



THE EFFECTS OF NANO-COMPOSITES IN BULK HETEROJUNCTION THIN-FILM ORGANIC SOLAR CELLS

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Preface

The research was carried out by the candidate under the supervision and guidance of Professor Genene Tessema Mola School of Chemistry and Physics in the College of Agriculture, Engineering, and Science University of Kwazulu-Natal Pietermaritzburg Campus. This research was financially supported by (ukzn), the national Research Foundation funds-SA and Ministry of Higher Education, Scientific Research-Sudan, and the University of Kordofan Sudan. This project has not been submitted for any University, all results reported herein are due to the investigation by the candidate

Signature (Student):.......... Date:12th October, 2020.


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Abstract

This thesis focuses on research that uses metal nano-particles or nano-composites as plasmonic materials that are incorporated at the various layers of organic solar cells, as a mechanism to improve device performances. The power conversion efficiency(PCE) of polymer-based solar cells has recently increased to as high as 17% using small molecules polymer acceptors. In this investigation, the improvement is the result of the effect the metal related nano-particles that were embedded at different layers of the solar cell device structure.

Poor light absorption, low charge carrier mobility, short exciton diffusion length, and device stability are challenges that still remain a major hurdle for organic photovoltaics before commercialization. The various layers of the organic solar cell must be optimized to overcome these problems. One of the strategies is to incorporate metal nano-particles in the photoactive medium of the solar cells to improve the optical absorption and aid collection of photo-generated charge carriers.

Metal nano-composites such as silver doped lanthanum phosphate($\text{LaPO}_4\text{:Ag}$) and metal-sulphide nano-particles (i.e. CuS , NiS , Ag_2S) were successfully synthesized and optimally used in the solar cell structure to be able to improve power conversion efficiency. The nano-particles were incorporated into the active layer and the hole transport layer of the fabricated solar cells while adopting the different architectural design of the devices. The metal nano-particles exhibited local surface plasmon resonance (LSPR) that influences both the charge transport processes as well as solar energy harvesting.

Dedication

To Almighty Allah for his guidance and gift of life.

Declaration 1- Plagiarism

Mohammed S.G Hamed, 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.
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Publications

Declaration - Publications

I declare that the contents of this dissertation each paper are indicated below.

1. **M.S.G Hamed**, G.T.Mola, Copper sulphide as a mechanism to improve energy harvesting in thin-film solar cell, Journal of Alloys and Compounds 802 (2019) 252-258. My role in this article was to conduct experiments, characterizations, analyze data, report results, and submit to the co-author for editing before submitting for publication.
2. **M.S.G Hamed**, S.O.Oseni, A.Kumar, G.Sharma, G.T.Mola, Nickel sulphide nano-composite assisted hole transport in thin-film polymer solar cells, Solar Energy 195 (2020) 310-317. My role in this article was to conduct experiments, characterizations, analyze data, report results, and submit to the co-authors for editing before submitting for publication.
3. **M.S.G.Hamed**, M.A. Adedeji, Y.Zhang, and G.T.Mola, Silver-sulphide nano-composite assisted photons capture in thin-film polymer solar absorber, Applied Physics A 126(3)1-9. My role in this article was to conduct experiments, characterizations, analyze data, report results ,and submit to the co-authors for editing before submitting for publication.
4. **M.S.G.Hamed**, G.T.Mola, Highly stable thin-film organic solar cells using poly crystallized silver doped LaPO_4 , Solar Energy 207 (2020) 157-164. My role in this article was to conduct experiments, characterizations, analyze data, report results ,and submit to the co-authors for editing before submitting for publication.

Publications have not included in the thesis

1. **M.S.G Hamed**, G.T.Mola, Mixed Halide Perovskite Solar Cells: Progress and Challenges, Critical Reviews in Solid State and Materials Sciences,(2020)1-28. My role in this review article was to collect the information and write the manuscript and submit to the author for modifying before submitting it for publication.
2. M.A. Adedeji, **M.S.G Hamed**, G.T.Mola Light trapping using copper decorated nano-composite in the hole transport layer of organic solar cell, Solar Energy 195 (2020) 310-317. My role in this article was preparation, fabrication, and analyze data, report results and submit to the co-authors for editing before submitting for publication.
3. M.W. Dlamini, **M.S.G.Hamed**, X.G. Mbuyise, G.T. Mola, Improved energy harvesting using well-aligned ZnS nano-particles in bulk-heterojunction organic solar cell, Journal of Materials Science: Materials in Electronics,31 (2020)9415-9422. My role in this article was the preparation, fabrication.
4. Makhosazane C.Mthethwa, **M.S.G.Hamed**, M.A. Adedeji, X.G. Mbuyise, Amit Kumar, Gaurav Sharma,Yong Zang, and G.T.Mola, Enhanced Thin-Film Organic Solar Cell Performance using Nickel Sulphide, (submitted article).My role in this article was the preparation, fabrication, and analysis of data, report results, and submit to the co-authors for editing before submitting for publication.

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List of Abbreviation

A	Acceptor
Ag	Silver
Au	Gold
Ag ₂ S	Silver sulphide
Al	Aluminum
BHJ	Bulk heterojunction
CuS	Copper sulphide
D	Donor
DSSCs	Dye-sensitized solar cells
EDX	Energy dispersive X-ray
E _g	Energy gap
ETL	Electron transport layer
FF	Fill factor
FTO	Fluorine-doped tin oxide
FWHM	Full width at half maximum
HTL	Hole transport layer
HOMO	Higher occupied molecular orbital
ITO	Indium tin oxide
J _{sc}	Short circuit current
J-V	Current density-voltage Curve
LaPO ₄ :Ag	Silver doped lanthanum phosphate

LiF	Lithium fluoride
LUMO	Lower unoccupied molecular orbital
LSPR	Localized surface plasmon resonance
LWF	Low work function
MoO ₃	Molybdenum oxide
NC	Nanocomposite
NiO	Nickel oxide
NiS	Nickel sulphide
NIR	Near-infrared
NPs	Nanoparticles
OFETs	Organic field-effect transistors
OLEDs	Organic light-emitting diodes
OSCs	Organic solar cells
P3HT	Poly (3-hexylthiophene)
PCE	Power conversion efficiency
PCBM	[6,6]-phenyl-C61-butyric acid methyl ester
PEDOT:PSS	Poly(ethylene-3-4-dioxy thiophene):poly styrene sulphonate
PL	Photoluminiscence
P_{max}	Maximum power
PSCs	Polymer solar cells
PTB7	poly4,6-(2-ethylhexyl-3-fluorothieno[3,4-b]thiophene-2-carboxylate) alt-2,6(4,8-bis(2-ethylhexyloxy) benzo[1,2-b:4,5-b']dithiophene)
PV	Photovoltaic
PVP	Polyvinyl pyrrolidone
SCLC	Space charge limited current

SEM	Scanning electron microscope
SPP	Surface plasmon polariton
R_s	Series resistance
R_{sh}	Shunt resistance
TEM	Transmission electron microscope
TFOPVs	Thin film organic photovoltaics
TiO ₂	Titanium oxide
UV-Vis	Ultra violet-visible
V_{max}	Maximum voltage
V_{OC}	Open circuit voltage
XRD	X-ray diffractometer
ZnO	Zinc oxide

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CHAPTER 1

Introduction

Today, the demand for more renewable energy sources has increased considerably because of worsening global environmental problem and unsustainable fossil fuel consumption. Hence, the use of renewable energy is expected to reach 20% of the overall energy production by 2040 (see Fig 1.1). The shift towards renewable energy sources such as wind and solar is necessary because of the fact that fossil fuels are ravaging the environment due to the emission of greenhouse gases such as carbon dioxide and others into the atmosphere. However, energy efficiency and increased use of renewable energy sources can lower carbon fuels, which are expected to help reduce the global carbon dioxide emission. The severity of environmental pollution, change of climate, and energy-security problems worldwide require enormous practical solutions transform the world's energy infrastructure to 100% clean, renewable energy that produces zero emissions. For example, each year, 4 to 7 million people die prematurely and hundreds of millions more become ill from air pollution [1–4]. On the other hand, indicate that the three main types of fossil fuels, natural gas, coal, and oil will be depleted in the next few decades, which is necessitating renewable energy sources for long-term sustainability. Renewable energy generation remains a balancing act between cost, efficiency, and environmental impact[5, 6].

Solar energy is the most abundant energy resource on earth, where every minute sunlight reaches the Earth's surface is enough to meet the world's energy demands for one year. Currently, the conversion of sunlight into energy can be achieved through photovoltaic (PV) cells, concentrated PVs, and solar thermal technologies. The sunlight provides the energy for almost all life on earth. Today, solar energy

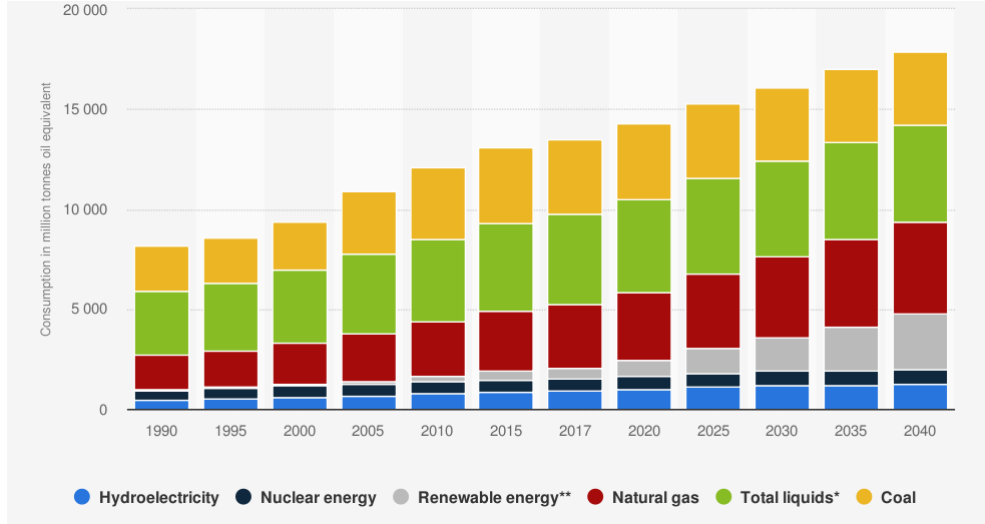


Figure 1.1: World energy consumption by energy source 2040 [4].

represents only a small fraction of total global electricity generation ($\approx 1\%$) but the use of solar PVs is rapidly expanding due to the annual decrease in the cost of such technologies. The conversion of solar energy into electricity by photovoltaic solar cells is one of the most promising approaches to cope with energy shortages. Photovoltaic can convert solar radiation directly into electrical energy using semiconductor converters that produce the photoelectric effect which is a physical and chemical phenomenon[7]. Solar cells can also be fabricated from different types of inorganic materials such as silicon or compound semiconductors. The past decade has seen a dramatic acceleration in the deployment of crystalline Silicon PVs, spurred by unprecedented reductions in manufacturing costs and State subsidies with an efficiency of up to 25% on the laboratory scale. However, the high cost and long energy payback time of these solar cells have limited them from competing with conventional fossil-fuel energies on larger scales. Therefore, it is necessary to introduce low-cost PV technologies; researchers have been focusing on solution-processed thin-film solar cells such as polymer thin-films solar cells, perovskite solar cells, quantum-dot photovoltaic [8, 9].

A semiconductor is a material whose conductivity lies between those of conductors and insulators. Generally, a material that has conductivity in the range from 10^{-8} - 10^3 S cm^{-1} is commonly considered to be a semiconductor. Variations in the

conductivity of materials arise from their difference in the energy band structures. The energy difference between the valence band and the conduction band is the energy gap (bandgap)[10].

There are two main types of organic semiconductors, polymers, and low-molecular-weight materials, also known as organic small molecules. The polymers are conjugated molecules connected via π -bonds, whereas, the small molecules are bonded to each other by weak van der Waal's force. The atomic configuration of an isolated carbon atom is $1s^2 2s^2 2p^2$, inorganic semiconductors, the s and p orbitals form 3 sp^2 orbitals which are sp^2 -hybridized, and the σ bonds. The fourth orbital, p_z , is vertical, to the plane crossed by the sp^2 orbitals. The bonding orbital is also called the highest occupied molecular orbital (HOMO), whereas, the anti-bonding orbital is called the lowest unoccupied molecular orbital (LUMO). The difference between the (HOMO) and the (LUMO) levels is known as the energy gap. The transference of energy between these levels can be excited by the light and depends on the ability of the charge carriers[11, 16] (see Fig 1.2a).

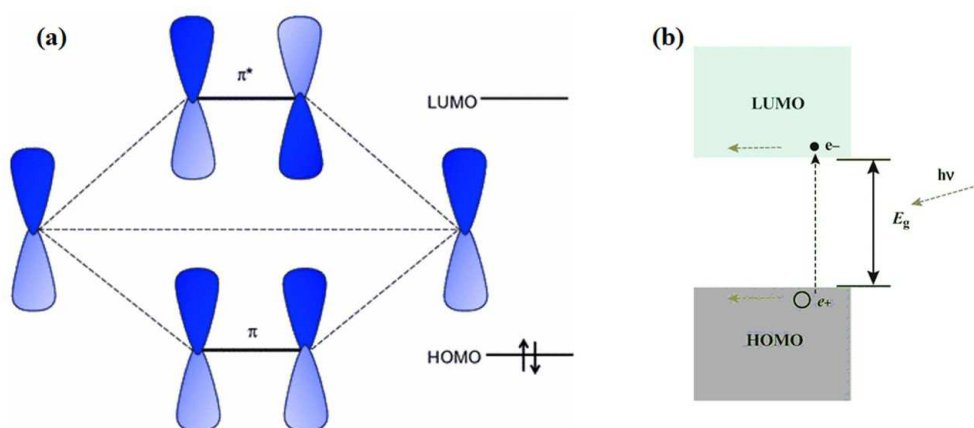


Figure 1.2: (a) The bonding π orbital and antibonding π^* orbitals in the conjugated polymer [11].(b) Schematic of the operating principle for photocurrent[14].

The ability to fine-tune the conductivity of organic semiconductors using molecular design has attracted interest and has inspired many interesting properties such as low-temperature process-ability, flexibility, various colors as well as cost-effective applications. There are three potential applications of conjugated polymers in the

area of optoelectronic devices such as organic field-effect transistors (OFETs), organic solar cells (OSCs), and organic light-emitting diodes (OLEDs). These can all be uniquely processed from solution[13].

Photovoltaic is the phenomenon of converting light energy into electrical energy by means of a semiconductor material, due to their exposure to photons with sufficient energy to release the electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). In general, the ultimate power conversion efficiency of organic photovoltaics is determined by the ability of the acceptor and donor molecules blend to harvest photons and transport charges. [14, 15].

In general, when the photon with energy higher or equal to the energy gap is absorbed by the material a quasi particle known as exciton will be generated. In the devices, incident photons with wavelength 400-900 nm can excite electrons from ground states to excited states in the donors and/or acceptors(see Fig 1.2b), the free charge carriers should be collected by the electrodes to form the photo-current.

Typically, all PVs are multilayer structures. For instance, in every photovoltaics, there is at least one or more active layers. This layer absorbs light and where the charged species that act as photocurrent carriers are formed. Accordingly, there are many ways to classify the photovoltaics, the most common method is through the materials used as an active layer. Generally, there are two important categories in the classification, the inorganic and the organic PVs. Currently, the PVs market is dominated by inorganic photovoltaics based on by silicon cells. But, the high-cost material, manufacturing processes, and heavy weight solar panel makes it costly for applications. The second category is the organic photovoltaics OPVs. The organic photovoltaics are increasingly attracted a lot of attention due to their several advantages over the traditional silicon-based solar cells, such as low-cost device production, mechanical flexibility, and low material weight. However, it did not yet reach the maturity needed to challenge the latter at the commercial level.

