic photovoltaic · ZnO:Ag nanoparticles · Surface plasmonic effect · Forward scattering

6.1 Abstract

The effect of silver doped ZnO (ZnO:Ag) nano-particles in the hole transport buffer layer of thin film organic solar cell (TFOSC) was studied in this article. Polymers molecules blend composed of poly(3-hexylthiophene-2,5-diyl):phenyl-C61-butyric-acid-methyl-ester (P3HT:PCBM) was used as a medium of solar absorber to investigate the effect of metal nano-particles in the transport layer. Furthermore, an additional improvement on the charge transport processes were expected by co-doping of dimethyl sulfoxide (DMSO) solvent ad-

ditive on the absorber layer of the solar cells. The optical properties of the absorber films of the devices showed significant enhancement of absorbency from the use of nano-particles and dimethyl sulfoxide. As a result, device performances have been boosted as determined from improved device parameters such as the fill-factor and short-circuit current density were increased by 16 % and 58 %, respectively. The power conversion efficiency (PCE) has increased from 2.56 % (pristine devices) to a maximum of 4.88 % for devices doped with 5 wt.% dimethyl sulfoxide and 1.5 mg ZnO:Ag nano-particles.

6.2 Introduction

Due to the rising cost and scarcity of fossil fuel and global warming challenges, renewable energy has attracted tremendous research attention from researchers around the globe. In particular, solar energy harvesting has become one of the most researched and promising technology in dealing with today's energy crisis. Bulk heterojunction (BHJ) organic solar cells are amongst the solar cell technologies that have recently emerged and gained remarkable progress in energy research [1]. The BHJ organic solar cells consists of polymer molecules that form an interpenetrating polymer network of donor:acceptor molecules sandwiched between two electrode for exclusive collection of electrons and holes. The short exciton diffusion length of ca. 10 nm and low carrier mobility in polymers limits the photoactive layer thickness to 120 - 250 nm [2]. As a result, most of the incident radiation in organic solar cells (OSCs) devices is not absorbed. Researchers have developed several techniques to improve photon harvesting and carrier transport process in OSCs while keeping fabrication costs and photoactive layer thickness at minimum. These techniques include the use of solvent additives [3, 4], incorporation of plasmonic nanoparticles at various layers of the device structure [5, 6] and thermal treatment of active layers. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is the most widely used hole transport buffer layer in OSC due to its solution processability, high optical transparency ($> 85\%$) in the visible light spectrum, high work function (4.8 - 5.2 eV), good electrical conductivity and reducing roughness of the indium-tin oxide (ITO) film [7, 8]. PEDOT:PSS has a wide range of applications in optoelectronics and biomedicine[9–11]. However, the acidity and hygroscopic nature of PEDOT:PSS may result in the etching of the ITO surface during spin coating and hydrolysis of the deposited PEDOT:PSS by moisture absorption can also etch the ITO that cause indium incorporation into the polymer [12, 13]. To improve on the drawbacks on PEDOT:PSS, several studies have reported enhancements on the PEDOT:PSS films by solvent additive [8, 12, 14, 15]. Ligang et al. used copper(I) thiocyanate (CuSCN) modified PEDOT:PSS to improve the efficiency and stability of perovskite solar cells [10]. The modified PEDOT:PSS exhibited lowered acidity and higher work function [10]. As a result, significantly enhanced PCE and improved long-term stability of inverted perovskite solar cells was observed. Similarly, Chenghao et al. also observed enhanced PCE and long-term stability when PEDOT:PSS was incorporated with metal oxide MoO_x and used in inverted polymer

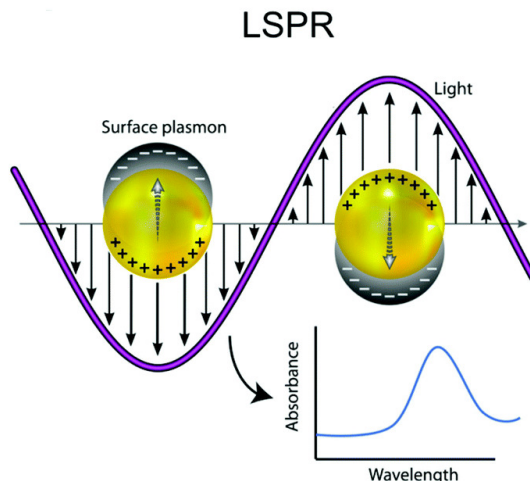


Figure 6.1: Schematic diagrams of localized surface plasmon resonance in spherical metallic NPs and possible resonance absorption [22].

solar cells [11]. Devices based on the modified PEDOT:PSS showed regulated wettability and work function, and enhanced power conversion efficiency of up to 19.64 % [11]. Dimethyl sulfoxide is the most commonly used solvent additive for PEDOT:PSS with conductivity enhancement from 0.04 S/cm to 117.41 S/cm at 15 wt.% of DMSO into PEDOT:PSS [15]. Similarly, Wilson et al. reported conductivity enhancement by a factor of 10^3 to 130 S/cm of inkjet printed PEDOT:PSS films [16]. Other studies have reported use of solvents such as sorbitol, ethylene glycol, tetramethylene sulfonate [15] and isopropyl alcohol [17]. Although the conductivities and optical transmittance of the buffer layer is reportedly to be improvable, the issue of optical absorption in OSCs still needs to be solved. Recently, plasmonic metal nanoparticles have been extensively used to enhance optical absorption of the photoactive layer either by the effect of localized surface plasmon resonance (LSPR) or forward scattering [1, 2, 7, 18–20]. The valence electrons of high free electron mobility nanostructures oscillate inherently against the restoring force due to the positively charge nuclei [21]. When the frequency of their oscillation matches that of the incident photons, localized surface plasmon resonance occurs [23]. Figure 6.1 shows a schematic representation of the oscillation of electron cloud around a metallic NP in the vicinity of an applied external electric field. A strongly localized and enhanced electric field is created in the subwavelength regime [24]. This enhanced electric field can be tens to thousands of times greater than that of incident light [25, 26]. When the electron cloud oscillations are coherent, a large oscillating dipole moment is created. The energy from the plasmonic metal is then transferred to the surrounding semiconductor via dipole-dipole coupling, which generates excitons below and near the semiconductor band edge [27]. Li et al. showed that electron-hole pairs can be created in a semiconductor via resonant energy transfer from plasmonic metal [27]. That is, energy is transferred by coupling the large plasmonic dipole to the electron-hole pair dipole in the semiconductor [25, 28]. The LSPR is confined in a very small volume around an isolated

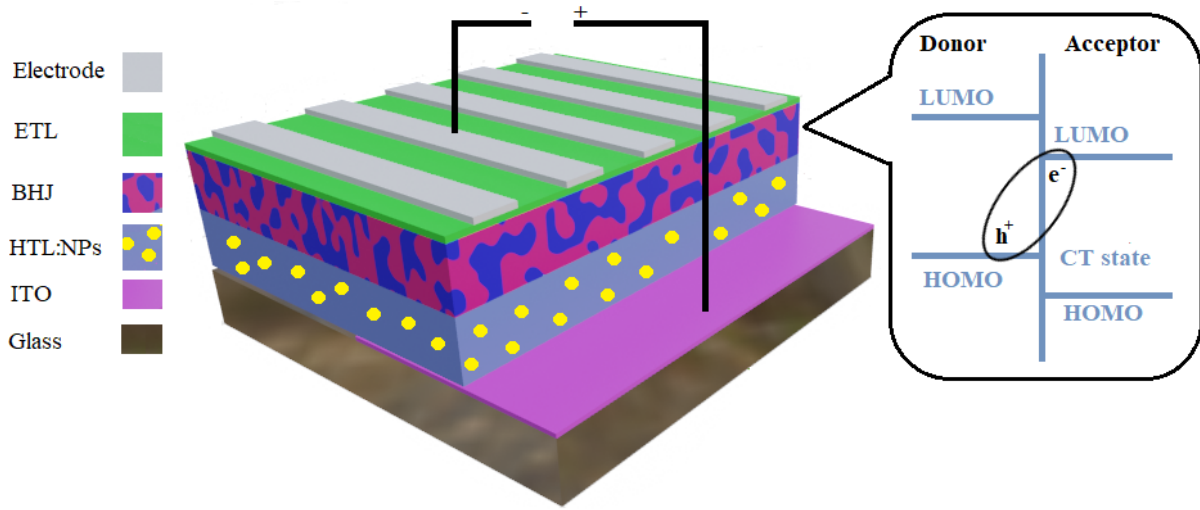


Figure 6.2: Schematic diagram for bulk heterojunction organic solar cell based on P3HT:PCBM with ZnO:Ag NPs nanoparticles incorporated into the anode buffer layer PEDOT:PSS.

nanoparticle [24] and hence decays exponentially with distance from the nanoparticle. The LSPR decays through radiative process via re-emitted photons or non-radiative process via excitation of hot electrons [21, 23]. Metallic nanoparticles of metals such as gold (Au), silver (Ag) and copper or combination of them have been used to improve the performance of OSCs [2, 7, 16, 19, 20]. However, due to the high cost and low scattering efficiency of Au [18], Ag NPs have dominated the OSCs research space. Silver has been used as a thin layer coating to other unstable or low scattering nanoparticles. Baek et al. found that a thin layer of Ag on Au NPs acted as a strong plasmonic scattering enhancer, thus creating a bimetallic Au@Ag nanocomposite possessing both a broad LSPR region and high scattering efficiency [5].

We report here on the use of silver doped zinc oxide (ZnO) nanoparticles as photocatalytic materials to improve OSCs optical properties by light scattering and LSPR. However, as the NPs are incorporated within the anode buffer layer, their LSPR effect in the photoactive layer will be insignificant as the near-field effect decays exponentially with distance from the NP. ZnO nanoparticles were doped with Ag to improve its photocatalytic properties. The Ag doping can improve the photocatalytic activity of ZnO NPs by creating a local electric field around the NPs and enhance its electrical properties by the optical vibration of surface plasmon [29, 30]. Furthermore, the higher light scattering coefficient of Ag can greatly improve the optical path length into the photoactive layer by forward scattering of the incident photons. ZnO is a wide band gap n-type semiconductor ($E_g = 3.37\text{eV}$) with excellent electrical and optical properties [31]. It is stable and environmentally friendly with its LSPR in the UV region due to its high band gap and large exciton binding energy [32]. It is therefore transparent to visible light. Due to its transparency and high electron mobility, ZnO has been widely applied in solar cells as an electron transport layer [33]. However, the solar spectrum

consists of only about 5 - 7 % of UV region and about 45 % of visible region [32, 34]. To improve the optical response of the ZnO NPs in the visible range, we doped the ZnO NPs with a noble metal silver. Silver is an excellent inexpensive and non-toxic visible light scatterer. Combining ZnO and Ag aims to form a superior photocatalyst that can perform both under UV and visible light to benefit from a wider spectrum range. Pragati et al. demonstrated that incorporation of noble metal NPs significantly enhances photocatalytic of ZnO under UV and visible light by promoting separation of photogenerated charge carriers [32]. This is achieved by delaying recombination process of the photogenerated electron-hole pairs [32].

6.3 Experimental

6.3.1 Synthesis of ZnO:Ag nanoparticles

The ZnO:Ag nanoparticles were synthesized using wet chemistry methods as detailed in [35]. In brief, a 1.25 g of ZnO nanopowder (< 50 nm particle size, containing 6 % aluminium as dopant, Sigma Aldrich) was dissolved in 20 mL aqueous solution of 0.25 M AgNO₃ (> 99 % AgNO₃, Merck (Pty) Ltd, South Africa) under continuous magnetic stirring at 50 - 60 °C under dark conditions. After 25 min of reaction at this temperature, the resulting precipitate of the solution was recovered by decanting out of the AgNO₃ solution followed by washing with hot distilled water several times and dried in air under suction. The powders were then further dried at 300 - 350 °C in an oven for 3 hours.