Recently, there are many approaches to improve the performance of organic photovoltaic, such as synthesizing new inorganic nanomaterials into the active layer

to enhance light absorption, using additives. Generally, the incorporation of metal nanoparticles in the active layer or buffer layer is a promising strategy to enhance the efficiency of organic photovoltaics.

1.1 Justification:

Fossil fuel has been the main source of energy for the daily livelihood of mankind for centuries. The residual from the use of fossil fuel negatively impacted the existence of life on earth due to the emission of carbon dioxide CO₂, and other poisonous gases into the atmosphere. On the other hand, the current predictions suggest that the three main types of fossil fuels, natural gas, coal, and oil, will be exhausted in the next few decades. Therefore, there is an urgent need to find sufficient alternative energy sources for sustainable energy supply to the world.

1.2 Aim of the thesis

The main aim of this research is to enhance the power conversion efficiency of organic solar cells based on P3HT:PCBM blend through the incorporation of optimized metal nano-particles at different layers of the device structure. The nano-particles are synthesized through simple wet chemical synthesis of plasmonic metal nanoparticles and blending the nanoparticles with the solar cells while maintaining low-cost fabrication processes to produce more environmentally stable devices.

1.3 Objectives of the thesis

- (a) To synthesis metal sulphide nanoparticles and other nano-composites.
- (b) To characterize the particles in terms of optical and morphological properties of

the synthesized nanoparticles by using high-resolution scanning electron transmission microscopy (HRSEM and HRTEM).

(c) To prepare, fabricate, and characterize thin-film organic solar cells.

(d) To optimize the solar absorber of polymer solar cells by incorporating plasmon metal nanoparticles.

(e) To optimize the hole buffer layer of polymer solar cells by incorporating plasmon metal nanoparticles.

1.4 Outline of this thesis

This research provides several advantages such as optimize the solar absorber and increasing interfacial roughness between the photoactive layer and hole transport layer of polymer solar cells and enhancing the power conversion efficiency by incorporating metal nanoparticles through their localized surface plasmon resonance effects, and light scattering.

This thesis contains 8 chapters involves the synthesis part, characterization, and incorporation of plasmon metal nanoparticles into thin-film solar cells which improves devices by enhancement the light absorption of solar cells.

Chapter 1 addresses a general introduction of solar energy and contributing to solving the global energy crisis and environmental problems. In addition to highlighting the reasons for doing research, objective, justification, and concludes with the description of the thesis outline.

Chapter 2 literature review presents a general introduction of photovoltaics, giving brief discussions of plasmonic metal nanoparticles organic solar cells, and specifically describes the mechanisms for plasmonic solar cells.

Chapter 3 the materials, experimental methods, and characterization tools used during this thesis. The list of all chemicals and solar cell fabrication are summarized.

Chapter 4 presents synthesized CuS nanoparticles, characterization and fabrication by incorporated in the solar absorber layer of the thin-film organic photovoltaic cell which provides better performance.

Chapter 5 Nickel sulphide (NiS) nano-composite were synthesized characterization and embedded in PEDOT:PSS as the hole transport layer of the thin-film organic solar cell to improve the charge carrier, which provides better performance.

Chapter 6 Silver sulphide nanoparticles (Ag_2S) (NPs) were successfully synthesized and characterized using high-resolution scanning and electron microscopy (HRSEM and HR-TEM), and incorporated in the inverted thin-film organic solar cell as a photoactive layer. the result is clearly shown enhanced the performance of the device, exhibited extraordinary environmental stability.

Chapter 7 the newly synthesized particles silver doped lanthanum phosphate ($\text{LaPO}_4\text{:Ag}$) were used in the solar absorber medium of inverted thin-film organic solar cells to assist in photons harvesting. The result has been shown to significantly improve power conversion efficiency. The improvement is due to the plasmon mechanism effect within the photoactive layer.

Finally, **chapter 8** is conclusions discussed research output and future development.

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CHAPTER 2

Literature review

2.1 General Introduction

Solar energy is one of the renewable energy resources that convert sunlight into electricity. It has been regarded as one of the most promising and cheap energy sources available in nature. Recently, photovoltaic research has contributed significantly to harness solar energy into electrical energy using semiconductor materials. There are various solar cell technologies available today to convert solar energy into electricity, such as crystalline Si, compound semiconductor-based cells, thin-film solar cells, organic photovoltaics (OPVs) cells, dye-sensitized solar cells (DSSCs), and perovskite solar cells. They are all contenders for the solar cell market in the future. However, organic photovoltaics (OPVs) based on organic semiconductors and small molecules, are particularly attractive due to their several advantages, such as low-cost fabrication of large areas, low-temperature fabrication, semi-transparency, and mechanical flexibility and electronic properties [1–8]. Organic photovoltaics (OPVs) are especially promising alternatives to solar energy harvesting due to the abundance of its constituent elements (basic materials), and ease of chemical synthesis. Because of the different optical properties of the polymer materials, it is possible to fabricate semi-coloured and transparent OPV devices. This technology is particularly attractive for the integrated PV market[9–11]. The most commonly known PV systems are mono- and polycrystalline PN-junction silicon solar cells with an efficiency of up to 25% on the laboratory scale. The main challenge with silicon-based solar cells is the high cost of device manufacturing. The thickness of the silicon wafer ranges from $200\mu\text{m}$ – $500\mu\text{m}$ which is thicker than OPV

solar absorber [12–15]. There are various types of device architectures in organic photovoltaics solar cells, the most widely used design is (1) is the bulk heterojunction architecture which consists of a blend of donor and acceptor materials. The distance between donor and acceptor molecules must be less than 10 nm for the effective dissociation of excitons. And therefore the losses due to exciton recombination can be expected to be low, which improved photon-generated currents, and also leads to improved power conversion efficiency[16–18]. Nevertheless, the performance of BHJ organic solar cells is very sensitive due to the nano-morphology of the photo-active film. The morphology may affect performance due to the occurrence of geminate and non-geminate charge carrier recombination. In order to improve the performance of the devices, the nano-morphology must be controlled by solvent additive, thermal annealing, solvent vapor annealing[19, 20]. (2) single-layer OPV which is consists of only one active material sandwiched between two electrodes, the active layer used usually p-type material and they require a Schottky barrier between p-type and metal to allow for the separation of excitons. The power conversion efficiency is very low[21, 22].(3)Bilayer heterojunction organic photovoltaics (see Fig 2.1a) comprising of an electron donor layer (D) and an electron acceptor layer (A) which are stacked by layer. The charge separation occurs at the donor-acceptor interface and the power conversion efficiency is limited due to the short diffusion length of excitons[23, 24]. (4)Tandem heterojunction solar cells consist of two or more solar subcells organic solar cells connected in series or parallel manner, with one wide bandgap and the other small bandgap with the complementary absorption over the broad range of the solar spectrum. Since tandem solar cells are the result of two sub-cells connected in series, the open-circuit voltage of cells is the sum of the two sub-cells. Therefore, Tandem solar cells demonstrated high power conversion efficiency (PCE) 17%[25, 26] compared with the Bulk heterojunction 16%[27]. But, the manufacturing of tandem is more expensive due to the formation of two subcells [28].

The recombination of photogenerated electron-hole pairs before migrating to the electrodes and the inability to utilize the entire visible light spectrum is considered to be the major factors for low PCE of organic solar cells. Most of the commonly

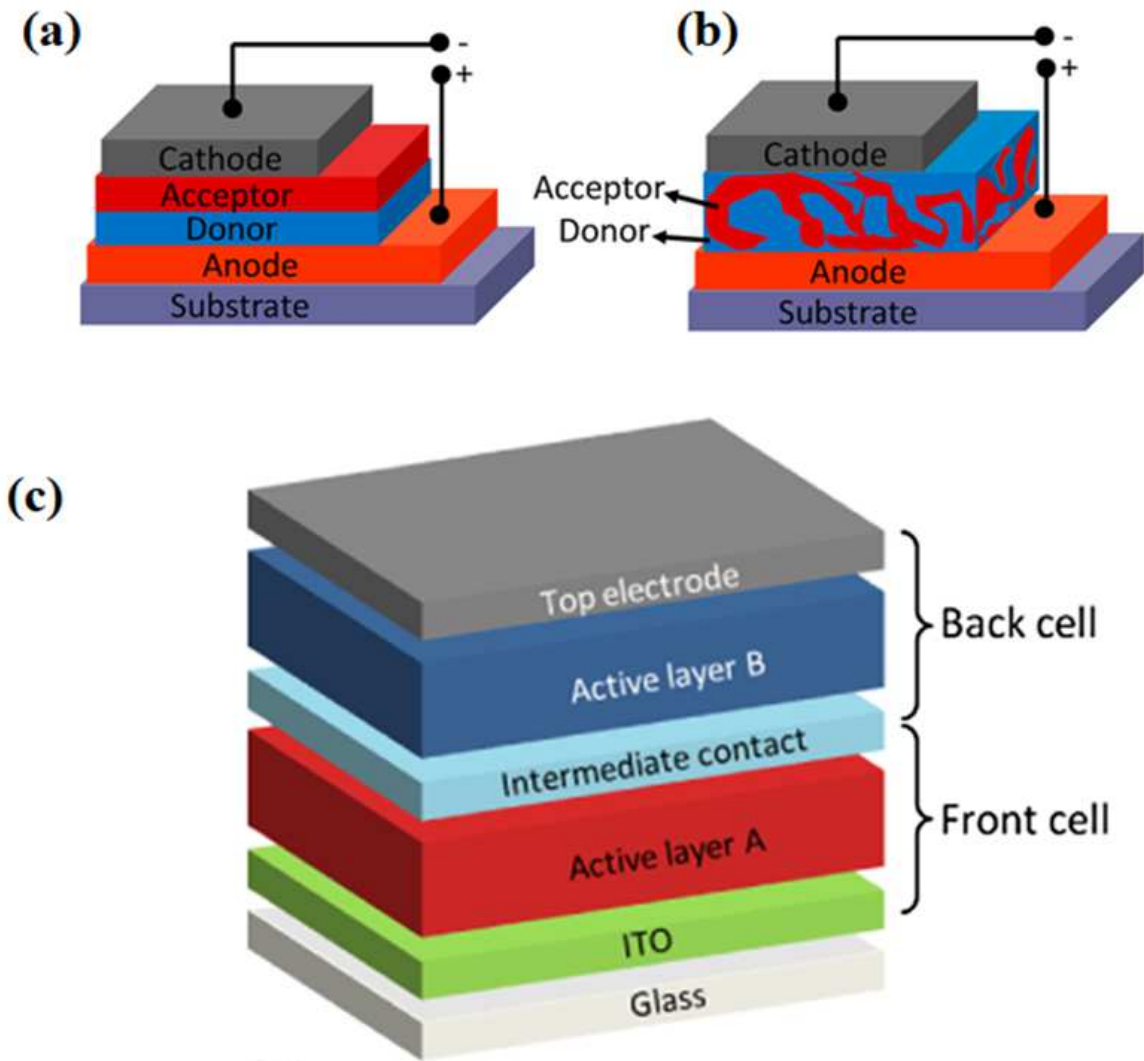


Figure 2.1: Schematic of the device structures (a) bilayer heterojunction, (b) bulk heterojunction[8] (c) Tandem heterojunction solar cells [29].

used organic semiconductors absorb in the range of near UV-visible light due to their large bandgap, which accounts for only about 4% of total solar radiation while the visible light contributes about 50%. Relatively, there are various strategies to improve the light-trapping in thin-film solar cells such as incorporating plasmon metallic nanoparticles in the active layer or buffer layer. These nanoparticles can help to enhance the light-matter interaction in the nanoscale which enhances the optical absorption and reduce recombination[30–33]. Plasmonic NPs are known to exhibit a strong absorption band in the UV-visible region due to the excitation of localized surface plasmon resonance (LSPR). The LSPR is a non-propagating excitations of conduction electrons of the metallic nanostructure to the electromagnetic

field[34, 35]. There are three methods to operational mechanisms for plasmonic solar cells to improve the light absorption to enhance exciton generation of organic solar cells (i) light scattering, in which the absorption enhancement is due to high-angle and/or multiple scattering, (ii) near-field can also be used to enhance the absorption of an active layer (iii) surface plasmon photonic SPPs[36, 37].

2.2 Working Mechanisms of organic solar cells

The photoactive layer in organic solar cells is composed of the mixture of p-type donor polymer and an acceptor fullerene or non-fullerene molecules. The energy band structure in semiconductor polymers is the highest occupied molecular orbitals (HOMO) are similar to the valence band and the lowest unoccupied molecular orbitals (LUMO) are analogous to conduction bands. However, the conventional structure's LUMO and HOMO has energetically low and high electron affinity, respectively, which leads to accepting electrons from the donors (see Fig 2.2). The fundamental working principle of the bulk-heterojunction (BHJ) organic solar cells and the mechanism of transforming photons into a photocurrent can be explained in at least four fundamental steps (see Fig 2.2).

(1) Photon absorption : the incident light is absorbed by the donor material in the photoactive layer, due to the high absorption coefficient (10^7m^{-1}) of conjugated polymers such as poly4,6-(2-ethylhexyl-3-fluorothieno[3,4-b]thiophene-2-carboxylate) alt-2,6(4,8-bis(2-ethylhexyloxy) benzo[1,2-b:4,5-b]dithiophene) (PTB7). Consequently, the thicknesses for the active layer of conjugated polymers between 100-200 nm are sufficient for a good absorption compared to silicon-based solar cells, active layer thicknesses of hundreds of micrometers are required due to the silicon is an indirect semiconductor. The absorbed light enters through the ITO or FTO coated glass substrate to the active layer, electron-hole pairs are generated by exciting electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The higher bandgap of the donor

conjugated polymers leads to lower absorption in the photoactive layer, and low photocurrent generation which shows lower power conversion efficiency. Therefore, the material with a lower bandgap may enhance the photon harvesting due to the better overlap with the solar spectrum[38–41].

(2)**Exciton generation and diffusion** : The photo-generated excitons need to overcome the binding energy of the charge-separated state and dissociate into free electrons and holes. To accomplish this, the excitons need to diffuse to the donor/acceptor (D/A) interface within the diffusion length without recombining to the ground state. The exciton diffusion lengths in conjugated polymers are typically around 10-20 nm.

(3)**Exciton dissociation into free electrons and holes at the interface**: when excitons reach D/A interface. The free charge carriers are separated by the energetic driving force. The hole is transferred into the donor through the backbone of the polymer chain and the electron is transferred into the acceptor domain. However, if this energy is larger than the binding energy of the exciton in the donor, then the dissociation procedure became more favorable.

(4) **Charge collection**: once the electron and hole have distributed within the donor and acceptor phases, the electrons are collected at the cathode and the holes at the anode driven by an internal electric field deriving from the Fermi level difference of the electrodes.

2.3 Device architectures of organic solar cells

The device performance of the organic photovoltaic is highly dependent on their architecture design and the materials used as buffer layers and electrodes. However,

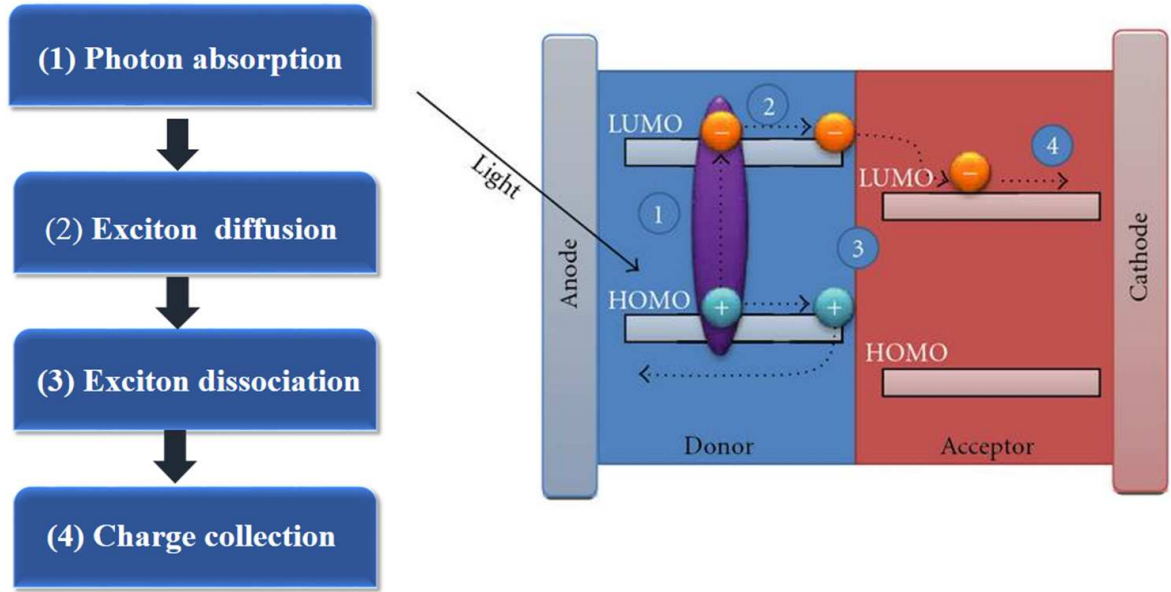


Figure 2.2: working principle of organic solar cells[41].

organic solar cells can be fabricated based on two types of device structures namely the conventional structure and the inverted structure. The conventional thin-film organic solar cells device consists of a bulk-heterojunction (BHJ) active layer, sandwiched between a transparent conducting electrode, such as indium tin oxide (ITO) or fluorine-doped tin oxide (FTO) glass, and a low work function (LWF) metal such as Al, Au, Ag as the cathode (see Fig 2.3). Usually, p-type conducting polymer, PEDOT:PSS, is commonly used on the top of ITO to improve the hole injection and electron blocking, while, the low work function metals such as Al and Ca/Al are often used as the top cathode to ensure effective electron extraction. The electron transport layer is commonly inserted between bulk-heterojunction and metal cathode which can be used LiF or Ca for electron extraction and improve the interfacial stability. However, organic solar cells' conventional architecture has suffered from some drawbacks in the stability and lifetime of the device [42, 43]. One of the major drawbacks of the conventional structure polymer solar cell is the short stability when exposed to air due to low-work-function metal (Al). Furthermore, in the conventional structure organic solar cells, the acidic nature of PEDOT:PSS interfacial layer which is in direct contact with the ITO can cause etching ITO film and result in a degradation of the device performance. The inverted device's architecture consists of n-type metal oxide semiconductors such as (ZnO, TiO₂). While that the

metal oxides have been used for efficient hole extraction on the top such as molybdenum oxide (MoO_3), vanadium oxide (V_2O_5), tungsten oxide (WO_3), and nickel oxide (NiO) are used to replace PEDOT:PSS. Inverted organic solar cells exhibit higher environmental stability of devices compared with the conventional architecture and provide higher flexibility in the design of multi-junction or tandem polymer solar cells [44–48].

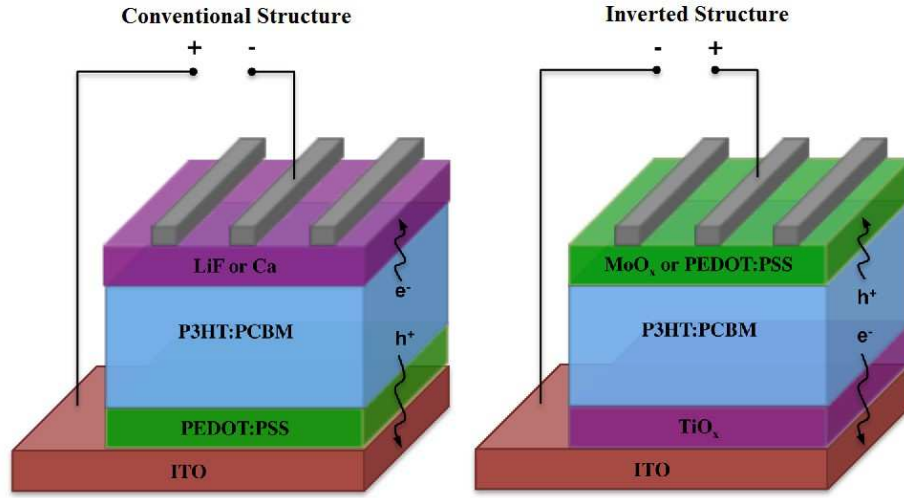


Figure 2.3: Typical device architecture for a conventional and inverted cell[43].

2.4 Current-voltage characteristics of the solar cells

Solar cells have a non-linear current-voltage (I-V) characteristics that describe the measured data. This relationship between the current and applied voltage can be described by various models. In most cases, a simple diode model is used from which the applied voltage and current relationship are derived and given by an equation:

$$I_{dark} = I_0(e^{\frac{qV}{kT}} - 1) \quad (2.1)$$

where I_0 is a constant, q is the electronic charge, k is the Boltzmann constant, and T is temperature. The total current of the solar cell device is the difference between the dark current that flows as a result of the applied potential difference (V) is given by the following:

$$I(V) = I_{SC} - I_{dark} = I_{SC} - I_0(e^{\frac{qV}{kT}} - 1) \quad (2.2)$$

In order to account the effect of a real solar cells depends on the ideal Shockley equation was extended by two-part of resistors represent by series resistance R_s and the parallel resistance R_p . The J-V characteristic in Figure 2.4 can be analyzed by the generalized Shockley equation corresponding to this equivalent circuit

$$J = \frac{1}{1 + \frac{R_s}{R_{sh}}} J_s \left(\exp\left(\frac{q(V - JR_s)}{nK_B T}\right) - 1 \right) - \left(J_{PH} - \frac{V}{R_{sh}} \right) \quad (2.3)$$

where J_s is the saturation current density, n is the ideal factor of the diode, q is the elementary charge, k_B is Boltzmann's constant, and T is the absolute temperature. The optional photocurrent J_{ph} is included by a parallel shift of the current-voltage curve down the current axis. The open-circuit and the short-circuit current density can also be calculated from this current equation, and can be presented as

$$V_{OC} = \frac{nK_B T}{q} \ln \left[1 + \frac{J_{PH}}{J_s} \left(1 - \frac{V_{OC}}{J_{PH} R_{sh}} \right) \right] \quad (2.4)$$

$$J_{SC} = \frac{1}{1 + R_s/R_{sh}} J_{PH} - J_s \left[\exp\left(\frac{|J_{SC}| R_s}{nK_B T/q}\right) - 1 \right] \quad (2.5)$$

The power conversion efficiency PCE is measured by using various parameters such as short circuit current (J_{SC}), the open-circuit voltage (V_{OC}), the fill factor (FF), and the efficiency (η). The power conversion efficiency PCE is generally defined as the percentage of the maximum output of electrical power to the incident light power (see Fig 2.4). Which is determined by the following formula

$$PCE = \frac{P_m}{P_{in}} = \frac{V_{OC} * J_{SC} * FF}{P_{in}} \quad (2.6)$$

Where P_m is a maximum power point, (J_{sc}) is the short-circuit current density, (V_{OC})

is the open-circuit voltage and (FF) is the fill factor, and P_{in} is the incident light power density. A standard test condition for solar cells is Air Mass 1.5 (AM 1.5) with an incident power density of $\sim 100 \text{ mWcm}^{-2}$ at a temperature of 25°C [49]. In solar cells, J_{sc} is directly related to the number of absorbed photons, which strongly depends on the absorption intensity and the absorption range of the active layer materials, exciton generation and dissociation, charge transport, and charge collection at the electrodes. The fill factor FF is defined as the ratio of the maximum power P_m to the produce of a short-circuit current density (J_{sc}) and open-circuit voltage (V_{OC}). The series resistance (R_s) and shunt resistance (R_{sh}) are two important factors that affect the FF of a cell. In general, R_s is producing from the bulk resistances of the active layer and electrodes and the contact resistance between the active layer and electrodes. While, the R_{sh} is derived from the current leakage induced by the pinhole in the cell, or the current leakage from the edge of the device.

$$FF = \frac{P_m}{V_{OC} * J_{SC}} \quad (2.7)$$

The V_{OC} is determined by the energy difference between the highest occupied molecular orbital (HOMO) energy level of the donor and the lowest unoccupied molecular orbital (LUMO) energy level. The acceptor components upon forming an ohmic contact are very important in organic materials and electrodes to collect the electrons in cathode and holes in anode in the bulk heterojunction (BHJ) organic solar cell. The schematic diagram and the charge transport channels in the organic polymer solar cells and energy levels alignments are shown in (Fig 2.3) such as planer layer has already been applied for organic solar cells[50–52].

2.5 Donor Materials

Conjugated polymers are the transcendent donor materials for PSCs because of their low bandgap and great portability. The most common categories of conjugated polymers that have been generally utilized as donors in organic solar cells are

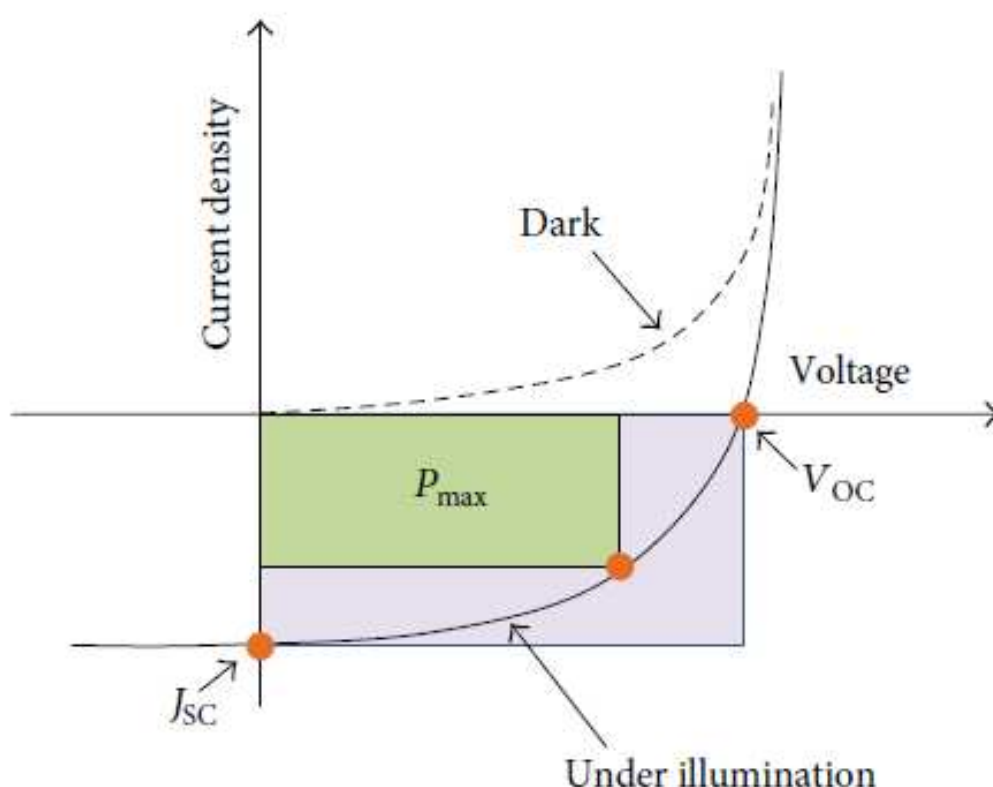


Figure 2.4: Current-voltage (I-V) characteristics of an organic photovoltaics[53].

the Poly(phenylene vinylene) (PPV), and Polythiophenes (PTs). The polythiophene (PT) subsidiaries are one of the most significant kinds of donor materials, and its derivatives are the main source of electron donor conjugated polymer that has attracted high research attention for photovoltaic applications[54, 55]. The poly[2-methoxy-5-(2-ethylhexyloxy)- p-phenylene vinylene] (MEH-PPV) (see Fig 2.5) is the first donor utilized in BHJ solar cells, due to the wide energy band gap 2.2 eV which are limits absorption to photons up to ≈ 600 nm, good solubility, mobility, and luminescence property[56]. Heeger et al. fabricated the BHJ device by blending MEH-PPV with a fullerene acceptor PC61BM, the device produced showed low J_{SC} due to poor harvesting of the solar spectra [57, 58].

The most popular polymer donor material, poly (3-hexylthiophene) (P3HT) molecules, is often utilized for the fabrication of thin-film organic solar cells. P3HT has higher charge carrier mobility (up to $0.2 \text{ cm}^2/(\text{V s})$), and therefore, this conju-

gated polymer exhibited much better photovoltaic properties[59]. Furthermore, P3HT has good stability in the ambient environment, and solubility in several organic solvents. Hence, BHJ devices containing P3HT together with fullerene derivatives have been used to produce stably inverted thin-film organic solar cells on glass substrate. Moreover, there are various strategies that have been developed to optimize the performance of P3HT-based PSCs such as post-annealing and solvent additives to improve the morphology [60]. On the other hand, the poly 4,6-(2-ethylhexyl-3-fluorothieno[3,4-b]thiophene-2-carboxylate) alt-2,6(4,8-bis(2-ethylhexyloxy) benzo[1,2-b:4,5-b']dithiophene) (PTB7) is another major donor polymer which is also widely used in organic solar cells. It has produced high efficiency and stable thin film organic solar cell[61, 62]. The 2,1,3-Benzothiadiazole (BT) is another major category of the donor conjugated polymer that has been widely used as an electron-deficient building block in conjugated polymers with D/A structure. The most popular Benzothiadiazole (BT) derivatives known to date is PCPDTBT which has is a narrow band gap polymer, strong and broad absorption band extending to the near-infrared region. It has been employed as donor BHJ in the thin film organic solar cell (TFOSC) and exhibited good hole mobility[63, 64]. Furthermore, other popular donor polymers which belongs to the group diketopyrrolopyrrole (DPP), are Benzo[1,2-b;4,5-b']dithiophene (BDT),and poly[2,3-bis-(3-octyloxyphenyl)quinoxalin-5,8-altthiophene2,5-diyl] (TQ1) [65–67] which has been employed in organic solar cells and exhibited high performance, good stability in inverted devices.