6.3.2 Device Fabrication and Characterisation

The BHJ OSC devices based on poly(3-hexylthiophene-2,5-diyl):phenyl-C61-butyric-acid-methyl-ester (P3HT:PCBM) blend (both from Ossila Co. Ltd.) photoactive layer were fabricated on unpatterned ITO coated glass substrates. The substrates were first partially etched with acid solution (HCL:H₂O:HNO₃ at 48%:48%:4%) to remove part of the ITO. They were then successively cleaned in ultrasonic bath with detergent, distilled water, acetone and isopropanol, respectively, for 10 min waiting time. The samples were then dried with pressurized nitrogen, transferred into an oven at 120 °C and dried for 30 min. Thin layers of PEDOT:PSS (i) without DMSO and NPs, (ii) 5 wt% DMSO and 1 mg ZnO:Ag NPs, and (iii) 5 wt% DMSO and 1.5 mg ZnO:Ag NPs, were spin coated onto the samples at 3500 rpm. The samples were dried again in the oven under ambient atmosphere. The solar absorber medium was prepared from P3HT:PCBM (1:1) blend in chloroform based solution at a concentration of 20 mg/mL. The solution was sonicated for 3 hours at 40 °C to ensure a good miscibility and inter-dispersion of the polymer-fullerene blend. The absorber films were then spin coated onto the PEDOT:PSS films at 1300 rpm for 40 sec. The samples were then dried in an oven at 90 °C under nitrogen atmosphere for 10 min before being transferred into a vacuum deposition chamber (Edwards Auto 306) for deposition of lithium fluoride (LiF) and

aluminium (Al). Thin layers of LiF (0.5 nm) and Al (80 nm) were deposited onto the samples at a base pressure of 10^{-6} mBar resulting in devices with one of the following structures: ITO/PEDOT:PSS:NPs/P3HT:PCBM/LiF/Al or ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al. Schematic diagram for device structure depicted in Fig. 2 shows the various layers of the organic solar cell based on ZnO:Ag NPs incorporated into PEDOT:PSS anode buffer layer.

6.4 Results and Discussion

6.4.1 Morphological and Optical properties of ZnO:Ag NPs

The newly synthesized ZnO:Ag NPs were characterised by powder XRD using a PANalytical Empyrean diffractometer operated at 40 mA and 45 kV. The XRD pattern was collected at 2θ values ranging from 20 - 70 degrees with a step size (2θ) of 0.026° and scan step time of 83.64 s. Twelve intense peaks appear within the measurement range as shown in Fig. 3 (a). These intense peaks at 31.77° , 34.43° , 36.26° , 47.55° , 56.60° , 62.87° , 66.39° , 67.96° and 69.10° correspond to a wurtzite ZnO structure and matched very well with card number 04-006-2557. The XRD pattern reveals ZnO as the dominant material in the sample as would be expected. This has also been observed by Yildirim et al. where ZnO was doped at different concentrations of Ag. At 0.3 at.%, Yildirim et al. observed ZnO as being the only crystalline phase without any noticeable Ag peaks [29]. At 1 at.%, a low-intense peak was then observed at $2\theta = 38.11^\circ$ [29]. In current experiment, several peaks corresponding to metallic silver were observed at $2\theta = 38.20^\circ$, 44.4° and 64.59° . Fig. 3 (a) shows the Ag peaks at 38.20° , 44.40° and 64.59° corresponding to (111), (200) and (220) Ag planes, respectively. These diffraction peaks correspond very well with literature results [34, 36, 37]. The presence of Ag peaks in the XRD pattern indicates successful formation of crystalline Ag NPs on the ZnO surface. The Ag peaks correspond to face centred cubic structure of silver based on the standard values for bulk silver (card no.: 00-901-2431). There are no other crystalline impurities observed in the XRD pattern.

The crystalline size (D) of the ZnO:Ag NPs was determined using the Debye-Scherrer's equation as

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (6.1)$$

where λ is the x-ray wavelength, β is the full width at half maximum (FWHM) of an x-ray diffraction peak. The crystallite sizes of the NPs ranged between 34 nm and 51 nm, and are shown in Table 6.1. The lattice parameters, a and c , of the ZnO hexagonal structure were determined using the equation [38]

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (6.2)$$

with the first-order approximation, $n = 1$;

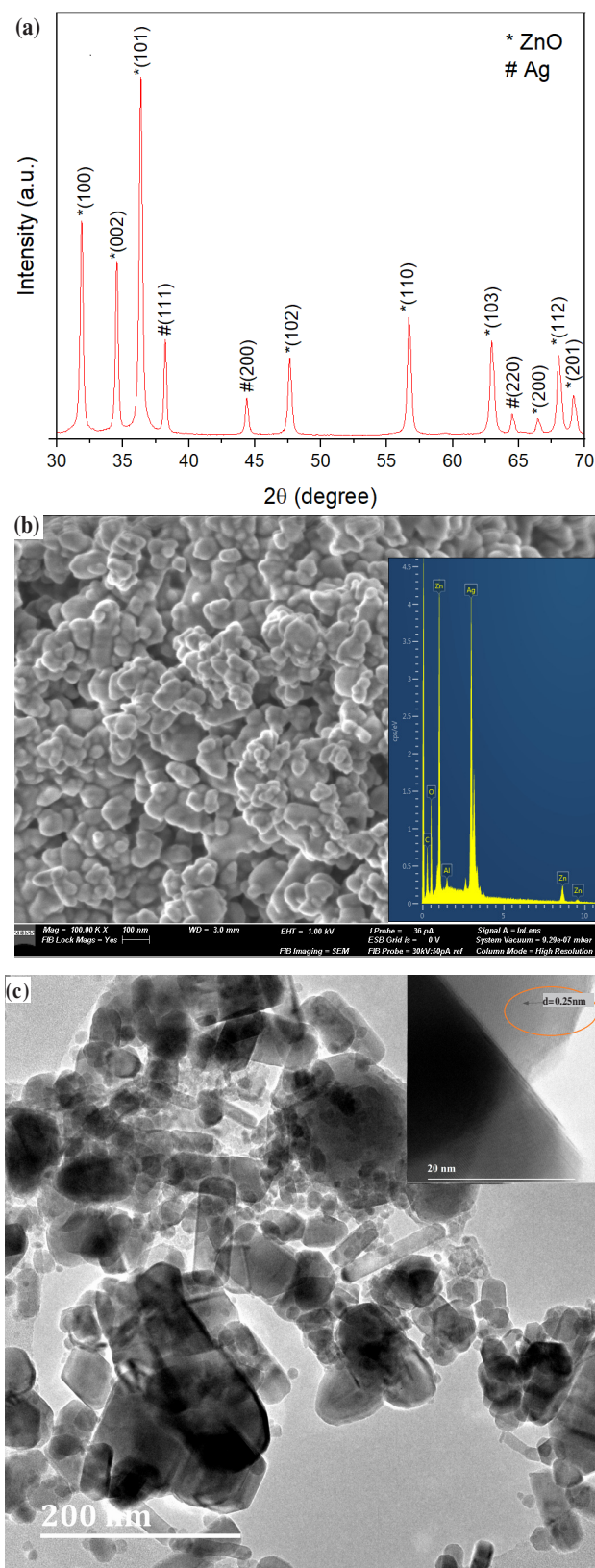


Figure 6.3: (a) X-ray diffraction pattern for ZnO:Ag nanoparticles. (b) Shows FIBSEM images of the synthesized ZnO:Ag NPs.

$$\sin^2\theta = \frac{\lambda^2}{4a^2} \left(\frac{4}{3}(h^2 + hk + k^2) + \left(\frac{a}{c}\right)^2 l^2 \right) \quad (6.3)$$

The a and c lattice parameters were determined for the (100) and (002) reflection planes, respectively, as follows

$$a = \frac{\lambda}{\sqrt{3}\sin\theta} \quad (6.4)$$

$$c = \frac{\lambda}{\sin\theta} \quad (6.5)$$

and were found to be $a = 3.23 \text{ \AA}$ and $c = 5.18 \text{ \AA}$. The lattices a and c match very well with lattice constants reported in literature for ZnO [38].

Table 6.1: Peak position, FWHM, d-spacing, crystallite size (D) and hkl values for the ZnO:Ag NPs annealed at 350 °C for 3 h under ambient

Pos.[° 2 θ]	FWHM	d _{hkl} (Å)	D(nm)	(hkl)
31.77	0.2303	2.80	35.88	100
34.43	0.2047	2.59	40.65	002
36.26	0.2047	2.47	40.85	101
47.55	0.2558	1.91	33.95	102
56.60	0.2184	1.62	41.34	110
62.87	0.2184	1.47	42.66	103
66.39	0.1872	1.41	50.74	200
67.96	0.1872	1.38	51.21	112
69.10	0.1872	1.36	51.55	201

The inter-planar spacings (d-spacing, d_{hkl}) were also determined from the XRD data using Bragg's Law [39]

$$n\lambda = 2d_{hkl}\sin\theta \quad (6.6)$$

where n is the order of diffraction. The d_{hkl} values are shown in Table 6.1. The obtained d-spacing values for the planes (100), (101) and (103) matched very well with literatures and card number JCPDS 36-14551 [40]. The calculated values are 2.80 Å, 2.47 Å and 1.47 Å and compare very well with 2.81 Å, 2.47 Å and 1.47 Å [40]. Similarly for the d-spacings shown in the Table 6.1 for the planes (110), (102) and (002), they matched very well with the values, 1.60 Å, 1.90 Å and 2.60 Å, from Yildirim et al. obtained by fast Fourier transform and inverse fast Fourier transform for the planes (110), (102) and (002) [29].

FIBSEM and HRTEM images of the ZnO:Ag NPs were taken and are shown in Fig. 3 (b) and Fig. 3 (c), respectively. Fig. 3 (b) shows randomly arranged irregular sized and shaped ZnO NPs coated with Ag. The FIBSEM images also show agglomeration of the nanoparticles into larger clusters. The EDS (insert of Fig. 3 (b)) confirms the presence of Zn, O, Ag and a very small amount of Al. The aluminium observed is due to the aluminium used as dopant to stabilise the ZnO NPs. The HRTEM image shown in Fig. 3 (c) confirms the nanocomposite consisted of differently shaped and sized ZnO NPs observed in the SEM

image Fig. 3 (b). These included irregular shapes, nanorods and nanospheres. The insert in Fig. 3 (c) shows a d-spacing of $d = 2.5 \text{ \AA}$ which closely matches with that of the (101) plane with d-spacing of $2.47 \text{ \AA}$ as obtained from the XRD data.

6.4.2 Optical absorption

The optical properties of the absorber films are affected by the shape, size and dielectric environment around the NPs. Figure 6.4 shows UV-vis spectrum of ZnO:Ag in deionized water suspension and from absorber films with/without the NPs in the PEDOT:PSS layer. The absorption spectrum of NPs powder (Figure 4 (b)) shows a sharp absorption peak at 364 nm corresponding to the ZnO. This absorption peak is due to band to band transition in ZnO molecules, where electrons are excited from the valence band to the conduction band [39]. The ZnO:Ag absorption peak is outside the range of absorbency of P3HT:PCBM blend. Therefore, both of them do not overlap on the photoactive layer absorption. The sharpness of the absorption peak of the NPs suggest nano-sized ZnO:Ag NPs with a narrow size distribution. The UV-vis spectra does not show any significant Ag absorption peak suggesting that the Ag layer was very thin and the NPs mainly consisted of ZnO. Nevertheless, according to the measured optical absorptions taken from absorber films with ZnO:Ag NPs, as provided in Fig. 4 (a), higher absorption intensities are recorded from doped films compared to the pristine one. Moreover, there are evidence of pronounced new peaks intensities at (650 – 750)nm and above 800 nm. The broad band absorbency near (650 – 750)nm could be attributed to LSPR from rod like structures of the nano-particles while the one above 800 nm could be due to far field scattering.