2.6 Acceptor Materials

Fullerene are C60 derivative comprehensively utilized as electron-accepting material in solution-processed thin-film organic solar cells (TFOSCs), as they showed great solubility in organic solvents. The simple fullerene PC60BM is one of the major acceptors which has been utilized frequently in BHJ as an acceptor and shows great electron mobility one of PC60BM molecule can accept up to four electrons[68]. Although PC60BM dissolves in chloroform and dichlorobenzene, it

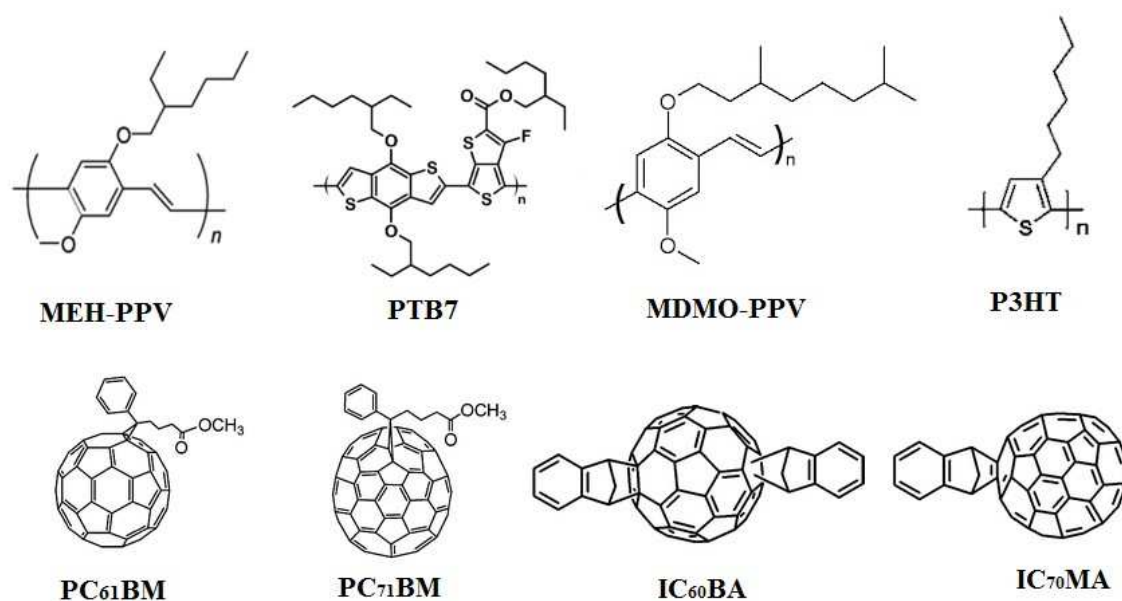


Figure 2.5: Chemical structures of conjugated polymers and fullerene and their derivatives.

exhibits very limited solubility in most of the normally utilized organic solvents. So as to improve its solubility and also to avoid severe phase separation of D/A blend, [6, 6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₀BM) is commonly applied in OPVs. In the previous decade, PC₆₀BM the derivative (PC₇₀BM), has been predominantly utilized as acceptors in OPVs. Both fullerenes PC₆₀BM, PC₇₀BM have strong absorption in the visible and ultraviolet region[69]. However, organic photovoltaic devices utilizing PC₇₀BM as the acceptor will absorb more sunlight, leading to an increased J_{sc} and subsequently improved PCEs. However, the energy level of the fullerene derivatives is significant for PSCs. The open-circuit voltage (V_{oc}) of PSCs is controlled by the difference between the LUMO energy level of the fullerene acceptors and the HOMO energy level of the polymer donors[70].

Besides, there are other fullerenes derivatives such as indene-fullerene monoadduct (ICMA) and indene-fullerene bisadduct (ICBA) are also other fullerene derivatives which were used as electron acceptor materials in OPVs (see Fig 2.5) [71]. Fan et al. investigated the Indene-C₇₀ Bisadduct (IC₇₀BA) with poly(3-hexylthiophene) (P3HT) based device, and obtained higher V_{oc} than that of pristine P3HT/PCBM-

based devices. The better performance of the optimized device was attributed to the higher crystallinity of P3HT and a better donor-acceptor interpenetrating network of the active layer[72]. Furthermore, devices in which fullerene and its derivatives are used as electron acceptor materials for OPV have proven to be very efficient.

2.7 Plasmonic metal nano-particles for solar energy harvesting

Plasmon nano-structures have been intensively used in different photonic devices such as organic photovoltaic cells, optoelectronics, chemical and biological sensing, light-emitting diodes, and photon detection [73, 74]. The metal nanoparticles (NPs) can be obtained by various synthetic methods such as wet chemical route, vapor deposition methods, and decomposition of the organometallic precursor. Metal nanoparticles have gained tremendous attention due to their attractive optical and electrical properties. In particular, metal nanoparticles (NPs) such as gold (Au) and silver (Ag) which exhibit strong absorption due to their relative localized surface plasmon resonance (LSPR), and scattering efficiency among noble metals in the visible range[75, 76].

Plasmonics has attracted great attention over the last few decades due to their alluring physical mechanisms arising from the interaction of light with the electron plasma on the surface of nano-structured metals. Metal nano-particles can assist in the light trapping process through different mechanisms such as the electric field and light scattering enhancement from metal nano-particles. In the case of electric field enhancement, there is a strong interaction between the incident light and metal nanoparticles which leads to the creation of an electromagnetic field around the nanoparticles. While in light scattering enhancement, the light is trapped in the solar absorber medium through multiple reflections by metal nano-particles. This metal nanostructure can be modified by coupling or concentrating the light onto an

active layer to enhance the absorption of the incident photons [79–81]. The incorporation of plasmonic nanostructures in solution-processed organic photovoltaic devices has been demonstrated as a means to enhance solar energy harvesting through different mechanisms as (1) light scattering, (2) localized surface plasmon resonance (LSPR), and (3) surface plasmon polariton (SPP).

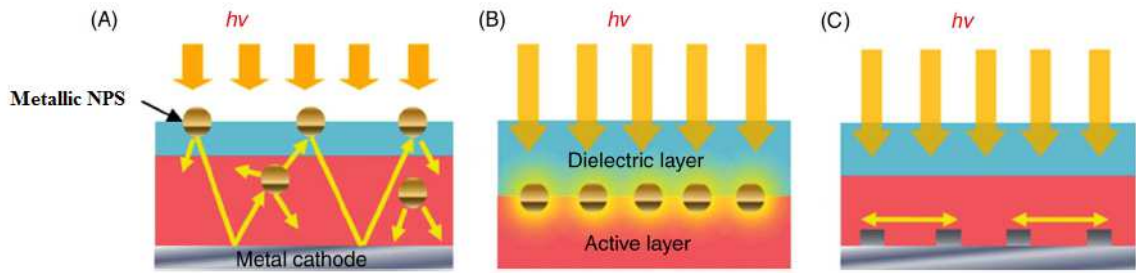


Figure 2.6: Different mechanisms for plasmonic solar cells to enhance the light absorption in the solar cells (a) Light Scattering Effect (b) Localized Surface Plasmon Resonance (LSPR) Effect (c) Surface Plasmon Polariton Effect [99].

2.8 Fundamentals properties of surface plasmons

2.8.1 Light scattering

Metal nano-particles in dielectric medium can act like effective scattering centres to change the direction of the incident beam in such a way that the light remain trapped in the medium. It is to be noted that the NPs scattering depends on the size and shape of the metallic nano-structures. [82]. Further, a relatively larger diameter (>50 nm) nano-particle behave in such a way that light scattered at a particular angular spread increases the path length through multiple scattering thus dispersing the electromagnetic waves of the incident light in the photoactive layer(see Fig 2.6a). Hence, organic solar cells consist of metal nano-particles placed at the surface of the buffer layer such that the nano-particles can enhance the absorber by scattering sunlight due to the reflected light at the top electrode back with NP(s) pass through within the photoactive layer, and therefore, generate more excitons(see Fig 2.6a),

and thus reduce reflection losses and increase the absorption of semiconductor material to convert it into the electricity, we can conclude the scattering is efficiency with increasing particle size [83–85].

2.8.2 Localized surface plasmon resonance (LSPR)

Localized surface plasmon resonance (LSPR) is a phenomenon associated with the collective excitation of free electrons on the surface of the metal nano-structures. The collective oscillation of the electrons leads to a resonant absorption due to the interaction between the electromagnetic field of incident light and the surface electron density on the surface of the metal nano-particles (NPs) as displayed in Fig (2.7a). When the incident light interacts with metal nano-particle which is smaller than the wavelength, the light show strong excitations due to the electric field in the form of localized surface plasmon resonances (LSPR)(see Fig 2.6b).[87]. The resonance wavelength of the metal nano-particles can be a shift over the wide spectral range from ultraviolet (UV), visible to near-infrared (NIR). The frequency of the resonance absorptions depends on the particle shape, size, geometry, and dielectric medium [97–100]. The polarizability (P) of a spherical NP can be expressed as:

$$P = 4\pi\epsilon_0\epsilon_m a^3 \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m} E_0 \quad (2.8)$$

$$\alpha = 4\pi a^3 \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m} \quad (2.9)$$

where a is the diameter of the NP and ϵ_p and ϵ_m are the dielectric constants of the surrounding dielectric medium and of the metal NP itself, respectively. According to eqn (2.8), we can see that when $|\epsilon_p + 2\epsilon_m|$ becomes a small, while $\epsilon_p(\omega) = -2\epsilon_m$ the particle polarizability will become very large. According to Drude's model for metallic nanoparticles, the dielectric reply of the metallic sphere $\epsilon_p(\omega)$ is a complex number and the real component of dielectric response can be related to the frequency with the following expression:

$$\varepsilon_p(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2} \quad (2.10)$$

where ω is the frequency of the electric field of metal nanoparticles, and $\gamma = 1/\tau$ and the τ is the relaxation time of the electron, ω_p is the plasmon frequency of bulk longitudinal electron excitations. The plasmon frequency can be defined by the equation:

$$\omega_p = \sqrt{\frac{n_e e^2}{\varepsilon_0 m_e^*}} \quad (2.11)$$

Where e is electric charge, m_e^* is the effective mass of the electron, ε_0 is the free-space dielectric constant, and n_e is the electron number density. From equation (2.10) and (2.11) we can obtain the surface plasmon resonance frequency (ω_{LSPR})[89–91, 96].

$$\omega_{LSPR} = \omega_p \sqrt{\frac{1}{1 + 2\varepsilon_m} - \frac{1}{\omega_p^2 \tau^2}} \quad (2.12)$$

We can observe from this relationship that plasmonic resonant frequency strongly depends on the dielectric. But for the novel metal ω_p by defined in the equation(2.11) mainly depends on the density of free electrons in the particle. Which is located in the deep ultraviolet region. The resonant frequency can be adjusted by changing the dielectric constant of the embedding medium: a higher index causes a redshift in the resonance[94–96].

2.8.3 Near-field effect

The incident light interaction with plasmonic nanoparticles results in local perform enhancement of electromagnetic fields. However, surface plasmon resonance is accompanied by strong near fields due to resonant enhancement in polarizability. These interaction is creating an electric field outside and inside of the metal nanoparticles. It can be inferred from the potential obtained using the Laplace

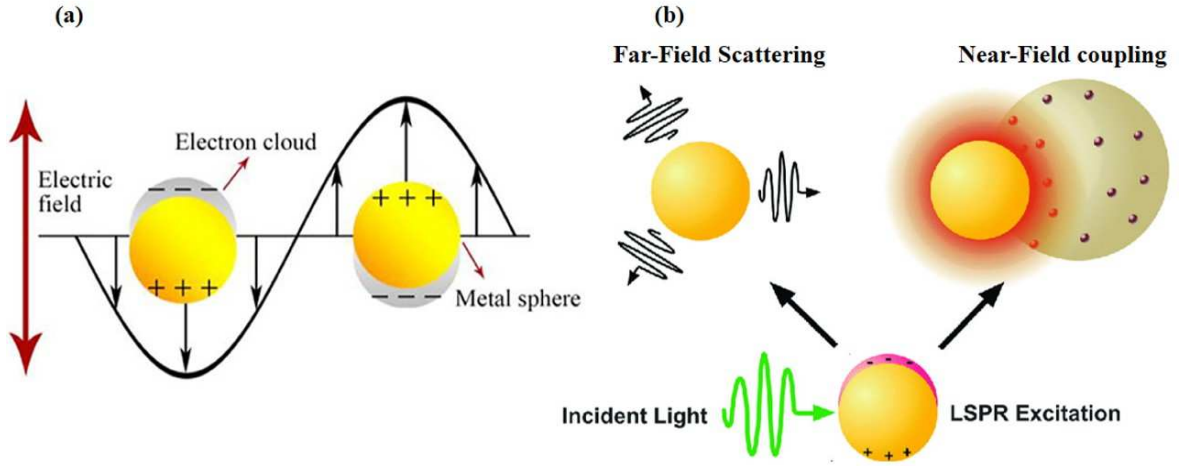


Figure 2.7: (a)Surface plasmon resonance oscillation for a sphere[86].
(b)Mechanisms of LSPR, far-field scattering and near-field[93].

Equation.

$$E_{in} = \frac{3\epsilon_m}{\epsilon_p + 2\epsilon_m} E_0 \quad (2.13)$$

$$E_{out} = E_0 + \frac{3\hat{n}(\hat{n} \cdot \vec{p}) - \vec{p}}{4\pi\epsilon_0\epsilon_m} \frac{1}{r^3} \quad (2.14)$$

Where r is the distance to the center of the spherical nanoparticles and $\hat{n}$ is the unit vector. The first term on the right-hand side of equation(2.14) represents the incident electric field and the second term represents the induced electric field within the spherical nanoparticles[89]. The near-field enhancement that plasmon nanoparticles can obtain near their surface is influenced by their morphology.

2.8.4 Far-field scattering effect

Another principle of the resonantly enhanced polarizability (P) can be used to trap the light inside solar cells, by light scattering and absorption, which increases the optical path length through the photoactive layer. Thus, it leads to improve performance. However, light incident on metal nanoparticles is scattered into the far-field, depending on the size and shape and material properties of the metal nanoparticles[93]. The extinction coefficient of the particles is defined as the sum of

the scattering and absorption. The scattering C_{sca} and absorption C_{abs} cross-sections are given by:

$$C_{sca} = \frac{1}{6\pi} * \left\{ \frac{2\pi}{\lambda} \right\}^4 |\alpha|^2 \quad (2.15)$$

$$C_{abs} = \frac{2\pi}{\lambda} Im[\alpha] \quad (2.16)$$

For the light-harvesting purposes in thin-film organic solar cells, the light scattering by the plasmonic nanoparticles should be greater than the parasitic absorption of the particle itself. In order to measure the scattering and absorption performances of the particles, We defined the efficiencies of scattering and absorption-through.

$$Q_{abs} = \frac{C_{abs}}{C_{abs} + C_{sca}} \quad (2.17)$$

$$Q_{sca} = \frac{C_{sca}}{C_{abs} + C_{sca}} \quad (2.18)$$

Thus, the absorption and scattering efficiency of the plasmonics nanoparticle depends on the particle size, shape, and type of the particle as well as its surrounding medium. Moreover, for photovoltaic cells application, the size of the nanoparticle should be smaller than particle size < 50 nm. Thus, LSPR can improve the power conversion efficiency of solar cells by increasing light absorption and exciton-generation.

2.8.5 Surface plasmon polariton (SPP)

Plasmonic effects in solar cells is to use metal nano-structured particles in thin-film solar cells to enhance photons harvesting through the effect of surface plasmon polariton. The surface plasmon polariton is occurring due to the collective oscillation of surface electrons that creates a strong, oscillating electric field that propagates along the surface. The oscillating electric field propagates into both metal and dielectric layers, where the dielectric portion will be improved and produces a photovoltaic enhancement[102]. The nano-particles are sandwiched at the interface of the metal electrode and dielectric medium and can spread with it for a few micrometers until the energy is lost in the metal or absorbed into the dielectric layer(see Fig

2.6c). SPP excitation at the metallic/dielectric interface can only be achieved when the momentum component in the photon momentum that coincides with that of SPP. The improvement of light absorption in solar cells is due to the strong propagation of the SPP at the interface, and this is particularly useful for thin-film organic solar cells [102, 103].

2.9 Metals nano-particles in the active layer of OPV

The plasmonic nano-structures embedded in the photoactive layer of thin-film organic solar cells can significantly improve the optical absorption and collection of photo-generated charge carriers through localized surface plasmonic resonance (LSPR) effect and light scattering in the medium. Consequently, the effects increases the power conversion efficiency (PCE). If the metal nano-particles are at the top surface of the active layer and have small diameters, they might excite free electrons through localized surface plasmon resonance. Moreover, metallic films at the back surface of a thin film photovoltaics absorber layer can couple sunlight by surface plasmon polariton [104–106].

Incorporation of the small amount of Au NPs into the active layer PTB7/PC₇₀BM is reported to have increased broadband plasmon-induced absorption enhancement ranging from 350 to 800 nm. The result has significantly enhanced the power conversion efficiency as high as PCE= 9.62%[107]. Tzounis et al. investigated the effect of bimetallic plasmonic nanoparticles Au@Ag(NPs) incorporated into PC3HT:PCBM exhibited improved device performance the PCE= 2.69% compared with the pristine device its efficiency PCE=2.24%. The improvement of performance due to the increased optical absorption attributed to the plasmonic nanoparticles (NPS), which has an average size of 40 nm. Oseni et al. incorporated two types of bimetallic nanocomposites such as silver:zinc (Ag:Zn) and silver:magnesium (Ag:Mg) into PTB7:PCBM blend photoactive layers in an inverted organic solar cells. The results showed that metal nano-composite improved optical and electrical properties and achieved PCE=3.90%, 4.96%, respectively. The im-

Table 2.1: Summary of the device performances plasmonic OPV devices with inclusion of metallic NPs in the active layer.

Device structure	Plasmonic nanostructure	V_{oc} (V)	J_{sc} (mAcm^{-2})	FF	PCE	Year	Ref
ITO/PEDOT:PSS/P3HT:PCBM-Ag@Cu/ LiF/Al	Ag@Cu NPs	0.60	11.90	54.40	3.87	2019	[37]
ITO/PEDOT:PSS/P3HT:PCBM:Ag@Au/ LiF /Al	Au:Ag	0.52	15.40	51.00	3.29	2019	[112]
ITO/PEDOT:PSS/Ag@SiO ₂ /PTB7:PC70BM /Al	Ag@SiO ₂	0.74	16.65	68.00	8.92	2013	[113]
ITO/PEDOT:PSS/Au@SiO ₂ /P3HT:PCBM /Al	Au@SiO ₂	0.62	10.60	57.00	3.80	2013	[114]
ITO/PEDOT:PSS/P3HT:ICBA-Au /Ca /Al	Au NPs	0.84	11.56	68.83	6.68	2015	[115]
ITO/PEDOT:PSS/P3HT:PCBM: Au/ Al	Au-NPs	0.60	9.45	56.65	3.20	2015	[115]
ITO/ZnO/P3HT:PCBM:Ag@SiO ₂ /MoO ₃ /Ag	Ag@SiO ₂	0.61	9.72	66.50	3.94	2015	[100]
ITO/PEDOT:PSS/P3HT:PCBM-Au/ Al	Au NPs	0.60	9.77	63.38	3.71	2012	[87]
ITO/TiO ₂ /PBDTTT-C-T:PC ₇₁ BM+Au /MoO ₃ /Ag	Au	0.76	18.39	62.87	8.79	2012	[88]
ITO/PEDOT:PSS/Ag@SiO ₂ /PTB7:PC ₇₁ BM /Ca /Al	Ag@SiO ₂	0.75	17.05	67.30	8.61	2018	[116]
ITO/PEDOT:PSS/PCDTBT:PC ₇₁ BM-Ag/ TiO _x /Al	Ag NPs	0.86	11.61	69.00	7.10	2011	[104]
ITO/PEDOT:PSS/P3HT:PCBM-Ag /Ca /Al	Ag NPs	0.64	9.93	64.08	4.07	2013	[105]
ITO/PEDOT:PSS/PTB7:PC ₇₁ BM-Au@Ag@SiO ₂ /Ca /Al	Au@Ag@SiO ₂ NC	0.75	18.07	70.8	9.56	2016	[106]
ITO/PEDOT:PSS/PBDTTT-C-T:PC ₇₁ BM-Ag@SiO ₂ /Ca /Al	Ag@SiO ₂ NPs	0.76	16.94	62.0	7.77	2017	[117]
ITO/PEDOT:PSS/P3HT:PCBM-Ag:Zn:Ni /LiF /Al	Ag:Zn:Ni NC	0.56	12.36	47.70	3.33	2019	[33]
ITO/ZnO/PTB7:PCBM-Ag:Zn:Ni/MoO ₃ / Al	Ag : Zn :Ni NC	0.73	14.76	46.93	5.06	2019	[119]
ITO/ZnO/PTB7:CdS:PCBM/MoO ₃ /Ag	CdS-NPs	0.74	14.20	64.65	6.80	2016	[120]
ITO/PEDOT:PSS/P3HT:PCBM-Ag:Zn /LiF /Al	Ag:Zn NPs	0.55	14.00	47.00	3.60	2017	[121]
ITO/rGO/ZnO/P3HT:PCBM-Ag /MoO ₃ /Ag	Ag-NPs	0.63	10.99	63.64	4.37	2016	[122]
ITO/rGO/ZnO/P3HT:PCBM-Au /MoO ₃ / Ag	Au-NPs	0.63	11.17	63.70	4.44	2016	[122]
ITO/TiO ₂ /PBDTTT-C-T:PC ₇₁ BM+Au/MoO ₃ / Ag	Au-NPs	0.88	16.01	48.10	6.83	2015	[123]
ITO/PEDOT:PSS/P3HT:PCBM:Zn-SnS/ LiF/ Al	Zn-SnS NPs	0.55	12.65	54.00	3.75	2020	[124]

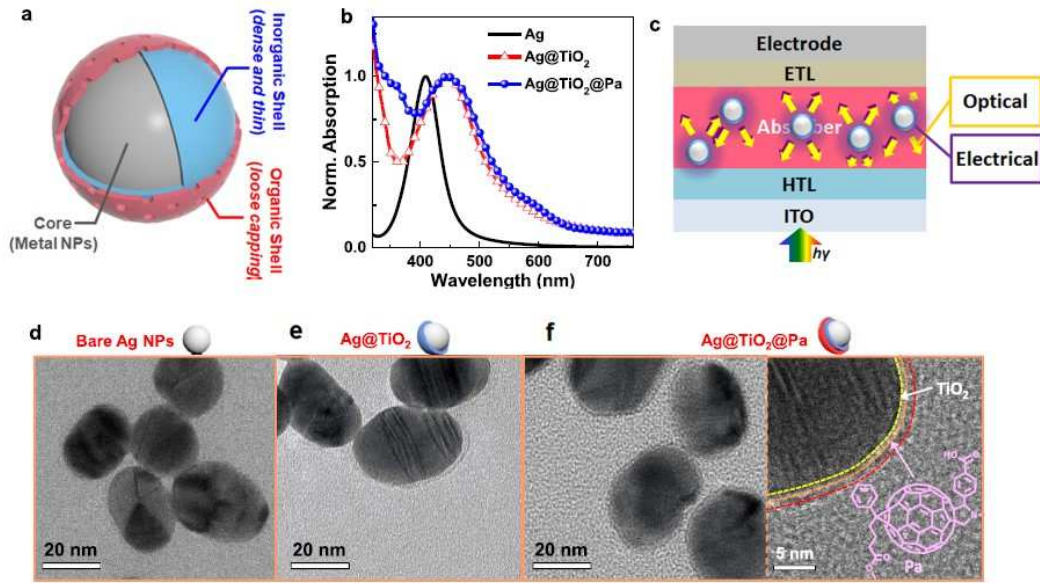


Figure 2.8: (a) Core-bishell design concept for metal nanostructures. (b) UV-vis spectra of parent Ag and Ag@TiO₂ as well as Ag@TiO₂@Pa. (c) The device structure of the plasmonic solar cell architectures. (d) TEM images as-obtained Ag NPs. (e) Ag@TiO₂. (f) TEM and HRTEM images of Ag@TiO₂ decorated with Pa [110]

provement of the performance is attributed to the LSPR and light scattering nature of Ag coupled with electrical and optical properties of the zinc and magnesium which have increased power conversion efficiency of the solar cells[49]. Yao et al. have studied the maximize light coupling into the active layer, by using core-bishell plasmonic nanoparticles (NPs) which are designed from metal-inorganic semiconductor-organic semiconductor nanostructure (Ag@TiO₂@Pa) (see Fig 2.8). The plasmonic nano-structures have been embedded into both active layers organic solar cells (OSCs) and perovskite solar cells (PSCs) to enhance optical absorption that resulted in improved device performance. On the other hand, the Ag NPs were decorated with a titania/ (Ag@TiO₂) with a fullerene shell that can activate efficient plasmon-exciton coupling and removes the exciton quenching. Moreover, Ag NPs within the photoactive layer may lead to improved light absorption with an increase in exciton generation by localized surface plasmon resonance and more efficient light scattering within the active layers. Meanwhile, the TiO₂ fullerene bishell enables the generated carriers to be transferred through NPs, this may lead to an increased carrier collection efficiency. The efficiency of both device (OSC), and (PSC)

has significantly improved with PCE reaching 13.0% and 20.2%, respectively[110].

2.10 Metal nano-particles in charge transport the buffer layer

The plasmonic metal nano-structures embedded in the buffer layers such as the electron transport layer (ETL) or hole transport layer (HTL), can also lead to incident light-trapping and/or scattering. The scattering is dependent on the location of the nano-structures. The feature of incorporating nano-particles within the hole transport layer to obtain higher performance is achieved due to better hole collection and reduction of recombination through various mechanisms [126]. For instance, when the nano-structures are embedded in the rear side of the buffer layer (see Fig 2.9), the scattering of light occurs and leads to total internal reflection within the photo-active layer which significantly increases the optical path length and the absorption of more photons in the active layer[128]. Moreover, the incorporation of nano-structures in the PEDOT:PSS hole transport layer also leads to significantly enhanced interfacial roughness between the photo-active and hole transport layers that reduces series resistance and increasing the photocurrent density. This is because metal NPs in PEDOT:PSS exhibits local surface plasmon resonance (LSPR)[129] and increases the conductivity of the medium. M.Tang et al. demonstrated that the of Cu-Au bimetallic NPs with core-shell structure embedded in PEDOT:PSS, hole transport layer of organic solar cells, is reported to have caused high device stability as well as broad optical absorbances compared to the pristine layer. The efficiency of the solar cells reported by the incorporation of Cu-Au core-shell nano-structures is PCE =8.48%. This significant improvement in device performance is due to LSPR and also light scattering[130].

Table 2.2: Summary of the device performances plasmonic OPV devices with inclusion of metallic NPs in the buffer layer.

Device structure	Plasmonic nanostructure	V_{oc} (V)	J_{sc} (mAcm^{-2})	FF	PCE	Year	Ref
ITO/PEDOT:PSS: Au@SiO ₂ /PTB7:PC ₇₁ BM/ LiF/ Al	Au@SiO ₂ NPs	0.78	18.75	65.16	9.55	2020	[125]
ITO/Au:ZnO/PBDTTT-C-T:PC ₇₁ BM /MoO ₃ /Ag	Au NPs	0.75	15.81	66.20	7.86	2015	[126]
ITO/ZnO:Ag-SiO ₂ /P3HT:PCBM /PEDOT:PSS/ Ag	Ag-NPs SiO ₂	0.58	14.14	46.00	3.54	2019	[127]
ITO/PEDOT:PSS: Au/PTB7:PC ₇₁ BM/ TiO _x :Au /Al	Au-NPs	0.76	17.17	61.40	8.01	2016	[128]
ITO/PEDOT:PSS: Au/PCDTBT:PC ₇₁ BM/ TiO _x :Au /Al	Au-NPs	0.89	12.03	62.90	6.75	2016	[128]
ITO/PEDOT:PSS: Au/P3HT:PCBM/ LiF/ Al	Au-NPs	0.63	8.94	62.00	3.51	2011	[129]
ITO/PEI/P3HT:ICBA/WO ₃ :Cu/Ag	Cu-NPs	0.87	11.79	62.20	6.38	2016	[131]
ITO/PEDOT:PSS: Au/PBDT-TS1:PC ₇₀ BM/ Ca/ Al	Au-NPs	0.82	18.72	67.34	10.29	2017	[132]
ITO/PEDOT:PSS: SiO ₂ / P3HT:PC ₆₁ BM /Al	SiO ₂ NPs	0.52	12.10	36.00	2.27	2017	[133]
ITO/PEDOT:PSS: Ag/PTB7:PC ₇₁ BM /Ca/ Al	Ag-NPs	0.68	14.70	63.20	6.40	2018	[134]
ITO/PEDOT:PSS: Cu/P3HT:PC ₆₀ BM/ TiO _x / Al	Cu-NPs	0.63	10.06	62.2	3.96	2014	[135]
ITO/PEDOT:PSS: Cu/PTB7:PC ₇₀ BM/ TiO _x / Al	Cu-NPs	0.63	10.06	62.2	3.96	2014	[135]
ITO/WO ₃ : Au@SiO ₂ /P3HT:PCBM/ LiF/ Al	Au@SiO ₂	0.61	4.72	54.00	1.58	2019	[136]
ITO/PEDOT:PSS: Ag/PTB7:PC ₇₀ BM /Ca /Al	Ag-NPs	0.71	16.40	68.80	8.01	2013	[137]
ITO/PEDOT:PSS: Au/PTB7:PC ₇₀ BM /Ca /Al	Au-NPs	0.71	16.70	68.80	8.16	2013	[137]
ITO/PEDOT:PSS: Au+Ag/PTB7:PC ₇₀ BM /Ca /Al	Au+Ag NPs	0.71	17.70	69.00	8.67	2013	[137]
ITO/PEDOT:PSS: Ag:Zn/P3HT:PCBM /LiF/ Al	Ag:Zn-NPs	0.59	15.3	53.00	5.0	2019	[138]

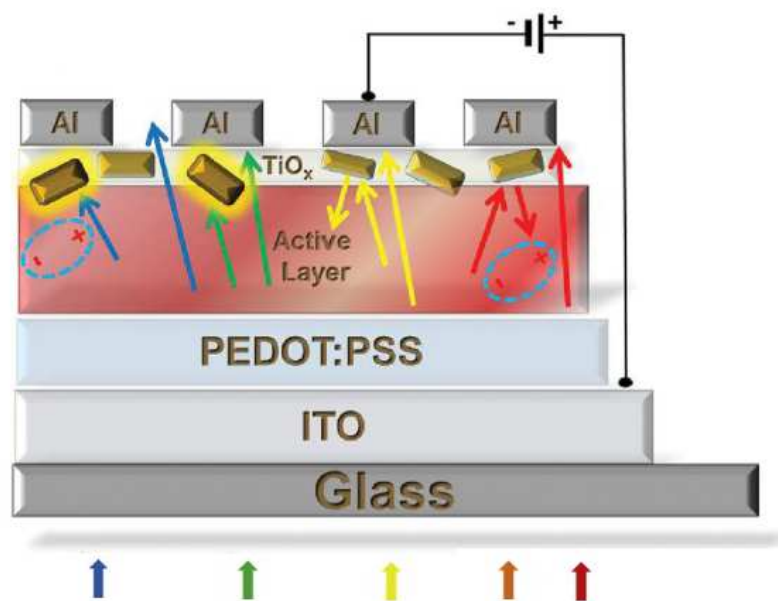


Figure 2.9: Structure of an OPV cell incorporating NPS in the rearward electron transport layer[128].

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CHAPTER 3

Materials and Methods

This chapter summarizes the list of all chemicals, experimental methods, and characterization that have been used in this thesis. Recently, nanostructured metal sulfides have been successfully incorporated in thin-film organic solar cell structures to improve the device's performance.