This enhanced absorbance is attributed to forward light scattering due to the NPs incorporation into hole transport buffer layer at the front electrode. Scattering of the incident light into the photoactive layer at different angles increases the optical path length thereby more photons get absorbed. This absorption enhancement is very crucial as it allows the photoactive layer thickness to be kept within the range 120 - 250 nm favourable for the short diffusion length and low carrier mobility in polymers. The doped OPV films show a red shift of the P3HT absorption peak in the range 510 - 565 nm. This red shift is attributed to thermal annealing of the thin films. Similar red shift in P3HT films upon thermal annealing has been reported before [41]. The difference in the red shifting in devices with 1.0 mg and 1.5 mg ZnO:Ag NPs is due to the fact that the later samples were kept longer time in the oven compared to the former. The UV-vis of the films with NPs show the ZnO:Ag absorption peak red shifted to 380 nm and 410 nm for PEDOT:PSS with 1.5 mg and 1.0 mg ZnO:Ag NPs, respectively. This LSPR shift is attributed to a change in the dielectric environment around the NPs.

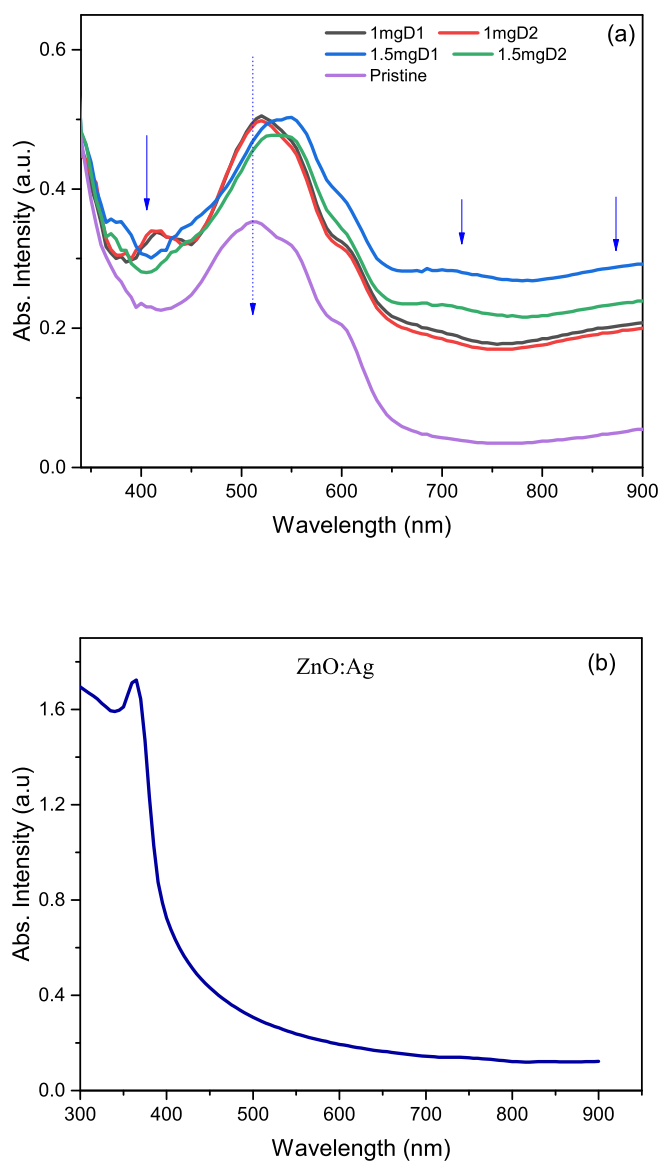


Figure 6.4: Optical absorption of (a) ZnO:Ag NPs in deionized water and (b) device films w/o ZnO:Ag NPs in PEDOT:PSS.

6.4.3 Device characterization

PEDOT:PSS films have been used extensively in OSC as charge transport buffer layer for selective conduction of holes. This is due to its noble properties such as mechanical flexibility, transparency to visible light, high electrical conductivity and solution processability. Several methods were used to enhance the properties of PEDOT:PSS a better role as HTL. These include doping with plasmon nanoparticles and/or use solvents additives such as dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), and ethylene glycol (EG) [42–45]. In particular, doping PEDOT:PSS with DMSO has been reported to improve its electrical conductivity by 100 fold at a doping concentration of 5 wt% [42, 46]. In this study, PEDOT:PSS was doped with 5 wt% DMSO to improve its electrical conductivity. The improved PEDOT:PSS conductivity is attributed to the rearrangement of the PEDOT:PSS morphology resulting to better connections between the conducting chains [47]. The structure of PEDOT chains changes from benzoid to quinoid upon treatment with DMSO, whereby the PEDOT chains with coiled structure attain a linear conformation [15, 48]. Keawprajak et al. studied the effects of solvent additives (TMS and DMSO) on molecular arrangements of PEDOT:PSS using Raman spectroscopy. Upon the addition of the additives on PEDOT:PSS, the Raman spectroscopy showed the disappearance of the vibration shoulder associated with the benzoid structure [15]. This conformational change of the PEDOT:PSS chains should then create better inter-connected pathways for charge transport perpendicular to the film [47]. Figure 5 shows a graphical representation of the J-V characteristics of the OSC devices measured under AM 1.5G illumination with/without ZnO:Ag doped HTL. The figure shows a significant increase in the short-circuit current density from ca. 10 mA cm^{-2} for pristine devices to a highest of ca. 16 mA cm^{-2} for devices with 1.5 mg ZnO:Ag NPs and 5 wt% DMSO in the PEDOT:PSS film.

This is an increase of close to 70 % in J_{sc} compared to that of the pristine devices. The open-circuit voltage remains relatively the same and only varies within the range of 0.55 V to 0.58 V which maybe due to well-established ohmic contact between the anode and the photoactive layer. The treatment of PEDOT:PSS with solvent additives may result in reduced work function. Zhang et al. reported a work function reduction on solvent treated PEDOT:PSS of about 0.2 - 0.3 eV lower than that of pristine PEDOT:PSS [47]. This reduction, in addition to leakage currents, may results in lowered V_{oc} . However, in this study the V_{oc} slightly increased from 0.55 V to 0.58 V at 5 wt% DMSO and 1 mg ZnO:Ag NPs doping. It however dropped again to as low as 0.55 V as the NP concentration was increased to 1.5 mg. This reduction can then be attributed to leakage current effects due to the increased metal NP concentration in the anode buffer layer. Metallic NPs can be used in OSCs to improve device performance either by utilising the near-field effect of LSPR or the far-field effect (forward light scattering) properties of NPs. However, the near-field around the NPs mainly distributes laterally along the thin film when incident light is normal to film and decays exponentially with distance from the plasmonic NP. Therefore, the near-field will

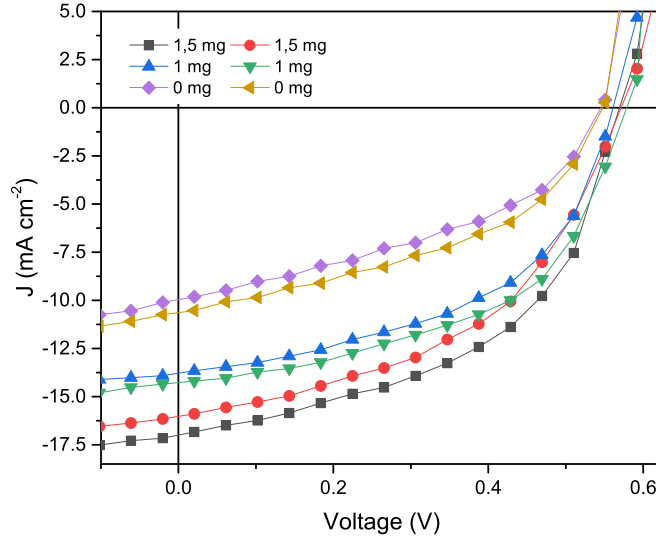


Figure 6.5: The current-voltage characteristic under AM 1.5G illumination at 100 mW/cm^2 of P3HT:PCBM based solar cells prepared with pristine PEDOT:PSS and PEDOT:PSS doped with 5 wt% and 1 mg or 1.5 mg ZnO:Ag NPs.

have insignificant effect on charge generation and dissociation in the photoactive layer when the NP are incorporated within the buffer layer. As a result, this study aims to utilize the far-field effect of the ZnO:Ag NPs to scatter incident light into the photoactive layer thereby increasing its optical path length. An increased optical path length will results to more photons being absorbed in the photoactive layer and improved device performance. This is evident on the pronounced peak intensities in Figure 4 (a). Table II shows a summary of device performance parameters for pristine, and DMSO and ZnO:Ag NP doped OPV devices. The devices with 1 mg and 1.5 mg ZnO:Ag NPs show significantly increased PCEs compared to pristine devices. The devices incorporated with NPs had also been doped with equal amounts (5 wt% of PEDOT:PSS) of DMSO. Therefore, the higher NP concentration greatly improved PCE to a maximum of 4.88 % for 1.5 mg of ZnO:Ag NPs. This increase corresponds to 90 % PCE enhancement from a PCE of 2.56 %. The FF increased from 43.95 % to 50.80 % and the J_{sc} increased from 10.65 mA cm^{-2} to a maximum of 16.88 mA cm^{-2} . The incorporation of the NPs into the buffer layer may increase its root-mean-square surface roughness thereby increasing the effective surface area between the buffer layer and the photoactive layer. This increased surface area may lead to enhancement in charge collection and ultimately in the FF and J_{sc} . ZnO has a wide band gap and high electron mobility than TiO_2 [49]. Hence, it can be used as an electron transport buffer layer. A high concentration of ZnO:Ag NPs in the hole transport layer would result to ZnO:Ag being in contact with the photoactive layer thereby leaking electrons into PEDOT:PSS and creating charge recombination. This would then lead to increased recombination of electron-hole pairs in the hole transport layer and reduce solar cell performance. It is to be noted

Table 6.2: Summary of performance parameters of BHJ devices based on P3HT:PCBM mixed with Ag@Cu plasmonic nanoparticles under AM 1.5G illumination at 100 mW/cm²

ZnO:Ag (mg)	V _{oc} V	J _{sc} mA cm ⁻²	FF (%)	PCE (%)	μ ₀ (cm ² V ⁻¹ s ⁻¹)
0	0.55	10.65	43.95	2.56	1.83×10 ⁻⁵
1	0.58	15.73	47.97	4.34	7.50×10 ⁻²
1.5	0.57	16.88	50.80	4.88	8.26×10 ⁻²

here that the effects of NPs are clearly demonstrated in the optical properties of the absorber films as discussed in the previous sections.

6.4.4 Charge Transport

To study the charge transport properties of the devices, their charge mobilities were calculated from the space charge limited current (SCLC). At steady-state conditions, charge inside the device saturates, charge injection then only occurs to replace charge extracted on the opposite electrode [50]. The SCLC region of current density measured under dark condition can be compared with Mott-Gurney law given as follows [50, 51]

$$J_{sclc} = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{L^3} \quad (6.7)$$

where ϵ_0 is the permittivity of free-space, ϵ_r is the dielectric constant of the medium and L is the layer thickness. Where charge changes with the applied electric field, μ is then given by

$$\mu = \mu_0 \exp(\gamma \sqrt{E}) \quad (6.8)$$

where μ_0 is the zero-field mobility, γ is the field-dependence effect factor, and $E=V/L$ is the applied electric field. Eq. 6.7 then takes the form

$$J_{sclc} = \frac{9}{8} \epsilon_0 \epsilon_r \mu_0 \exp(0.89\gamma \sqrt{V/L}) \frac{V^2}{L^3} \quad (6.9)$$

taking into account that the field is not uniform across the semiconductor layer. The charge mobility, μ_0 , and field-dependence factor, γ , can then be obtained in practical by fitting the Mott-Gurney law in Eq. 6.9 to the J-V experimental data obtained from the SCLC region where $J \propto V^2$. The SCLC method for obtaining charge mobility is very prone to misinterpretation [51] and mobility values can vary by more than one order of magnitude on nominally identical devices [50]. The obtained charge mobilities are summarised in Table 6.2.