3.1 Materials

Chemicals used in this research copper nitrate hydrate, silver nitrate hexahydrate, nickel (II) nitrate hexahydrate, lanthanum(III) nitrate hexahydrate, orthophosphoric acid (H_3PO_4), sodium sulfide nonahydrate (Na_2S), thiourea ($\text{CH}_4\text{N}_2\text{S}$), Polyvinyl Pyrrolidone (PVP), ethanol, and sodium hydroxide (NaOH)

3.1.1 Synthesis of CuS

The synthesis begins with the preparation of various solutions of chemicals in 50 mL of deionized water. The solutes such as 3.0 g of PVP, 1.95 g (0.5 M) of ($\text{Na}_2\text{S}\cdot 6\text{H}_2\text{O}$), and 0.5 M (4.689 g) ($\text{Cu}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$) are dissolved in 50 mL of deionized water in separate flasks. The solutions are then stirred at room temperature and eventually mixed together in a drop-wise manner while stirring the copper nitrate $\text{Cu}(\text{NO}_3)_2$ solution. The mixture of the solutions was further stirred at 450-500 rpm at room temperature until a gel-like solution is formed. The precipitate was centrifuged twice at 4500 rpm for 5 min followed by washing successively with deionized water

and ethanol, respectively. This precipitate was dried in an oven at 100 °C for 2-3 h. The resultant copper sulfide nanoparticles (CuS)(see Fig 3.1).

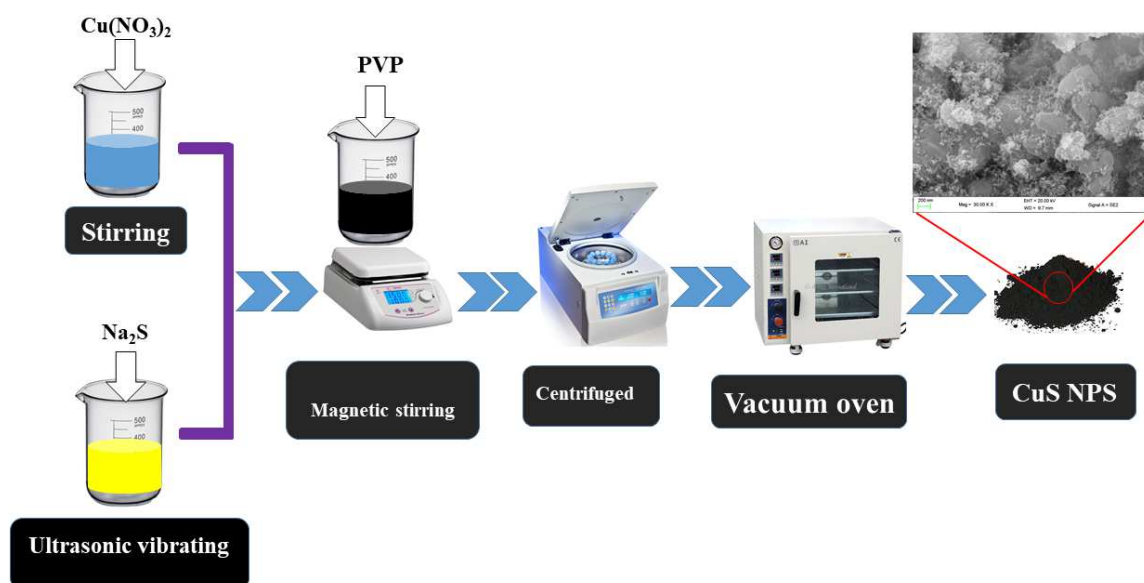


Figure 3.1: Synthesis of copper sulfide nanoparticles (CuS)

3.1.2 Synthesis of NiS

0.2 M from $(\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ and $(\text{CH}_4\text{N}_2\text{S})$ each and dissolved in deionized water in separate flasks and, stirred for two hours to attain a complete mixing. The two solutions were mixed. The resulting mixture is a deep green solution turned into black colour after adding drop-wise 0.1 M of NaOH which was dissolved in 50 mL deionized water. Then, the precipitated particles were centrifuged and washed with distilled water and ethanol, respectively. The filtered precipitate was dried at 80 °C for 24 h and was annealed at 300 °C for 30 min which resulted in the formation of nickel sulphide nanoparticles. The resultant Nickel sulphide nanoparticles (NiS).

3.1.3 Synthesis of Ag_2S

1.698 g (0.1 M) of silver nitrate hexahydrate ($\text{AgNO}_3 \cdot 6\text{H}_2\text{O}$), 0.4g (0.1 M) of sodium sulfide ($\text{Na}_2\text{S} \cdot 6\text{H}_2\text{O}$) and 3.0 g of PVP were dissolved in 50 mL of deionized water

solvent, separately. The solutions of sodium sulfide and PVP were mixed into silver nitrate solution by drop-wise while stirring using a magnetic stirrer. The resulting product was centrifuged, and dried in an oven at 80 °C for 2-3 h. The resultant silver sulfide nano-particles (Ag_2S).

3.1.4 Synthesis of $\text{LaPO}_4\text{:Ag}$

0.1 mol of lanthanum nitrate $\text{La}(\text{NO}_3)_3$, 0.05 mol of silver nitrate AgNO_3 were dissolved in 25 mL of deionized water, separately. 0.1 mol of orthophosphoric acid H_3PO_4 dissolved in 48 mL of deionized water. The silver nitrate was then added into lanthanum nitrate solution in drop-wise while continuous stirring. Then orthophosphoric acid slowly added by drop-wise into the above mixture. The resulting product was filtered, washed, and dried in an oven at 70 °C for 2 h. The resultant silver sulfide nano-particles ($\text{LaPO}_4\text{:Ag}$).

3.2 Characterization techniques

3.2.1 UV-Vis spectroscopy

The optical absorption was measured by UV-vis spectrometer (Rayleigh 1601), the optical absorption was run in the range 250-900 nm. All the nanoparticles were dissolved in different solvents, such as deionized water, ethanol, Aston, and then they were transferred into a quartz cell and the absorption data was recorded in nanometres (nm).

3.2.2 SEM and TEM electron microscopy

Scanning electron microscope (SEM: JEOL JSM6100), transmission electron microscope (TEM: JEOL JEM 1010), applied to investigate the surface morphology and composition of the metals nanoparticles.

3.2.3 XRD analysis

The crystal structure was characterized by powder X-ray diffraction analysis using a PERT-PRO diffractometer with filtered Cu-K α 1 radiation source ($\lambda=0.15406$ nm) to structural phase at 2θ values, ranging from 15-90.

3.3 Solar Cell Fabrication

3.3.1 Regular structure

Unpatterned ITO coated glass substrate was used in the preparations of conventional thin-film solar cells which begins by partially etching the ITO with an acid solution (HCl:H₂O: HNO₃ at 48%:48%:4%). The substrates were then cleaned successively with detergent, deionized water, acetone, and isopropanol for 10 min each, respectively [1, 2]. They were then dried under a nitrogen flow and then immediately baked in an oven at 120°C for 20 min. A thin layer of PEDOT:PSS hole transport layer (HTL) was spin-coated on the ITO substrate at 3500 rpm for 60 s which then annealed at 120°C on a hotplate for 20 min. The solution of the photoactive layer was prepared in chloroform solvent using P3HT and PC61BM blend at a 1:1 ratio by weight at a concentration of 20 mg/mL. The mixture was stirred for 4 hrs at 40°C to enhance the miscibility of the molecules. The photoactive films were spin-coated at 1200 rpm for 40 s and annealed at 90°C for 5 min in an N₂ filled furnace. Finally, the LiF electron transport layer and aluminum Electrodes were deposited

on the active layer under a vacuum pressure lower than 4.0×10^{-6} Pa at a thickness of 0.5 nm and 85 nm, respectively.

3.3.2 Inverted structure

First, the substrates were then cleaned successively with detergent, deionized water, acetone, and isopropanol for 10 min each, respectively [1, 2]. A thin layer of ZnO electron transport layer (ETL) was spin-coated on the substrate at 3500 rpm for 60 s. The ZnO film was dried at 100°C on a hotplate for 20 min under ambient conditions. The photoactive layer was spin-coated on ETL from the solution of P3HT and PC61BM blend 1:1 ratio by weight at a concentration of 20 mg/mL. The mixture was stirred for 4 hrs at 40°C to enhance the miscibility of the molecules. The photoactive films were spin-coated at 1200 rpm for 40 s and annealed at 90°C for 5 min in an N₂ filled furnace. Finally, the hole transport layer (MoO₃) and aluminum electrodes were deposited at a thickness of 8 nm and 85 nm, respectively.

3.3.3 J-V characteristics

J-V of all the devices was measured using solar simulation systems, the solar simulator is a light source with a broadband optical output similar to that of the sun over the response range of different solar cell technologies. The primary applications of these solar simulators are testing photovoltaic cell performance, consists of a computer interfaced with a Keithley (HP2420) source meter and a solar simulator (model SS50AAA) under a AM 1.5 illumination and operating at a light intensity of 100 mW/cm² [3, 4]. The solar simulator was controlled by a computer using an application I-V measurement software, the computes solar cell parameters such as I_{sc} , V_{oc} , I_{max} , V_{max} , P_{max} , FF, R_{sh} , R_s and η cell conversion efficiency, complete light and dark I-V curves, and it is saved them automatically on the hard disk drive.

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CHAPTER 4

Copper sulphide as a mechanism to improve energy harvesting in thin film solar cell

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Copper sulphide as a mechanism to improve energy harvesting in thin film solar cells

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ABSTRACT

Copper sulphide nano-particles (CuS) was successfully synthesized and incorporated in the thin film organic solar cell (TFOSC). The photo-active film of TFOSC is composed of poly(3-hexylthiophene) (P3HT) and (phenyl-C61-butyric acid methyl)(PC₆₁BM) blend. The synthesized nano-particles were characterized using high-resolution scanning and tunnelling electron microscopy (HRSEM and HR-TEM), respectively. Copper sulphide nano-particles were used within the photo-active layer of the newly fabricated TFOSC to assist in solar energy harvesting by way of improved optical absorption and charge transport processes. The concentration of CuS in the solar absorber medium of the devices play a critical role in attaining improved power conversion efficiency. The best device performance was attained at the concentration of 3% CuS by weight in the polymer blend matrix. The result is clearly evident on the measured enhanced short-circuit current density (J_{sc}) of the solar cells. Consequently, the power conversion efficiency (PCE) has grown by 69% compared to pristine type solar absorber films. The best power conversion efficiency recorded in this investigations was 5.04% which is an important development in the ambient condition device fabrication.

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4.1 Abstract

Copper sulphide nano-particles (CuS) was successfully synthesized and incorporated in the thin film organic solar cell (TFOSC). The photo-active film is composed of poly(3-hexylthiophene) (P3HT) and (phenyl-C61-butyric acid methyl)(PC₆₁BM) blend. The synthesised nano-particles (CuS) were characterized using high-resolution scanning and tunnelling electron microscopy (HRSEM and HR-TEM), respectively.

Copper sulphide nano-particles were used within the photo-active layer of the newly fabricated TFOSC to assist in solar energy harvesting by way of improved optical absorption and charge transport processes. The concentration of the CuS in the solar absorber medium of the devices play a critical role in attaining improved power conversion efficiency. The best device performance was attained at the concentration of 3 % CuS by weight in the polymer blend matrix. The result is clearly evident on the measured enhanced short-circuit current density (J_{sc}) of the solar cells. Consequently, the power conversion efficiency(PCE) has grown by 69% compared to pristine type solar absorber films. The best power conversion efficiency recorded in this investigations was 5.04% which is an important development in the ambient condition device fabrication.

4.2 Introduction

Solution processable-thin film organic photovoltaics (TFOPVs) is relatively new solar cell technology that offers a number of advantages over traditional silicon based solar cells in terms of the ease of device fabrication, low-cost, semi-transparency, mechanical flexibility and abundance of raw materials [1–13]. Organic solar cell research has made significant stride in terms of improving power conversion efficiency and device stability in the past 20 years. At present, the power conversion efficiency of TFOSC reached a record level over 13% which is well beyond the minimum required PCE for mass production [5, 6]. Organic semiconductors can be regarded as wide bandgap semiconductors in an intrinsic phase whose conductivity can go down to “insulators” (with energy band gaps ≥ 3 eV) and possess low intrinsic charge carrier density at room temperature. However, the conductivity of polymer semiconductor can improve as high as metals through the process of doping because of their tunable energy band gap. This attractive features of the polymers have brought enormous potential applications in photonic and electronics devices. Conjugated polymer has relatively high hole and low electron mobilities in an intrinsic phase that leads to imbalance carrier transport which can be reduced

by the incorporation of fullerene derivatives such as PCBM as electron acceptor. The introduction of bulk heterojunction (BHJ) device architecture, in the preparations of OSC, resulted in tremendous progress in achieving highly efficient solar cells. The device performance of polymer solar cells can be affected by a number of factors such as fabrication methods, materials used, film thicknesses and morphology [10, 11, 14–16].

The most popular polymer blends in the fabrication thin film organic solar cells are P3HT:PC₆₁BM, PTB7:PC₇₁BM, PCDTBT:PC₆₁BM etc. These polymer blends have exhibited a very promising photovoltaic characteristics that could lead to the realization of mass cheap device production [17, 18]. Moreover, a water soluble conducting polymer known as poly(3,4-ethylenedioxythiophene)-polystyrene-parasulfonic acid (PEDOT:PSS) is commonly used as a hole transport buffer layer because of its good conductivity, high light transmittance and suitable work function (~ 5.0 eV) [19–23]. In fact, inorganic p-type semiconductors such as metal oxides and CuS are also been used as a hole transport layer in TFOSC that have produced even better device performance and stability. CuS is also widely applied in thin films and composite materials. Recently, it proved to be a good counter electrode for quantum dot sensitized solar cells [24–26].

In thin film solar cells, the ability to harvest solar energy is mainly dictated by the nature of the solar absorbing medium of the device. Low band gap conjugated polymers are the most successful solar absorbers in the preparations of OSC, which have optical absorption in visible and near infrared regions where the intensity of the solar radiation is high. Thus, in order to assist the effort of solar harvesting, there is a growing interest in the use of metal nanoparticles in organic photovoltaic research by way of exploiting the property of localized surface plasmonic resonances (LSPR) of metal nanoparticles [27, 28]. Recently, metals such as Au, Ag nanoparticles and trimetallic (Ag:Zn:Ni) nano-composites have been successfully incorporated in thin film organic solar cell structure to improve the performance of devices. [29–34]. In most cases, reports suggest that the incorporation metal nanostructures in polymer matrix increased photons harvesting that resulted in enhanced device performance. Lei et al. have fabricated solar cells using a thin layer of CuS film as hole transport-

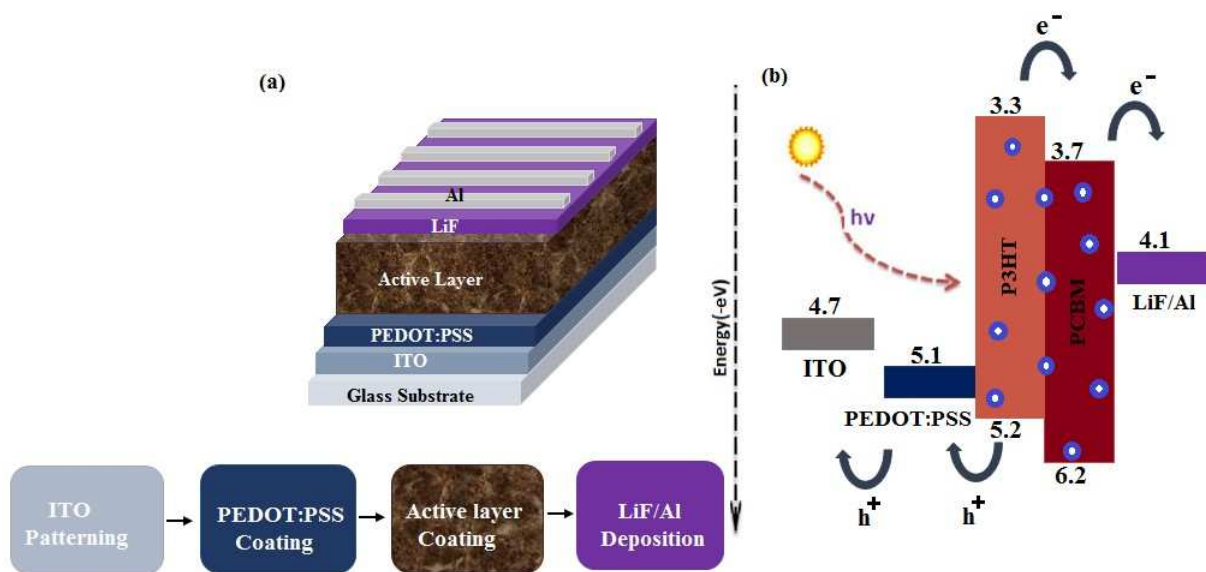


Figure 4.1: (a) Schematic diagram for bulk heterojunction organic solar cell based on P3HT:PC₆₁BM active layer doped with CuS nano-particles. (b) energy level diagram of the materials used in device fabrication.

ing layer (HTL) because of its high hole mobility and good transparency and high environmental stability [35]. The authors have reported that the CuS hole transport layer produced enhanced fill factor $FF = 56\%$, $V_{oc} = 0.55V$, $J_{sc} = 10.96 \text{ mAcm}^{-2}$ and a power conversion efficiency (PCE) = 3.4% [35]. In this article, we are reporting a better device performance by employing a newly synthesized copper sulphide (CuS) nano-particles in the photoactive layer of P3HT:PC₆₁BM based organic solar cells. The fabricated devices showed significant improvement in terms of charge collection that leads to enhanced power conversion efficiency.

4.3 Experimental section

4.3.1 Materials

The chemicals required for the synthesis of copper sulfide nano-particles are obtained from commercial sources and used as received. These are copper nitrate

hydrate (>99.999% $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$), sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 6\text{H}_2\text{O}$), 98.0%), and Polyvinyl Pyrrolidone (PVP) molecular weight 25000-30000 (from Merck, Germany). The polymer molecules such as poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)(PEDOT:PSS), poly(3-hexylthiophene)(P3HT), and phenyl- C_{61} -butyric acid methyl ester (PC_{61}BM) were purchased from Ossila Ltd.(UK).

4.3.2 Synthesis Of CuS Nanoparticles

The synthesis of copper sulfide nano-particles begins with the preparation of various solutions of chemicals in 50 mL of deionized water. The solutes such as 3.0g of PVP, 1.95g(0.5M) of ($\text{Na}_2\text{S} \cdot 6\text{H}_2\text{O}$) and 0.5M(4.689g) ($\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) are dissolved in 50 mL of deionized water in a separate flasks. The solutions are then stirred at room temperature and eventually mixed together in drop-wise manner while stirring the copper nitrate $\text{Cu}(\text{NO}_3)_2$ solution. The mixture of the solutions was further stirred at 450-500 rpm at room temperature until gel like solution is formed. The gel was then kept in an open air for 2-3 hours for precipitation. The precipitate was then centrifuged two or three times at 4500 rpm for 5 min followed by washing successively with deionized water and ethanol, respectively. This precipitate was dried in vacuum oven at 100°C for 2-3 hours. The residual of the precipitation is a powder of metal copper sulfide nano-particles (CuS). The synthesised CuS nano-particles were then characterized in terms of structural, optical and morphological properties by various spectrometer like scanning electron microscope (SEM:JEOL JSM6100), transmission electron microscope (TEM:JEOL JEM 1010) and high-resolution transmission electron microscope (HR-TEM:JEOL JEM2100), X-ray diffraction(XRD) analysis and Raman spectroscopic.

4.3.3 Device Fabrication

Bulk heterojunction thin film solar cells were fabricated which are composed of different layers of materials as glass/ITO/PEDOT: PSS/P3HT: PC_{61}BM :CuS/LiF/AL.

Schematic diagram provided in Fig 4.1 shows the various layers of materials that forms the solar cell. The device fabrication begins by etching unpatterned ITO-coated glass substrates using a warm acid solution containing HCl:H₂O:HNO₃ at 48%:48%:4% by volume. The substrates were then cleaned successively with detergent, deionized water, acetone, and isopropanol for 10 minutes each, respectively. They were then annealed in an oven at 120°C for 30 minutes. [37, 49]. A thin layer of PEDOT:PSS was spin-coated on partially etched glass substrates at 3500 rpm for 60s. The PEDOT:PSS film was dried at 120°C on a hotplate for 30 min. The solution of the active layer was prepared in chloroform solvent using P3HT and CBM blend 1:1 ratio by weight. The CuS nano-particles were added in the blend solution at the concentration of (3 %) and (5 %) by weight in a separate solutions. The solutions were stirred on a hot plate at an average temperature of 45°C for 3-4 hours. The photo-active films were spin-coated at 1200 rpm for 40 s and annealed at 90°C for 5 min in a N₂ filled furnace. Finally, a thin layer of LiF and aluminium electrode were deposited using Edward Auto 306 deposition unit at 0.4 nm and 60 nm, respectively. The current density-voltage (J-V) data are collected using Keithley HP2420 source meter and a solar simulator (model SS50AAA) operating at AM1.5 and 100 mW/cm². The photo-active film optical properties were studied using UV-vis spectrometer (Rayleigh 1601).

4.4 Results and discussion

4.4.1 Characterizations of CuS

SEM and TEM electron microscopy

The surface morphology and composition of the copper sulfide nano-particles was investigated by high-resolution scanning and electron microscopy (HRSEM and HRTEM). The HRSEM image provided in Fig.4.2(b) shows the various structure of CuS nano-particles formation as described by the different shapes and sizes. The

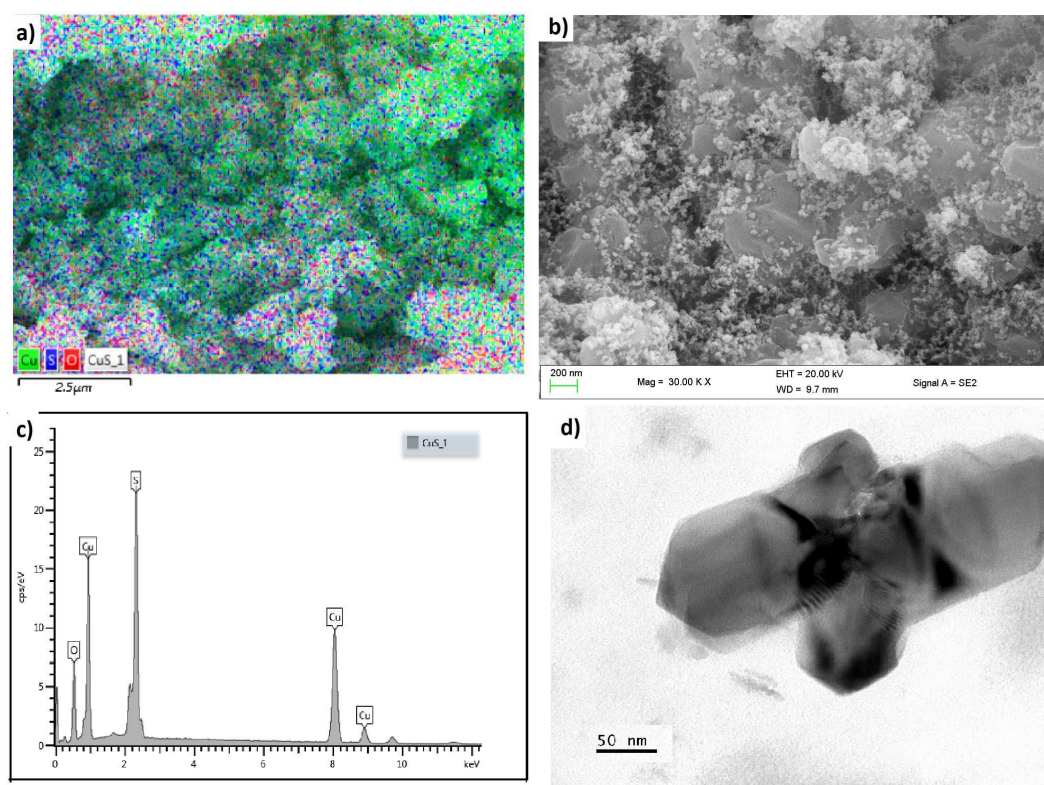


Figure 4.2: (a) and (b) are HRSEM images taken from CuS powder while (d) is its HRTEM image. (c) is an energy dispersive X-ray (EDX) spectrum of CuS

elemental mapping given in Fig. 4.2 (a) clearly showed uniform distribution of elements of copper and sulfur in the powder form. Fig.4.2(d) is the TEM images taken from CuS powder suspended in distilled water. A drop of suspension was transferred onto the HRTEM sample holder and the images taken are an indicative of the formation of large sized CuS clusters. The CuS nano-particles possesses hexagonal like structure as confirmed by XRD data discussed in the following section. This kind of hexagonal structure of copper sulfide nano-particles has been reported by the previous investigations [38]. The elemental analysis carried out using EDX (see Fig.4.2(c)) confirm the existence of copper, sulfur and small trace of oxygen element. The presence of oxygen may be due to the partial oxidation of the metal element due to exposure to the ambient environment.

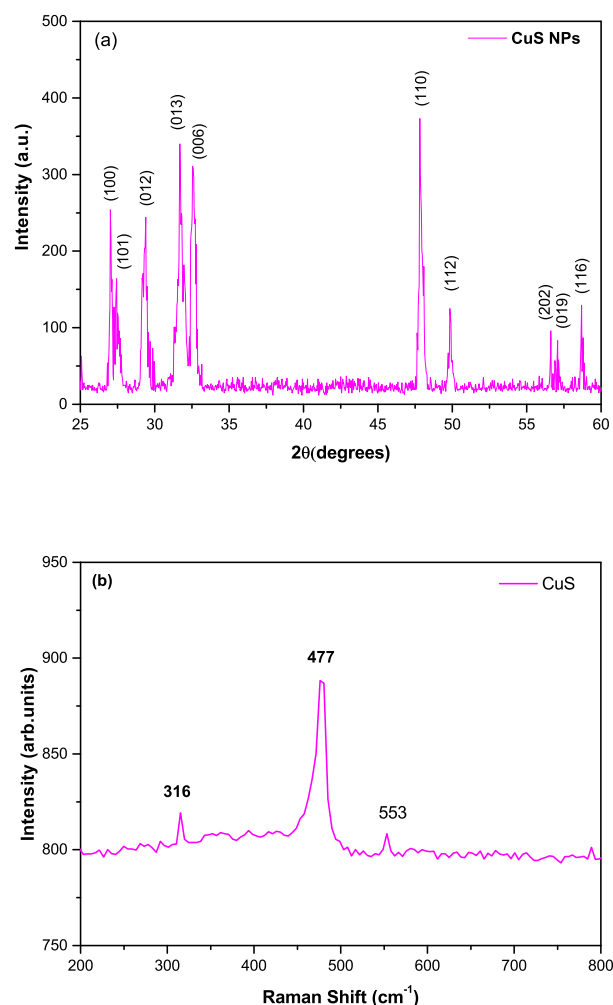


Figure 4.3: (a)X-ray diffraction pattern of CuS nano-particles (b)Raman spectra of the CuS indicating the possible bond stretching of the molecules

X-ray diffraction and Raman spectroscopic

The XRD data were measured from copper sulfide nano-particles powder is given by Fig.4.3(a). According to the spectrum provided in Fig. 4.3a, four prominent peaks are observed at the diffraction angles $2\theta = 27.059^\circ$, 27.608° , 32.67° , 47.835° and 59.113° . These peaks corresponds to the X-ray reflections from lattice planes (100), (101), (006), (110), (116), respectively. The planes represents hexagonal phase of the CuS covellite with cell parameters, $a = 3.802\text{\AA}$ and $c = 16.4299\text{\AA}$. Comparison of the data with the standard diffraction pattern (JCPDS Card No.06-0464) confirmed the existence of CuS and the associated crystal structure is found to be similar to those

Table 4.1: XRD data of CuS nanoparticles

Peak No.	2 θ (degree)	hkl	FWHM(β)	d(nm)
1	27.02	(100)	0.32607	25.05
2	27.45	(101)	0.32607	25.07
3	29.39	(012)	0.30794	26.67
4	31.69	(013)	0.336	24.57
5	32.55	(006)	0.34034	24.31
6	47.81	(110)	0.5627	15.44
7	49.84	(112)	0.14155	61.88
8	56.62	(202)	0.07822	115.61
8	57.08	(019)	0.05607	161.28
9	58.78	(116)	0.09138	99.77

reported in literatures [39–41]. Subsequently, the crystallite size of the particles was calculated using the Debye Scherrer formula (equ. 1) for the highest peak at the (110) crystal plane of hexagonal CuS nano-particles.

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (4.1)$$

where, λ is the wavelength of the X-ray(1.5405Å), k is the Scherrer constant ($k = 0.89$), β is the full width at half maximum (FWHM) of the diffraction peak in radians and θ is the Bragg angle corresponding to the maximum of the diffraction peak in degrees. The particle size was estimated to be in the range between 15.44 nm and 161.28 nm as provided in Table 1 which agrees with the information derived from HRTEM images.

Fig.4.3b shows the Raman spectrum of copper sulfide phases nanoparticles, a sharp peak is observed at 477 cm^{-1} which is attributed to S-S stretching of the vibration mode of S_2 molecule. A peak centered at 316 cm^{-1} is representing Cu-S bond stretching. Another weak signal around 553 cm^{-1} is attributed to oxygen related defect. Moreover, CuS belongs to a hexagonal crystalline system, a $p63/mmc$ space group, containing six formula units per unit cell. Each element has different Wyck-off symbols, two copper atoms have 2d, 4f and two sulphur atoms have 4e and 4c, respectively. Where only 14 are Raman active modes denoted by $\Gamma=2A1g + 4E2g + 2E1g$. These can be grouped as $\Gamma_{Cu1} = A1g + E2g + E1g$, $\Gamma_{Cu2} = E2g$, $\Gamma_{S1} = A1g + E2g + E1g$, $\Gamma_{S2} = E2g$ for copper and sulphur respectively [42].