Upon the incorporation of the NPs in the hole transport layer, the field dependent charge mobility μ increased by three orders of magnitude from 10⁻⁵ cm²V⁻¹s⁻¹ to 10⁻² cm²V⁻¹s⁻¹ with the concentration of 1.5 mg ZnO:Ag NPs yielding the highest charge mobility of $\mu=8.26 \times 10^2$ cm²V⁻¹s⁻¹. This suggest that hole and electron mobilities were increased

and a more balanced charge transport was attained. Balanced charge transport could result in reduced effects of space charge formation and alleviate charge recombination in the devices [52]. Arbab et al mentioned that good distribution of NPs in the transport layer may also favour inter-facial contacts with the anode which is responsible for improved charge transport process manifested in improved FF and V_{oc} [7].

6.5 Conclusion

Silver coated ZnO NPs were successfully incorporated into PEDOT:PSS hole transport layer together with 5 wt.% DMSO solvent additives. The various structures of the NPs are evident on the TEM and SEM images, which are in a good agreement with the analysis of XRD data taken from NPs powder. The V_{oc} of the devices with or without the NPs and DMSO remained relatively unchanged in the range of 0.55 - 0.59 V. However, the devices' FF and J_{sc} have shown increment by 16 % and 58 %, respectively, due to the forward light scattering effect of the NPs embedded within PEDOT:PSS. Solvent additive DMSO also enhanced the conductivity of the PEDOT:PSS thereby improving charge transport processes in the doped devices. The NPs and solvent treatment of the PEDOT:PSS resulted in improved device performance with growth in PCE from 2.56 % to 4.88 %. The ZnO:Ag nano-particles are environmentally stable and are compatible to roll to roll device fabrication.

Bibliography

References

- [1] Mbuyise, X. G., Arbab, E. A. and Mola, G. T., 2019. The effect of a trimetallic nanocomposite in the solar absorber layer of organic solar cells. *RSC advances*, 9(11), pp.6070-6076.
- [2] Dlamini, M. W. and Mola, G. T., 2019. Near-field enhanced performance of organic photovoltaic cells. *Physica B: Condensed Matter*, 552, pp.78-83.
- [3] Liu, Z., Seo, S. and Lee, E. C., 2017. Correlation between the performance of organic bulk-heterojunction solar cells and the molecular structures of alcohol solvents. *Journal of Applied Polymer Science*, 134(1).
- [4] Kwon, S., Kang, H., Lee, J. H., Lee, J., Hong, S., Kim, H. and Lee, K., 2017. Effect of processing additives on organic photovoltaics: recent progress and future prospects. *Advanced Energy Materials*, 7(10), p.1601496.
- [5] Baek, S. W., Park, G., Noh, J., Cho, C., Lee, C. H., Seo, M. K., Song, H. and Lee, J. Y., 2014. Au@ Ag core-shell nanocubes for efficient plasmonic light scattering effect in low bandgap organic solar cells. *ACS nano*, 8(4), pp.3302-3312.
- [6] Chen, B., Zhang, W., Zhou, X., Huang, X., Zhao, X., Wang, H., Liu, M., Lu, Y. and Yang, S., 2013. Surface plasmon enhancement of polymer solar cells by penetrating Au/SiO₂ core/shell nanoparticles into all organic layers. *Nano Energy*, 2(5), pp.906-915.
- [7] Arbab, E. A. A. and Mola, G. T., 2019. Metals decorated nanocomposite assisted charge transport in polymer solar cell. *Materials Science in Semiconductor Processing*, 91, pp.1-8.
- [8] Zhang, W., Bi, X., Zhao, X., Zhao, Z., Zhu, J., Dai, S., Lu, Y. and Yang, S., 2014. Isopropanol-treated PEDOT: PSS as electron transport layer in polymer solar cells. *Organic Electronics*, 15(12), pp.3445-3451.
- [9] Jeong, W., Gwon, G., Ha, J. H., Kim, D., Eom, K. J., Park, J. H., Kang, S. J., Kwak, B., Hong, J. I., Lee, S. and Hyun, D. C., 2021. Enhancing the conductivity of

- PEDOT: PSS films for biomedical applications via hydrothermal treatment. *Biosensors and Bioelectronics*, 171, p.112717.
- [10] Xu, L., Li, Y., Zhang, C., Liu, Y., Zheng, C., Lv, W., Li, M., Chen, Y., Huang, W. and Chen, R., 2020. Improving the efficiency and stability of inverted perovskite solar cells by CuSCN-doped PEDOT: PSS. *Solar Energy Materials and Solar Cells*, 206, p.110316.
- [11] Duan, C., Liu, Z., Yuan, L., Zhu, H., Luo, H. and Yan, K., 2020. PEDOT: PSS-Metal Oxide Composite Electrode with Regulated Wettability and Work Function for High-Performance Inverted Perovskite Solar Cells. *Advanced Optical Materials*, 8(17), p.2000216.
- [12] Kadem, B. Y., Al-Hashimi, M., Hasan, A. S., Kadhim, R. G., Rahaq, Y. and Hassan, A. K., 2018. The effects of the PEDOT: PSS acidity on the performance and stability of P3HT: PCBM-based OSCs. *Journal of Materials Science: Materials in Electronics*, 29(22), pp.19287-19295.
- [13] Wong, K. W., Yip, H. L., Luo, Y., Wong, K. Y., Lau, W. M., Low, K. H., Chow, H. F., Gao, Z. Q., Yeung, W.L. and Chang, C.C., 2002. Blocking reactions between indium-tin oxide and poly (3, 4-ethylene dioxythiophene): poly (styrene sulphonate) with a self-assembly monolayer. *Applied physics letters*, 80(15), pp.2788-2790.
- [14] Hu, Z., Zhang, J. and Zhu, Y., 2014. Effects of solvent-treated PEDOT: PSS on organic photovoltaic devices. *Renewable Energy*, 62, pp.100-105.
- [15] Keawprajak, A., Koetnuyom, W., Piyakulawat, P., Jiramitmongkon, K., Pratontep, S. and Asawapirom, U., 2013. Effects of tetramethylene sulfone solvent additives on conductivity of PEDOT: PSS film and performance of polymer photovoltaic cells. *Organic Electronics*, 14(1), pp.402-410.
- [16] Wilson, P., Lekakou, C. and Watts, J. F., 2013. In-plane conduction characterisation and charge transport model of DMSO co-doped, inkjet printed Poly (3, 4-ethylenedioxythiophene): Polystyrene sulfonate (PEDOT: PSS). *Organic Electronics*, 14(12), pp.3277-3285.
- [17] Namkoong, G., Younes, E. M., Abdel-Fattah, T. M., El-Maghraby, E. M., Elsayed, A. H. and Elazm, A. A., 2015. Aging process of PEDOT: PSS dispersion and robust recovery of aged PEDOT: PSS as a hole transport layer for organic solar cells. *Organic Electronics*, 25, pp.237-244.
- [18] Baek, S. W., Park, G., Noh, J., Cho, C., Lee, C. H., Seo, M. K., Song, H. and Lee, J. Y., 2014. Au@ Ag core-shell nanocubes for efficient plasmonic light scattering effect in low bandgap organic solar cells. *ACS nano*, 8(4), pp.3302-3312.

- [19] Mola, G. T. and Arbab, E. A., 2017. Bimetallic nanocomposite as hole transport co-buffer layer in organic solar cell. *Applied Physics A*, 123(12), p.772.
- [20] Tang, M., Sun, B., Zhou, D., Gu, Z., Chen, K., Guo, J., Feng, L. and Zhou, Y., 2016. Broad-band plasmonic Cu-Au bimetallic nanoparticles for organic bulk heterojunction solar cells. *Organic Electronics*, 38, pp.213-221.
- [21] Li, S., Miao, P., Zhang, Y., Wu, J., Zhang, B., Du, Y., Han, X., Sun, J. and Xu, P., 2021. Recent advances in plasmonic nanostructures for enhanced photocatalysis and electrocatalysis. *Advanced Materials*, 33(6), p.2000086.
- [22] Masson, J. F., 2020. Portable and field-deployed surface plasmon resonance and plasmonic sensors. *Analyst*, 145(11), pp.3776-3800.
- [23] Clavero, C., 2014. Plasmon-induced hot-electron generation at nanoparticle/metal-oxide interfaces for photovoltaic and photocatalytic devices. *Nature Photonics*, 8(2), pp.95-103.
- [24] Liu, J., He, H., Xiao D., Yin S., Ji W., Jiang, S., Luo, D., Wang, B. and Liu Y., 2018. Recent advances of plasmonic nanoparticles and their applications. *Materials*, 11(10), p.1833.
- [25] X. C. Ma, Y. Dai, L. Yu and B. B. Huang, 2016. Energy transfer in plasmonic photocatalytic composites. *Light: Science & Applications*, 5(2), pp.e16017-e16017.
- [26] Linic, S., Christopher, P. and D. B. Ingram, 2011. Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy. *Nature materials*, 10(12), pp.911-921.
- [27] Li, J., Cushing, S. K., Meng, F., Senty, T. R., Bristow, A. D. and Wu, N., 2015. Plasmon-induced resonance energy transfer for solar energy conversion. *Nature Photonics*, 9(9), pp.601-607.
- [28] Kholmicheva, N., Romero, L. R., Cassidy, J. and Zamkov, M., 2018. Prospects and applications of plasmon-exciton interactions in the near-field regime. *Nanophotonics*, 8(4), pp.613-628.
- [29] Yildirim, Ö. A., Unalan, H. E. and Durucan, C., 2013. Highly efficient room temperature synthesis of silver-doped zinc oxide (ZnO: Ag) nanoparticles: structural, optical, and photocatalytic properties. *Journal of the American Ceramic Society*, 96(3), pp.766-773.
- [30] Wu, J. J. and Tseng, C.H., 2006. Photocatalytic properties of nc-Au/ZnO nanorod composites. *Applied Catalysis B: Environmental*, 66(1-2), pp.51-57.
- [31] Sarma, B. and Sarma, B. K., 2018. Role of residual stress and texture of ZnO nanocrystals on electro-optical properties of ZnO/Ag/ZnO multilayer transparent conductors. *Journal of Alloys and Compounds*, 734, pp.210-219.

- [32] Fageria, P., Gangopadhyay, S. and Pande, S., 2014. Synthesis of ZnO/Au and ZnO/Ag nanoparticles and their photocatalytic application using UV and visible light. *Rsc Advances*, 4(48), pp.24962-24972.
- [33] Wang, P., Wang, H., Mao, Y., Zhang, H., Ye, F., Liu, D. and Wang, T., 2020. Organic ligands armored ZnO enhances efficiency and stability of CsPbI₂Br perovskite solar cells. *Advanced Science*, 7(21), p.2000421.
- [34] Saravanan, R., Karthikeyan, N., Gupta, V. K., Thirumal, E., Thangadurai, P., Narayanan, V. and Stephen, A. J. M. S., 2013. ZnO/Ag nanocomposite: an efficient catalyst for degradation studies of textile effluents under visible light. *Materials Science and Engineering: C*, 33(4), pp.2235-2244.
- [35] Jadhav, J. and Biswas, S., 2016. Surface plasmon enhanced near-UV emission in monodispersed ZnO: Ag core-shell type nanoparticles synthesized by a wet chemical method. *Superlattices and Microstructures*, 91, pp.8-21.
- [36] Jabbar, A. H., Al-janabi, H. S. O., Hamzah, M. Q., Mezan, S. O., Tumah, A.N. and Ameruddin, A. S. B., 2020. Green Synthesis and Characterization of Silver Nanoparticle (AgNPs) using Pandanus Atrocarpus Extract". *International Journal of Advanced Science and Technology*, 29(3), pp.4913-4922.
- [37] Aravind, M., Ahmad, A., Ahmad, I., Amalanathan, M., Naseem, K., Mary, S.M.M., Parvathiraja, C., Hussain, S., Algarni, T.S., Pervaiz, M. and Zuber, M., 2021. Critical green routing synthesis of silver NPs using jasmine flower extract for biological activities and photocatalytical degradation of methylene blue. *Journal of Environmental Chemical Engineering*, 9(1), p.104877.
- [38] Bindu, P. and Thomas, S., 2014. Estimation of lattice strain in ZnO nanoparticles: X-ray peak profile analysis. *Journal of Theoretical and Applied Physics*, 8(4), pp.123-134.
- [39] AL-Asady, Z. M., AL-Hamdani, A. H. and Hussein, M. A., 2020, March. Study the optical and morphology properties of zinc oxide nanoparticles. In *AIP Conference Proceedings* (Vol. 2213, No. 1, p. 020061). AIP Publishing LLC.
- [40] Kuriakose, S., Choudhary, V., Satpati, B. and Mohapatra, S., 2014. Enhanced photocatalytic activity of Ag-ZnO hybrid plasmonic nanostructures prepared by a facile wet chemical method. *Beilstein journal of nanotechnology*, 5(1), pp.639-650.
- [41] Mihailetschi, V. D., Xie, H. X., de Boer, B., Koster, L. A. and Blom, P. W., 2006. Charge transport and photocurrent generation in poly (3-hexylthiophene): methanofullerene bulk-heterojunction solar cells. *Advanced Functional Materials*, 16(5), pp.699-708.

- [42] Wilson, P., Lekakou, C. and Watts, J. F., 2013. In-plane conduction characterisation and charge transport model of DMSO co-doped, inkjet printed Poly (3, 4-ethylenedioxythiophene): Polystyrene sulfonate (PEDOT: PSS). *Organic Electronics*, 14(12), pp.3277-3285.
- [43] Dimitriev, O. P., Grinko, D. A., Noskov, Y. V., Ogurtsov, N. A. and Pud, A. A., 2009. PEDOT: PSS films—Effect of organic solvent additives and annealing on the film conductivity. *Synthetic metals*, 159(21-22), pp.2237-2239.
- [44] Yeo, J. S., Yun, J. M., Kim, D. Y., Kim, S. S. and Na, S. I., 2013. Successive solvent-treated PEDOT: PSS electrodes for flexible ITO-free organic photovoltaics. *Solar energy materials and solar cells*, 114, pp.104-109.
- [45] Crispin, X., Jakobsson, F. L. E., Crispin, A., Grim, P. C. M., Andersson, P., Volodin, A. V., Van Haesendonck, C., Van der Auweraer, M., Salaneck, W. R. and Berggren, M., 2006. The origin of the high conductivity of poly (3, 4-ethylenedioxythiophene)-poly (styrenesulfonate)(PEDOT-PSS) plastic electrodes. *Chemistry of Materials*, 18(18), pp.4354-4360.
- [46] Kim, J. Y., Jung, J. H., Lee, D. E. and Joo, J., 2002. Enhancement of electrical conductivity of poly (3, 4-ethylenedioxythiophene)/poly (4-styrenesulfonate) by a change of solvents. *Synthetic Metals*, 126(2-3), pp.311-316.
- [47] Hu, Z., Zhang, J. and Zhu, Y., 2014. Effects of solvent-treated PEDOT: PSS on organic photovoltaic devices. *Renewable Energy*, 62, pp.100-105.
- [48] Ouyang, J., Xu, Q., Chu, C. W., Yang, Y., Li, G. and Shinar, J., 2004. On the mechanism of conductivity enhancement in poly (3, 4-ethylenedioxythiophene): poly (styrene sulfonate) film through solvent treatment. *Polymer*, 45(25), pp.8443-8450.
- [49] Dehghan, M. and Behjat, A., 2019. Deposition of zinc oxide as an electron transport layer in planar perovskite solar cells by spray and SILAR methods comparable with spin coating. *RSC advances*, 9(36), pp.20917-20924.
- [50] Blakesley, J. C., Castro, F. A., Kylberg, W., Dibb, G. F., Arantes, C., Valaski, R., Cremona, M., Kim, J. S. and Kim, J. S., 2014. Towards reliable charge-mobility benchmark measurements for organic semiconductors. *Organic Electronics*, 15(6), pp.1263-1272.
- [51] Röhr, J.A., Moia, D., Haque, S. A., Kirchartz, T. and Nelson, J., 2018. Exploring the validity and limitations of the Mott–Gurney law for charge-carrier mobility determination of semiconducting thin-films. *Journal of Physics: Condensed Matter*, 30(10), p.105901.

-
- [52] Li, J., Zhang, X., Liu, C., Li, Z., He, Y., Zhang, Z., Shen, L., Guo, W. and Ruan, S., 2017. The role of polymer dots on efficiency enhancement of organic solar cells: Improving charge transport property. *Optics Communications*, 395, pp.127-132.

Chapter 7

Manganese doped zinc sulphide nanoparticles as scattering centres in P3HT PCBM based solar cells

7.1 Abstract

Manganese doped zinc sulphide (ZnS:Mn) nanoparticles (NPs) were successfully synthesized via a simple solution process and incorporated into the photoactive layer of P3HT:PCBM based organic photovoltaic devices (OPVs). The structural, morphological and optical properties of the NPs were investigated using X-ray diffraction (XRD), scanning electron microscopy, energy dispersive spectroscopy and optical spectroscopy. The XRD pattern of the ZnS:Mn NPs shows the formation of a zinc wurtzite crystalline structure similar to that of undoped ZnS. Incorporation of the ZnS:Mn NPs into the photoactive layer of OPVs at 1.5 wt% and 3 wt% concentration improved the device optical absorption and current density leading to an improved power conversion efficiency (PCE). The concentration of 5 wt% increased optical absorption but deteriorated the electrical properties of the devices. The short-circuit current density increased by a maximum of 34 % with the PCE increasing by a maximum of 41 % compared to pristine devices.

7.2 Introduction

Donor/acceptor bulk heterojunction based photovoltaic devices have been investigated tremendously in the past few decades and have shown great potential as next generation of renewable energy sources due to their advantages of low cost, potential for roll-to-roll fabrication, flexibility and low weight [1, 2]. Organic photovoltaics (OPVs) have shown tremendous increase in their power conversion efficiencies (PCEs) to over 16 % [3, 4] in the past few years. Such PCEs for OPVs put them on par with the efficiencies of their inorganic counter parts with PCE values typically in the range 15 - 18 % [5]. However, due to the relatively low carrier

mobility ($\mu \approx 10^{-4} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) [3, 5, 6] and typically short diffusion lengths (5 - 10 nm) in OPV materials, the active layer thickness is limited to about 150 nm or less for better charge carrier diffusion and extraction at the electrodes. The thin photoactive layer limits optical absorption and severely hinders efficiency enhancement in OPVs. To overcome this drawback, several strategies have been employed to improve optical absorption in OPVs while keeping the photoactive layer thickness very thin. These include the use of metal gratings, reflective back electrode, and metallic nanoparticles (MNPs). Of most interest is the use of MNPs which can enhance light trapping and photon management in OPV devices. Depending on their size, shape and distribution in OPV devices, MNPs can enhance device efficiency either by absorbing light through localized surface plasmon (near-field) creating very large electric field around the MNPs or by scattering light (far-field) in different directions inside the device. Light scattering by the nanoparticles (NPs) can significantly increase optical path length inside OPV devices [5, 7–10], thereby enhancing photon absorption. Local surface plasmon resonance (LSPR) is the periodic oscillation of conduction electrons on the metal NP surface and exists at the metal-dielectric interface [11]. The LSPR depends on the size, shape, distribution and the wavelength of the incident light. The large electric field created by LSPR around the NPs can excite electron-hole pairs in the photoactive layer via coupling of the large plasmonic dipole to the electron-hole pair dipole [12]. This intense electric field quickly decays with distance from the metallic NPs. The most widely used metallic NPs are gold (Au) and silver (Ag) due to their excellent LSPR and light scattering properties [5, 7, 9]. However, due to their scarcity and cost, several alternative NPs which are abundant and cheaper have also been investigated. We report here results of zinc sulphide (ZnS) doped with manganese incorporated into the photoactive layer of P3HT:PCBM based OPVs. ZnS is one of the semiconductors with promising opto-electronic properties. It has been doped with several transition metals such as manganese and copper [13–15].

7.3 Materials and Methods

7.3.1 Materials:

Chemical materials used for the fabrication of OPVs were purchased and used as received without further processing except the synthesis of ZnS:Mn NPs. Poly(3-hexylthiophene) (P3HT), phenyl-C₇₁-butyric acid methyl ester (PCBM) and PEDOT:PSS were purchased from Ossila Co. Ltd. Zinc nitrate hexahydrate and sodium sulphide nonahydrate were purchased from Sigma-Aldrich and Merck, respectively. Manganous chloride tetrahydrate was purchased from Associated Chemical Enterprises, Johannesburg. Polyvinylpyrrolidone (PVP, (C₆H₉NO)_n, MW of 25 000 - 30 000) LAB.

7.3.2 Synthesis and characterization of ZnS nanoparticles:

The ZnS:Mn NPs were synthesized using a simple solution method in air as explained in [16] with some modifications. In this study, 2.5 g of sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) was dissolved in 12.5 mL deionized water and stirred for 1 hour at room temperature. On separate beakers, 2 g of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 0.5 g of manganous chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) were each dissolved in 12.5 mL deionized water and stirred. The zinc nitrate and manganous chloride solutions were then mixed together and then poured into the sodium sulphide solution and stirred for 4 hours at room temperature. The resulting precipitate was centrifuged and separated from the solution. It was then washed with methanol repeatedly to remove impurities. The precipitate was then dried overnight at 150 °C in a convection oven. The morphology and elemental composition of the ZnS:Mn NPs powder were investigated using a scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDAX) analysis. X-ray diffraction data of ZnS:Mn was then acquired on a PANalytical Empyrean diffractometer operated at 45 kV and 40 mA. The pattern was collected from 2θ values of 20 to 65 degrees, step size of 0.02 degrees and an acquisition time of 127 seconds per step.

7.3.3 Device Fabrication

P3HT:PCBM blend based organic solar cells mixed with ZnS:Mn plasmonic nanoparticles were fabricated on unpatterned ITO coated glass substrates. The substrates were first partially etched with acid solution ($\text{HCL}:\text{H}_2\text{O}:\text{HNO}_3$ at 48%:48%:4%) to remove part of the ITO. They were then successively cleaned in ultrasonic bath with detergent, distilled water, acetone and isopropanol, respectively, for 10 min waiting time. The samples were then dried in an oven at 120 °C for 30 min. A thin layer of PEDOT:PSS was spin coated onto the samples at 3500 rpm. The samples were dried again in the oven under ambient atmosphere. Three P3HT:PCBM (1:1) blend solutions with 1.5 wt%, 3 wt% or 5 wt% of ZnS:Mn NPs were prepared in chloroform and sonicated for 3 hours at 40 °C to ensure good dispersion of the NPs and miscibility of the polymer-fullerene blend.

The P3HT:PCBM solutions incorporated with ZnS:Mn NPs were then spin coated onto the PEDOT:PSS film at 1300 rpm for 40 sec. The samples were then dried in oven under nitrogen atmosphere for 10 min before being transferred into a vacuum deposition chamber (Edwards Auto 306) for deposition of lithium fluoride (LiF) and aluminium (Al). Thin layers of LiF (0.5 nm) and Al (80 nm) were deposited onto the samples at a base pressure of 10^{-6} mBar resulting in devices with the following structure; ITO/PEDOT:PSS/P3HT:PCBM:NPs/LiF/Al. Schematic diagram for device structure depicted in Fig. 7.1 shows the various layers of the organic solar cell based on ZnS:Mn plasmonic nanoparticles incorporated into P3HT:PCBM active layer.

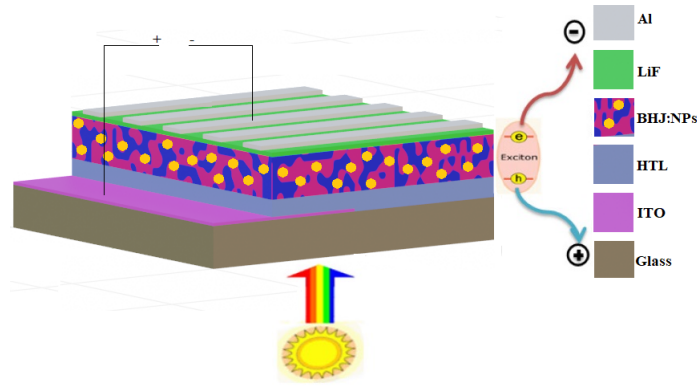


Figure 7.1: Schematic device structure for P3HT:PCBM OPV incorporated with ZnS:Mn NPs.

7.4 Results and Discussion

7.4.1 Structural and Morphological Analysis of ZnS:Mn NPs

Fig 7.2 shows the X-ray diffraction pattern of pristine and manganese doped zinc sulphide NPs measured at $\lambda = 1.5406 \text{ \AA}$. The XRD pattern for ZnS:Mn NPs shows three prominent diffraction peaks at 2θ values of 28.96° , 48.55° and 56.77° were indexed as cubic zinc blende structure. These peaks correspond to reflections from (111), (220) and (311) planes. These planes match very well with literature JCPDS no. 05-0566 [16] and JCPDS no. 77-2100 [17]. There is no significant impurity phase observed in the XRD spectra indicating that the Mn atoms replaced Zn atoms in the ZnS maintaining the zinc blende structure of ZnS. The broadening of the peaks illustrates the formation of nanosized particles. The d_{hkl} spacing values for the three prominent reflections were determined using Bragg's law

$$2d_{hkl}\sin\theta = n\lambda \quad (7.1)$$

The d-spacing values, 3.08, 1.87 and 1.62 $\text{\AA}$ obtained matched very well with literature values of 3.07, 1.88 and 1.60 $\text{\AA}$ [18]. The lattice parameter, a , of the ZnS:Mn NPs were determined using the standard formula for a cubic structure given by

$$\frac{1}{d_{hkl}} = \frac{h^2 + k^2 + l^2}{a^2} \quad (7.2)$$

The obtained lattice parameters are shown in Table 7.1 and range between 5.30 $\text{\AA}$ and 5.37 $\text{\AA}$ with an average of $a = 5.34 \text{ \AA}$. Particle size, D_{size} , was determined using the Debye-Scherrer formula

$$D_{size} = \frac{0.91\lambda}{\beta(2\theta)\cos(\theta)} \quad (7.3)$$

where λ (0.15406 nm) is the wavelength of the X-rays, β is the full width at half maximum in radians and θ is the Bragg angle. The crystalline size values obtained ranged between 1.32 - 1.81 nm and are shown in Table 7.1.

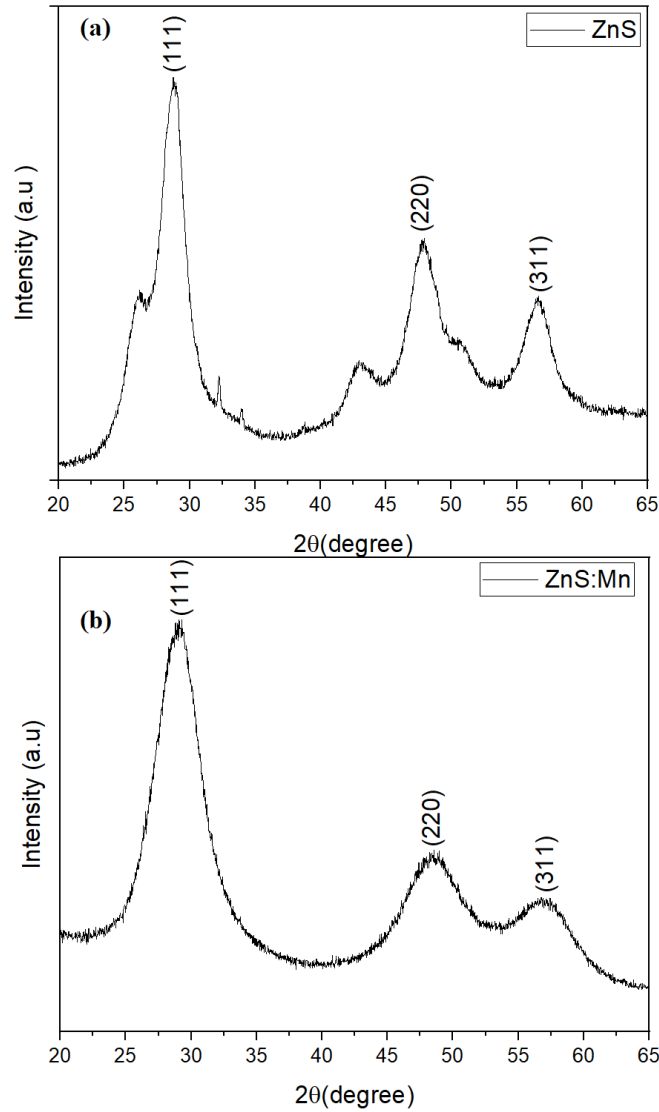


Figure 7.2: X-ray diffraction pattern for (a) ZnS and (b) ZnS:Mn nanoparticles.

The reflections from the (111), (220) and (311) planes, occurring at 2θ at 28.85° , 47.81° and 56.54° respectively, were used for the crystalline size calculation and the results are shown in Table 7.1.

Doping ZnS with Mn atoms at low concentration did not significantly alter its structure as observed in Fig. 7.2 (a) and (b). The ZnS:Mn diffraction peaks are slightly shifted to higher angles when compared to undoped ZnS. However, the d-spacings and lattice parameters of both materials remained on average the same. This is despite the fact that Mn^{2+} ions ($0.80 \text{ \AA}$) are larger than those of Zn^{2+} ions ($0.74 \text{ \AA}$) [15, 17]. The difference in the radii of the two ions is less than 10 %, therefore when the concentration of Mn^{2+} ions replacing Zn^{2+} ions is very small, the crystal structure of the doped ZnS changes only slightly [15].

HR-TEM was used to characterize the ZnS:Mn NPs. Fig. 7.3 shows the HR-TEM image obtained using a JEOL 400CX TEM. The HR-TEM image shows ZnS:Mn formed by differently oriented ZnS:Mn crystallites. These NPs agglomerate to form large clusters which is observed in the SEM analysis. Lattice fringes measured using the HR-TEM give average

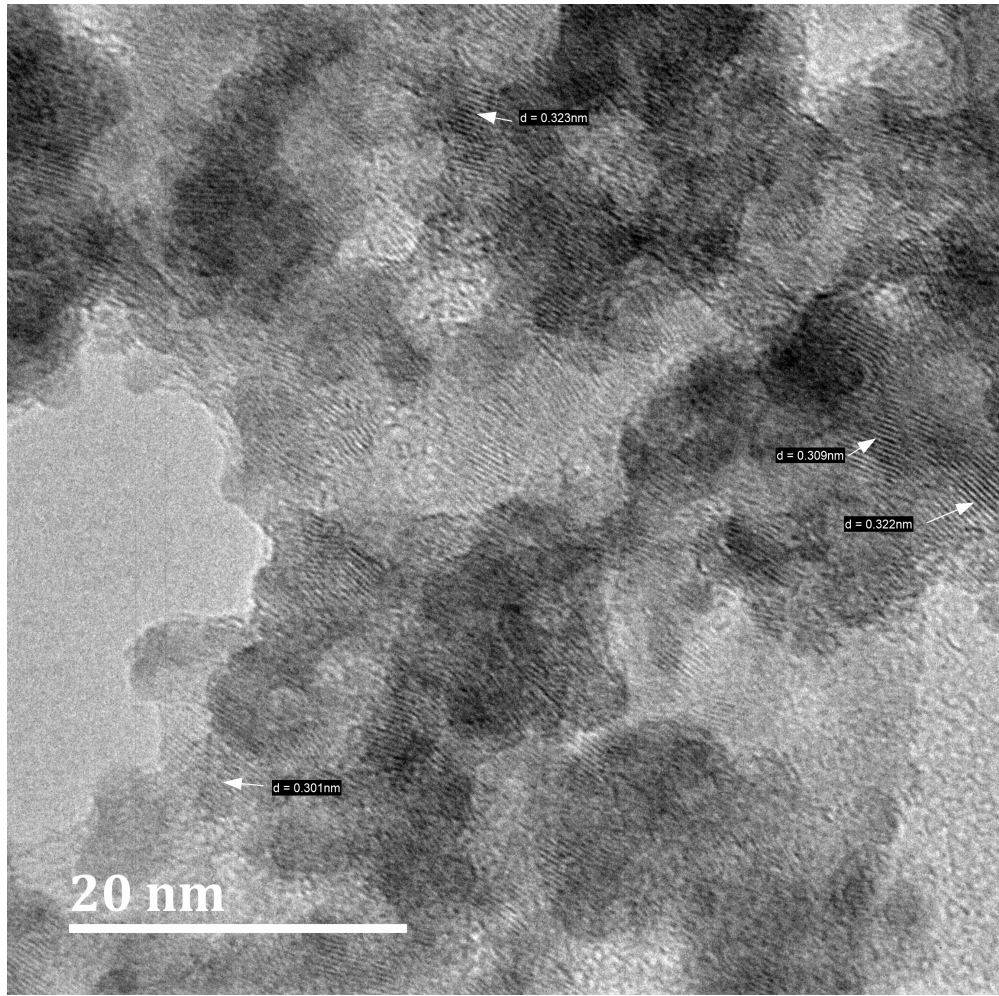


Figure 7.3: Transmission electron microscopy analysis of the ZnS:Mn nanoparticles showing d-spacing for the (111) plane.

Material	Pos. [2θ]	FWHM	hkl	d_{hkl} [Å]	a [Å]	D_{size} [nm]
ZnS:Mn	28.96	5.21401	111	3.08	5.34	1.57
	48.55	6.55523	220	1.87	5.30	1.33
	56.77	4.98388	311	1.62	5.37	1.81
ZnS	28.85	1.6265	111	3.09	5.35	-
	47.81	2.8259	220	1.90	5.37	-
	56.54	2.6397	311	1.63	5.37	-

Table 7.1: Inter-planar spacing (d_{hkl}) from XRD data card with corresponding (hkl) and lattice parameter values for ZnS.

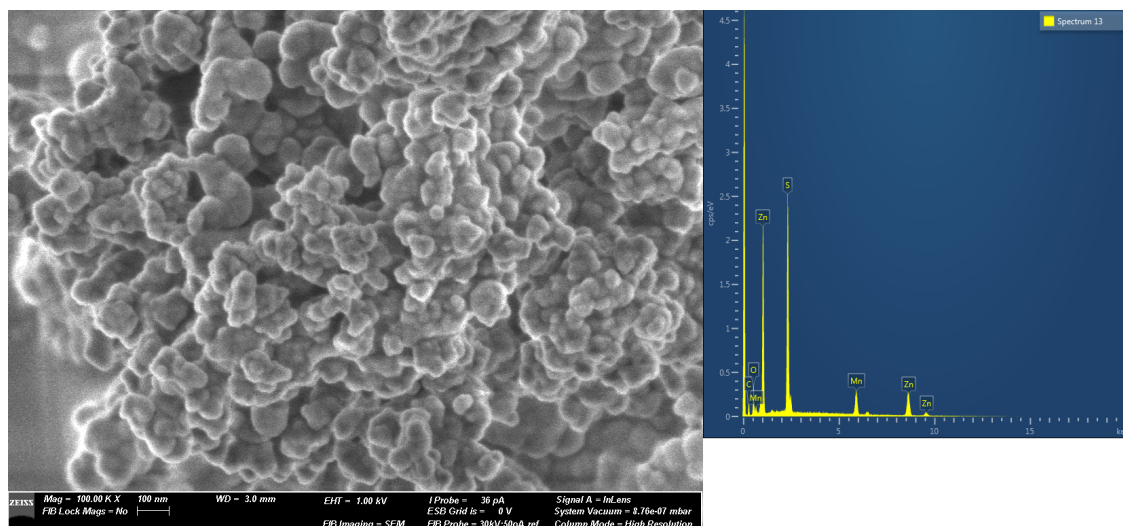


Figure 7.4: Scanning electron microscopy and energy dispersive spectra analysis of the ZnS:Mn nanoparticles.

d-spacing of 3.12 Å. This lattice plane spacing closely matches the d-spacing obtained from XRD analysis for the (111) planes of ZnS:Mn and ZnS NPs, see Table 7.1. The ZnS:Mn NPs were characterized for their morphology using scanning electron microscopy (SEM) imaging. Fig. 7.4 shows the SEM image and energy dispersive spectra (EDS) of the NPs. The SEM image shows differently sized particles agglomerated together to form flower-like particles. The EDS analysis confirms the presence of zinc, sulphur and manganese. In addition, traces of oxygen and carbon appear due to oxidation and the carbon tape sample holder used.

7.4.2 Optical absorption of the photoactive film

ZnS:Mn NPs were incorporated into the P3HT:PCBM photoactive layer blend to utilize their near-field and far field effect to enhance photon absorption of the OPV devices. Metallic NPs can be used as far-field scatterers of incident light and confine freely propagating plane waves of the incident photons into the photoactive layer. This effect can effectively increase the optical path length of the incident light while keeping the photoactive layer thickness within the charge carrier diffusion length. Secondly, the near-field effect of the NPs can absorb light which then induces a strong electromagnetic field in the vicinity of the plasmonic NP. This enhanced near-field which can be 100 times stronger than the electric field of the incident light can aid in the creation of additional electron-hole pairs within the photoactive layer [10]. Fig 7.5 shows the optical absorption spectra of ZnS:Mn NPs in deionized water and P3HT:PCBM films incorporated with 0 wt%, 1.5 wt%, 3 wt% and 5 wt% ZnS:Mn NPs. The ZnS:Mn NPs show good absorption in the wavelength range 300 - 400 nm with an absorption shoulder at ca. 370 nm. The absorption spectra then shows a long absorption tail extending towards the longer wavelengths which is due to far-field scattering effect by the NPs. The increased absorption intensity in the range 340 - 675 nm of the films incorporated with ZnS:Mn NPs is attributed mainly to light scattering by the NPs.

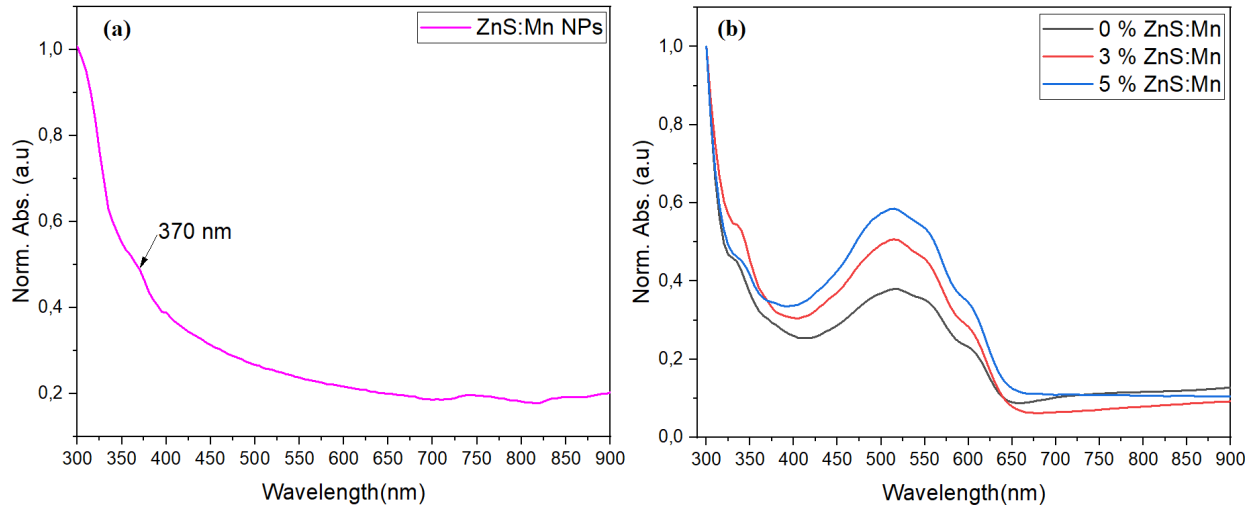


Figure 7.5: Optical absorption spectra of the (a) ZnS:Mn NPs in deionized water and (b) P3HT:PCBM films w/o ZnS:Mn NPs.

Fig 7.5(b) shows UV-vis of P3HT:PCBM films incorporated with ZnS:Mn NPs. The absorption intensity in the wavelength range 340 - 650 nm increases with increasing ZnS:Mn NP concentration in the P3HT:PCBM photoactive layer blend. However, the J-V characteristics of the devices showed that the enhanced optical absorption did not guarantee for enhanced power conversion efficiency. Devices with 5 wt% ZnS:Mn NPs showed tremendous enhancement in optical absorption but performed poorly (see Table 7.2). This suggests that high NP concentration in the active layer may have caused charge carrier recombination at their surface resulting to exciton quenching and degradation of the device performance.

7.4.3 Electrical Properties

The device performances were determined from the electrical properties which are derived from the measured current-voltage (J-V) characteristics of the OPV devices. In this study, four types of devices with the device structures Glass/ITO/PEDOT:PSS/P3HT:PCBM:NPs/LiF/Al were fabricated. The NPs concentration in the active was set at 0 wt% (Pristine), 1.5 wt%, 3 wt% and 5 wt%. Fig 7.6 shows the J-V characteristics of the OPV devices under AM1.5 illumination. The open-circuit (V_{oc}) of the devices slightly increased from 0.51 V for pristine devices to 0.55 V for devices incorporated with the NPs. This slight increase of V_{oc} may be due to slow recombination rate and enhanced electron collection efficiency. It is expected that the incorporation of the ZnS:Mn NPs will affect the device morphology. However, the relationship between morphology and V_{oc} is still not clear and is still a topic for debate. The open-circuit voltage is affected by a number of factors such as donor-acceptor interface, morphology, electrodes work function, defects of states, crystallinity, carrier density, charge transfer states, density of states and ideality factor [19]. Incorporation of the NPs in the photoactive layer may increase its surface roughness. Li et al [20] reported surface roughness increase of a P3HT:PCBM layer from 11.707 nm to 14.257 nm upon addition of Ag

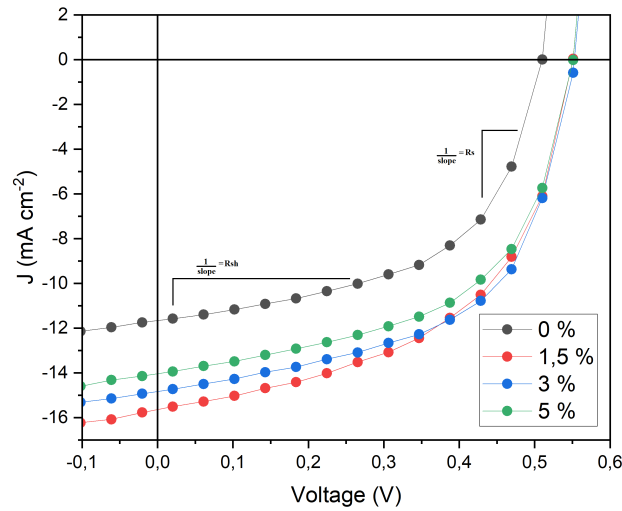


Figure 7.6: The J-V characteristics of P3HT:PCBM devices w/o ZnS:Mn NPs

nanomaterials. This surface roughness increase may be beneficial for the J_{sc} as the effective contact area between the photoactive layer and hole/electron transport layer is increased. However, this interface increase which is beneficial for J_{sc} may be compensated by corresponding increase in recombination current [18]. Nevertheless, incorporation of the ZnS:Mn NPs in the active layer increased the short-circuit current density of the devices from 11.65 mA/cm^{-2} for pristine devices to a highest J_{sc} of 15.60 mA/cm for a NP concentration of 1.5 wt%.

As the NP concentration in the photoactive was increased to 3 wt% and 5 wt%, the J_{sc} of the devices started to drop. The significant enhancement of the J_{sc} by incorporation of the ZnS:Mn in the photoactive layer improved the power conversion efficiency (PCE) of the devices. The PCE increased from 3.23 % for pristine devices to a highest value of 4.54 % for 1.5 wt% ZnS:Mn NPs doping. The concentration of 3 wt% yielded a PCE value of 4.53 % comparable that obtained with a doping of 1.5 wt% ZnS:Mn (see Table 7.2). The performance enhancement observed upon incorporation of the NPs is attributed to their LSPR and light scattering effects. Light scattering by the NPs incorporated into the photoactive layer confines incident photons within the photoactive layer increasing its effective optical thickness and hence absorption. This leads to more excitons in the photoactive layer being produced and create more charge flow. The ZnS:Mn NPs, as by their optical absorption spectra were able to scatter the incident light over a wide wavelength range increasing the photoactive layer optical thickness. The improved J_{sc} led to the increased PCE for devices with 1.5 wt%, 3 wt% and 5 wt% ZnS:Mn NPs corresponding to a 41 %, 40 % and 32 % enhancement, respectively. High NP concentration in the photoactive layer may become impurities and cause defects which lead to high recombination rate and leakage currents. The NPs may become recombination centers quenching excitons. Even though devices with 5 wt% ZnS:Mn possessed the highest optical absorption, the high concentration of NPs in the photoactive layer started to degrade the electrical properties of the devices and hence

their PCE started dropping. The device fill-factors (FF) remained relatively unchanged within the range 52 - 55 %. The PCE also depends on this important parameter, FF, which is more sensitive and is determined by comprehensive and complicated courses, including charge generation, transport, recombination and extraction [21]. Furthermore, the FF is affected by device morphology, thickness and regioregularity of the conjugated polymer and morphology of the active/transport layers interface. P3HT forms crystalline domains due to its regioregularity. The crystallinity of the P3HT can be tuned by thermal annealing. For this study, the devices were all annealed at a same temperature and equal annealing times. Therefore, the regioregularity of the device films is expected to be comparable and hence has no significant effect on the device fill-factors. The FF can be determined from the series resistance (R_s) and shunt resistance (R_{sh}) of a device. The series and resistances are determined from the inverse of the slope of the J-V curve as shown in Fig 7.6. The J-V curves in Fig 7.6 show relatively similar slopes in the first quadrant hence the comparable fill-factors. We therefore attribute the PCE enhancement to the increased J_{sc} due to enhanced optical absorption by the incorporation of the ZnS:Mn NPs.

Device (wt%)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	μ_o (cm ⁻² V ^{-$\frac{1}{2}$} s ⁻¹)
0	0.51	11.64	54.35	3.23	9.93×10^{-3}
1.5	0.55	15.60	52.80	4.54	1.15×10^{-2}
3	0.55	14.79	55.37	4.53	1.01×10^{-2}
5	0.55	14.00	55.05	4.25	8.47×10^{-3}

Table 7.2: Summary of best performed solar cell devices based on P3HT:PCBM blend at different concentrations of ZnS:Mn NPs.

7.4.4 Charge Transport

The charge transport properties of the devices were studied using J-V measurements performed under dark current conditions. The space charge limited current (SCLC) method was used to determine charge mobility(μ_0) of the devices. The SCLC method assumes that charge transport in the devices is bulk limited and not electrode limited. Charge carrier mobility was determined using the modified Mott-Gurney law given by

$$J = \frac{9}{8} \epsilon \epsilon_o \mu_o \exp \left(0.89 \gamma \sqrt{\frac{V}{L}} \right) \frac{V^2}{L^3} \quad (7.4)$$

where ϵ is the relative dielectric permittivity of the material, ϵ_o is the permittivity of free space, L is the active layer thickness, γ is the field activation factor and V is the voltage drop across the sample corrected by the built-in voltage (V_{bi}).

Equation 7.4 was fitted (see Fig. 7.7) to the experimental data obtained from the SCLC region of the J-V measurements where $J \propto V^2$. The obtained data is shown in Table 7.2. The charge mobility was enhanced by the addition of the ZnS:Mn NPs from the order of 10^{-3}

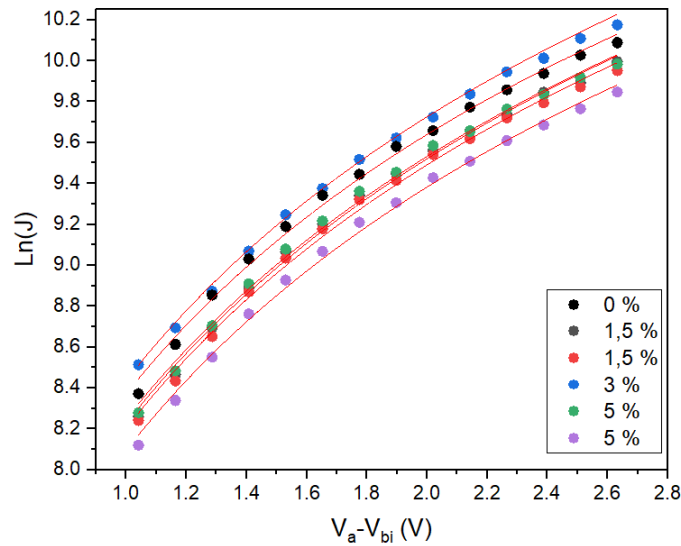


Figure 7.7: Charge transport property curves obtained by fitting the experimental data to the Mott-Gurney Law at Space-Charge-Limited Current region.

$\text{cm}^{-2} \text{V}^{-\frac{1}{2}} \text{s}^{-1}$ to $10^{-2} \text{cm}^{-2} \text{V}^{-\frac{1}{2}} \text{s}^{-1}$. Incorporation of 1.5 wt% ZnS:Mn NPs increased charge mobility by 16 % from $9.93 \times 10^{-3} \text{cm}^{-2} \text{V}^{-\frac{1}{2}} \text{s}^{-1}$ to $1.15 \times 10^{-2} \text{cm}^{-2} \text{V}^{-\frac{1}{2}} \text{s}^{-1}$. However, as the NP concentration was increased from 1.5 wt% to 5 wt% the charge mobility deteriorated back to the order of 10^{-3} . This deterioration suggests increased charge recombination in the photoactive layer which may be due to NP overloading. It should however be noted that the SCLC method is very prone to misinterpretation [17] and mobility values can vary by more than one order of magnitude even on normally identical devices [21]. The mobility values are consistent with the PCE values where concentrations of 1.5 and 3 wt% showed the highest PCE values. The PCE values of devices with 5 wt% ZnS:Mn NPs were very poor compared to those obtained with doping concentrations of 1.5 wt% and 3 wt% consistent with the charge mobility values obtained.

7.5 Conclusion

We successfully doped ZnS with a small concentration of manganese. The effect of ZnS:Mn NPs in the incorporated within the photoactive layer of P3HT:PCBM based devices was then studied. The optical absorption of the devices films was significantly improved and increased with increasing NPs concentration. J-V characteristic studies revealed improved current density resulting to increased PCE for devices with 1.5 wt% and 3 wt% NP concentration. However, higher concentration (5 wt%) had undesirable effects and degraded the J-V characteristics and reduced the PCE of the devices. The enhancements at 1.5 wt% and 3 wt% ZnS:Mn concentration resulted to a maximum J_{sc} of 15.6mA cm^{-2} and a maximum PCE of 4.54 %.

Bibliography

References

- [1] M. S. Hamed, M. A. Adedeji, Y. Zhang and G. T. Mola, 2020. Silver sulphide nanoparticles enhanced photo-current in polymer solar cells. *Applied Physics A*, 126(3), pp.1-9.
- [2] Z. Guan, H. W. Li, Y. Cheng, Q. Yang, M. F. Lo, T. W. Ng, S. W. Tsang and C. S. Lee, 2016. Charge-transfer state energy and its relationship with open-circuit voltage in an organic photovoltaic device. *The Journal of Physical Chemistry C*, 120(26), pp.14059-14068.
- [3] S. Wilken, O. J. Sandberg, D. Scheunemann and R. Österbacka, 2020. Watching space charge build up in an organic solar cell. *Solar RRL*, 4(3), p.1900505.
- [4] L. Zhu, M. Zhang, G. Zhou, T Hao., J. Xu, J. Wang, C. Qiu, N. Prine, J. Ali, W. Feng and X. Gu, 2020. Efficient organic solar cell with 16.88% efficiency enabled by refined acceptor crystallization and morphology with improved charge transfer and transport properties. *Advanced Energy Materials*, 10(18), p.1904234.
- [5] L. Feng, M. Niu, Z. Wen and X. Hao, 2018. Recent advances of plasmonic organic solar cells: Photophysical investigations. *Polymers*, 10(2), p.123.
- [6] M. Mall, P. Kumar, S Chand. and L. Kumar, 2010. Influence of ZnS quantum dots on optical and photovoltaic properties of poly (3-hexylthiophene). *Chemical Physics Letters*, 495(4-6), pp.236-240.
- [7] M. A. Alkhalayfeh, A. A. Aziz and M. Z. Pakhuruddin, 2021. An overview of enhanced polymer solar cells with embedded plasmonic nanoparticles. *Renewable and Sustainable Energy Reviews*, 141, p.110726.
- [8] A. Tooghi, D. Fathi and M. Eskandari, 2020. High-performance perovskite solar cell using photonic-plasmonic nanostructure. *Scientific Reports*, 10(1), pp.1-13.
- [9] C. C. Wang, W. C. Choy, C. Duan, D. D. Fung, E. I. Wei, F. X. Xie, F Huang. and Y. Cao, 2012. Optical and electrical effects of gold nanoparticles in the active layer of polymer solar cells. *Journal of Materials Chemistry*, 22(3), pp.1206-1211.

- [10] F. Enrichi, A. Quandt and G. C. Righini, 2018. Plasmonic enhanced solar cells: Summary of possible strategies and recent results. *Renewable and sustainable energy reviews*, 82, pp.2433-2439.
- [11] P. Mandal and S. Sharma, 2016. Progress in plasmonic solar cell efficiency improvement: A status review. *Renewable and Sustainable Energy Reviews*, 65, pp.537-552.
- [12] X. C. Ma, Y. Dai, L. Yu and B. B. Huang, 2016. Energy transfer in plasmonic photocatalytic composites. *Light: Science & Applications*, 5(2), pp.e16017-e16017.
- [13] B. Bodo, D. Prakash and P. K. Kalita, 2012. Synthesis and Characterization of ZnS: Mn Nanoparticles. *International Journal of Applied Physics and Mathematics*, 2(3), p.181.
- [14] V. D. Mote, V. R. Huse, Y. Purushotham, S. S. Shah and B. N. Dole, 2012, June. Synthesis and characterization of Mn doped ZnS nanometer-sized particles. In *AIP Conference Proceedings* (Vol. 1447, No. 1, pp. 217-218). American Institute of Physics.
- [15] R. Zhang, Y. Liu and S. Sun, 2012. Synthesis and characterization of high-quality colloidal Mn^{2+} -doped ZnS nanoparticles. *Optical Materials*, 34(11), pp.1788-1794.
- [16] G. Murugadoss, 2012. Luminescence properties of co-doped ZnS: Ni, Mn and ZnS: Cu, Cd nanoparticles. *Journal of Luminescence*, 132(8), pp.2043-2048.
- [17] V. D. Mote, Y. Purushotham and B. N. Dole, 2013. Structural, morphological and optical properties of Mn doped ZnS nanocrystals. *Cerâmica*, 59(352), pp.614-619.
- [18] N. Saravanan, G.B. Teh, S.Y.P. Yap and K. M. Cheong, 2008. Simple synthesis of ZnS nanoparticles in alkaline medium. *Journal of Materials Science: Materials in Electronics*, 19(12), pp.1206-1208.
- [19] N. K. Elumalai and A. Uddin, 2016. Open circuit voltage of organic solar cells: an in-depth review. *Energy & Environmental Science*, 9(2), pp.391-410.
- [20] X. Li, W. C. H. Choy, H. Lu, W. E. Sha and A. H. P. Ho, 2013. Efficiency enhancement of organic solar cells by using shape-dependent broadband plasmonic absorption in metallic nanoparticles. *Advanced Functional Materials*, 23(21), pp.2728-2735.
- [21] X. Guo, Q. Fan, J. Wu, G. Li, Z. Peng, W. Su, J. Lin, L. Hou, Y. Qin, H. Ade and L. Ye, 2021. Optimized active layer morphologies via ternary copolymerization of polymer donors for 17.6% efficiency organic solar cells with enhanced fill factor. *Angewandte Chemie International Edition*, 60(5), pp.2322-2329.

Chapter 8

Conclusion

We have successfully synthesized metallic NPs via simple colloidal chemistry. These NPs were then used to assist solar energy harvesting using P3HT:PCBM blend solar absorber of OPVs. The NPs were incorporated at various functional layers of the device structure such as photo-active layer and charge transport buffer layer. We employed different concentrations of the NPs in this investigation, which clearly showed improved solar cell performance at optimum doping level. The incorporation of the NPs tremendously improved the optical and electrical properties of the investigated OPV devices. This was attributed to the LSPR and near field enhanced light scattering phenomena due to the presence of metal NPs.

Characterisation of the synthesised NPs were carried out using HRSEM, HRTEM and XRD, which showed the NPs form larger clusters of different sizes and shapes. EDS analysis confirmed the chemical composition of the NPs with low level of impurities concentration. This was also confirmed by XRD analysis which showed no crystalline diffraction peaks corresponding to impurities. The HRTEM and XRD measurements were used to determine the inter-planar spacings of the materials and the results agreed very well with one another and also with literature values. The XRD diffraction analysis showed the Zn based nanocomposites, ZnS, ZnO:Ag and ZnS:Mn, formed the zinc wurtzite crystalline structure.

The incorporation of the NPs into OPV devices significantly increased the power conversion efficiency mainly due to better collection of photo-current. This is due to the occurrence of LSPR absorption and light trapping in the photo-active medium. The solar cell performances were found to be dependent on type and concentration of the NPs. The optimum NP concentrations differed for different NPs. For instance, the optimum concentration for Ag@Cu in P3HT:PCBM blend was found to be 10 wt% whereas it was found to be 8 wt% for ZnS. The Ag@Cu NPs in the photoactive layer increased the J_{sc} from 7.5 mA cm^{-2} to 11.9 mA cm^{-2} with a maximum PCE of 3.87 %. On the other hand, the ZnS NPs at 8 wt% increased the J_{sc} further to 15.65 mA cm^{-2} with a maximum PCE of 4.00 %. When ZnS was doped with Mn and incorporated into the photo-active layer, the optimum concentration

reduced to a mere 1.5 wt%. However, the PCE was further increased to 4.54 %. The J_{sc} remained relatively the same at 15.60 mA cm^{-2} . However, the FF was increased from 46.43 % to 55.05 %.

Metal NPs have also been incorporated within the HTL to scatter incident light into photo-active layer. The scattered light then enters the photo-active layer at different incident angles thereby increasing its optical path length and improve photon harvesting. In this study, we incorporated silver coated ZnO NPs into PEDOT:PSS HTL to scatter light into the photo-active layer. Significant enhancement in the optical absorption of the devices was observed. This resulted to significant enhancements in the devices' J_{sc} and PCE. In addition to the ZnO:Ag NPs in the HTL, DMSO was also used as solvent additive in PEDOT:PSS to improve on its acidity and hydroscopic nature. A 5 wt% DMSO concentration was used for both devices with 1 mg and 1.5 mg ZnO:Ag NPs. The J_{sc} and PCE were increased to maximums of 16.88 mA cm^{-2} and 4.88 % at a concentration of 1.5 mg ZnO:Ag NPs. These enhancements surpassed those observed on devices with Cu@Ag, ZnS and ZnS:Mn NPs in the photoactive layer. For all the devices fabricated, the open-circuit voltage did not show any significant change upon the addition of the NPs. More than 95 % of the fabricated devices had V_{oc} in the range 0.55 - 0.60 V.

In this study, we used the NP concentration as our control parameter and we did not vary the NP sizes. For further studies, the NP sizes could be varied during the synthesis process to tune the LSPR of the NPs. Each nano-composite could also be tried at different device locations to determine the optimum location. In this study, we used each nano-composite at one location only, either in the photo-active layer or in the HTL.