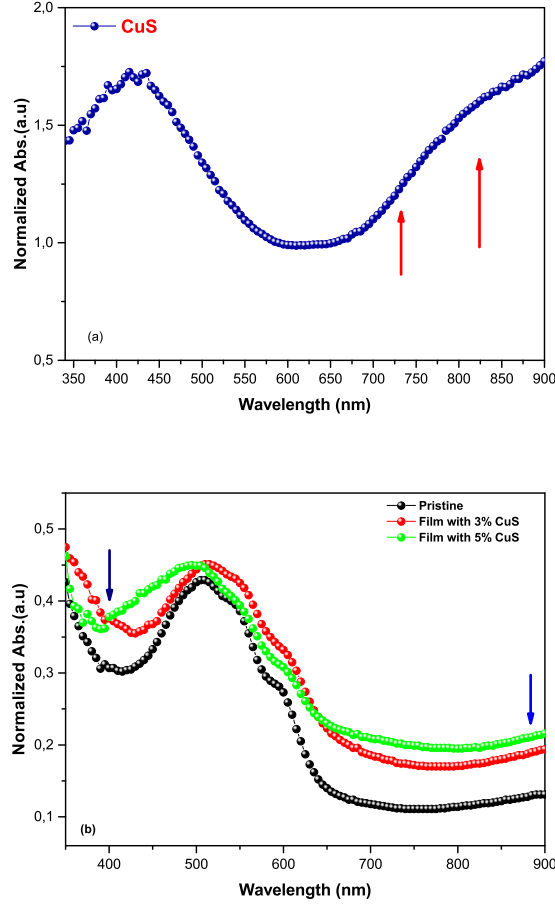


Figure 4.4: (a) Optical absorption of (a) CuS suspension in deionized water. (b) Optical absorption of spectra of P3HT:PC₆₁BM films prepared at different CuS concentration

4.4.2 Optical absorption

The optical absorptions were measured from CuS powder suspension in deionized water as provided in Fig 4.4(a). CuS nano-particles exhibit two strong peaks of absorption in the visible and near-infrared (NIR) regions. The optical absorption windows (350-550 nm) is the result of the excitation of carriers from valance to conduction band of the bulk CuS whereas the absorption in infrared region is attributed to LSPR absorptions and scattering by copper and copper related clusters. The broad absorption band in the infrared regions is due to the dependence of the LSPR effect on the nature, shape and size of the nano-particles [43]. The energy

band gap of CuS (inset) was calculated using Tauc's equation in the high absorption region of the semiconductor.

$$(\alpha h\nu)^2 = \beta(h\nu - E_g) \quad (4.2)$$

where β is a constant, E_g is the optical energy gap, h is Plank's constant, α is the absorption coefficient. The plot of $(\alpha h\nu)$ vs. $(h\nu)$ is the direct allowed transition [44, 45]. Based on the intercept of the straight line at $(\alpha h\nu)^2 = 0$, the energy band gap CuS is determined to be 2.18 eV, which is similar to the value reported in the literatures.

A similar measurements were conducted on the photoactive film composed of P3HT:PC₆₁BM blend with and without CuS doping Fig.4.4(b). The optical absorption taken from the pristine film showed a typical P3HT:PC₆₁BM blend with clear vibronic shoulder around 550 nm and 600 nm, respectively. However, copper sulfide doped films evidently showed broadening of the absorption bands and possible red-shift on the onset of absorption. This is an indication for possible changes in the energy band structure of the polymer film due to the interaction with metal nano-particles. The presence of CuS nanoparticles is evident in the polymer film by the new absorption pattern around 400 nm and 900 nm. These two areas of absorbency coincided with the absorption peaks of copper sulfide in deionized water. Therefore, CuS nano-particles at the concentration as little as 3 % and 5 % by weight have indeed contributed positively in harvesting the incident photons in the film.

4.4.3 J-V Characteristics

The current-voltage characteristics (J-V) of the solar cells were taken under ambient laboratory condition in which the devices were not encapsulated. Fig 4.5 clearly shows the different performances of the device fabricated using P3HT:PC₆₁BM solar absorber containing various concentrations of CuS nano-particles. The measured solar cells parameters are summarized in Table 2. The incorporation of CuS nano-

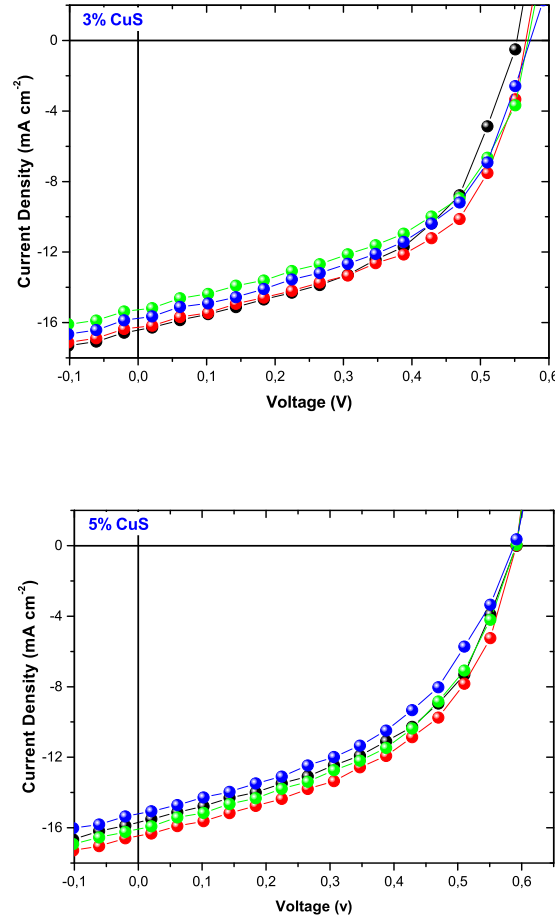


Figure 4.5: The J-V characteristics of the best performing devices prepared with CuS doped photoactive layer (a) 3 % CuS (b) 5 % CuS concentrations by weight.

particles in the photo-active layer exhibited better performance than the pristine P3HT:PC₆₁BM-based active layer without the inclusion of CuS nano-particles. The best power conversion efficiency recorded in this investigations was 5.04 % at CuS concentration of 3% by weight. The incorporation of CuS nano-particles in the photo-active layer clearly enhanced the collection of the photo-current as reflected by improved short circuit current (J_{sc}) and fill factor (FF). This suggests that better charge carriers transportation to the electrode must have been the main reason for improved device performance. In deed, high J_{sc} could also implying low charge carrier recombination. Increasing the concentration of CuS to 5 % still was favourable in producing more photocurrent, but, reduces the device fill factor which negatively impacted the overall PCE (see Table 2). In fact, the solar cell rectification has been severely compromised by high CuS concentration beyond 5 %. Therefore, the

optical absorption of the solar absorber layer of the device has been enhanced at the optimum doping level of CuS, which is associated with occurrence of multiple

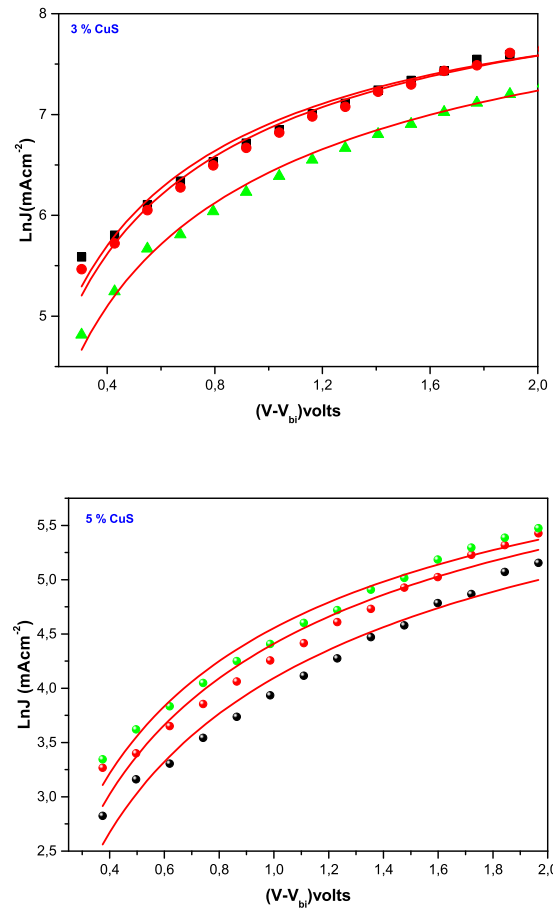


Figure 4.6: The space charge limited current of the P3HT:PC₆₁BM active layer prepared with different CuS (a) 3 % and (b) 5 % concentration by weight

lights scattering at the large sized nanoparticles or due to the excitation of localized surface plasmon resonance modes of smaller sized of nanoparticles. Moreover, the hexagonal structure of large sized CuS nano-particles are an ideal scatterer of light inside active medium and also can generally serve as alternative charge percolation channel for holes. These could certainly assist in improving the performance of organic solar cells. Nevertheless, the high concentration of metal nano-particles is unfavorable for TFOSC because of significant charge recombination which reduces the external quantum efficiency of the devices [46–48].

Table 4.2: The parameters of P3HT:PC₆₁BM based solar cells fabricated at various CuS nanoparticles concentrations.

Device	V _{oc} (V)	J _{sc} (mAcm ⁻²)	FF	PCE%	R _s (Ωcm ²)
0	0.56	12.37	42.56	2.98	429
3	0.56	19.44	46.33	5.04	150
3	0.57	15.76	49.50	4.45	186
3	0.55	16.45	50.04	4.55	69
3	0.57	16.29	50.49	4.68	92
5	0.59	15.73	47.23	4.40	80
5	0.59	16.74	46.72	4.63	155
5	0.59	16.07	47.00	4.45	192
5	0.59	15.21	45.50	4.07	220

4.4.4 Charge carrier transport

The charge transport properties of the photo-active films doped with CuS nanoparticles have been investigated using the measured Space Charge Limited Current (SCLC) taken under dark. The SCLC data were compared with Mott-Gurney's law that employs field dependent mobility equation (3):

$$J = \frac{9}{8} \epsilon \epsilon_0 \mu_0 \frac{V^2}{L^3} \exp(0.89\gamma \sqrt{\frac{V}{L}}) \quad (4.3)$$

where ϵ is the relative dielectric permittivity ϵ_0 is the permittivity of free space, μ_0 is the zero-field mobility; g is the field activation factor, L is the active layer thickness and V is the applied voltage drop across the sample which is corrected for built-in potential V_{bi} [49, 50]. According to Fig.4.7 the plots of space charge limited current data were fitted with Eq (3) that suggest agreement with experimental data (see Fig.4.6). The zero field mobility(μ_0) and field activation factor γ derived from the fit to the data are very well in agreement with literature (see Table 3). The zero mobility value of the device with P3HT:PC₆₁BM and 3 %, and 5 wt% of CuS nanoparticles are two order of magnitudes higher than the pristine device. This is a clear evidence to the enhancement of photo-current J_{sc} due to the suppression of charge recombination processes.

Table 4.3: The charge transport parameters of organic solar cells based on P3HT:PC₆₁BM blend at various CuS doping levels.

(P3HT:PC ₆₁ BM:CuS)	$\mu_0(\text{cm}^2\text{S}^{-1}\text{V}^{-1})$	$\gamma(\text{cmV}^{-1})$
0	5.60×10^{-4}	-5.90×10^{-5}
3	5.61×10^{-3}	-7.11×10^{-4}
3	1.75×10^{-2}	-2.22×10^{-3}
3	1.17×10^{-2}	-1.49×10^{-3}
5	1.67×10^{-4}	-2.16×10^{-5}
5	2.55×10^{-4}	-3.30×10^{-5}
5	1.93×10^{-3}	-2.50×10^{-4}

4.5 Conclusion

In summary, CuS nano-particles were synthesized by wet chemistry process. The synthesised CuS nano-particles is found to form different shapes and sizes as demonstrated by various spectroscopic methods. The CuS nano-particles were incorporated in the solar absorber layer of thin film organic photovoltaic cell composed of P3HT:PC₆₁BM blend. The result is clearly showed enhanced photovoltaic parameters such as J_{sc} , FF, and PCE. Such improvement is the result of enhanced optical absorption assisted by localized surface plasmonic resonances as well as multiple light scattering of CuS nano-particles within the active layer. The plasmon resonance of the hexagonal phase of CuS is beneficial to efficient photons harvesting in the medium. As a consequence, significant increment in the power conversion efficiency was found as high as 69 %. The best device performance found was at the concentration 3 % CuS by weight, which has resulted in PCE = 5.04% under ambient condition. However, significant improvement were recorded from all the device doped with metal nano-particles compared to the pristine type photo-active layer. The metal nano-particles are compatible with roll-to-roll devices preparation which potentially reduces the cost of device fabrication.

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CHAPTER 5

Nickel sulphide nano-composite assisted hole transport in thin film polymer solar cells



Nickel sulphide nano-composite assisted hole transport in thin film polymer solar cells



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ABSTRACT

Nickel sulphide (NiS) nano-composite were synthesized and used as dopant in the hole transport layer of the thin film organic solar cell (TFOSC). The nano-particles are intended to assist in the charge transport processes at the interface between the active layer and the anode. Thin film solar cells were fabricated using photo-active layer composed of poly-3-hexylthiophene (P3HT) and (6-6) phenyl-C61-butyric acid methyl ester (PCBM) blend. The solar cells employed NiS doped PEDOT:PSS hole transport layer (HTL) which are investigated in terms of changes in optical and electrical properties of the films. The electrical properties of the newly fabricated solar cells showed significant improvement in photo-generated current as the result of reduced charge carrier recombination and enhanced charge transport processes at the interface. This in turn boost the power conversion efficiency (PCE) of the devices by 95% compared to the devices without NiS doped HTL. The observed PCE enhancement is attributable to the excitation of the localized surface plasmon resonance exhibited by the presence of NiS in hole transport layer. It is noted in the investigation that the performance of the solar cell is dependant on the concentration of NiS nano-particles in PEDOT:PSS layer. As consequence, the highest recorded PCE in this study was 6.03% at 0.1% NiS by weight, which is encouraging result for device fabrication in ambient laboratory condition.

5.1 Abstract

Nickel sulphide (NiS) nano-composite were synthesized and used as dopant in the hole transport layer of the thin film organic solar cell (TFOSC). The nano-particles are intended to assist in the charge transport processes at the interface between the active layer and the anode. Thin film solar cells were fabricated using photo-active

layer composed of poly-3-hexylthiophene (P3HT) and (6-6) phenyl-C61-butyric acid methyl ester (PCBM) blend. The solar cells employed NiS doped PEDOT:PSS hole transport layer (HTL) which are investigated in terms of changes in optical and electrical properties of the films. The electrical properties of the newly fabricated solar cells showed significant improvement in photo-generated current as the result of reduced charge carrier recombination and enhanced charge transport processes at the interface. This in turn boost the power conversion efficiency (PCE) of the devices by 95% compared to the devices without NiS doped HTL. The observed PCE enhancement is attributable to the excitation of the localized surface plasmon resonance exhibited by the presence of NiS in hole transport layer. It is noted in the investigation that the performance of the solar cell is dependant on the concentration of NiS nano-particles in PEDOT:PSS layer. As consequence, the highest recorded PCE in this study was 6.03% at 0.1% NiS by weight, which is encouraging result for device fabrication in ambient laboratory condition.

5.2 Introduction

Organic semiconductors have attracted considerable research interest in the past two decades due to their prominent features for potential applications in photonic devices. The material's light weight, mechanical flexibility, low cost, tunable optical and electronic properties [1–3] are among the few attraction for thin film organic solar cells. Solution processable TFOSCs research has gained significant progress in terms of attaining high power conversion efficiency that stands close to 16 % at present [4–7]. The main challenge that TFOSC is facing today are the poor charge collection and instability of the polymer molecules under ambient environemt. A number of research efforts towards the synthesis of new polymers and efficient device architectures have made significant progress in the realization of TFOSC. For instance, the bulk-heterojunction (BHJ) design of the solar absorber is the most effective device structure known to date to address the issue of poor charge transport in polymer medium. BHJ film is formed by the blend of p-type polymer (donor) and

fullerene (acceptor) molecules. However, BHJ is still lags behind due to the challenging trade-off between the film thickness and maximizing photon harvesting. Photons induced excitation of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) levels is the principal mechanism for the generation of charge carriers in polymer medium. This is followed by excitons diffusion into the donor/acceptor (D/A) interfaces for the dissociation into free charge carriers. Once the charge separation has occurred at the D/A interfaces, parting holes and electrons are distributed within the donor and acceptor phases, respectively. The holes and electrons are then transferred to their respective electrodes driven by an internal electric field formed by the workfunctions difference of the metal electrodes [8–13]. The popular semiconductor polymer known as poly-3-hexylthiophene (P3HT) has the property of assembling in a semi-crystalline structure through an orderly fashion that assist in improving charge carrier mobility and high optical absorption [14–17]. However, there are several important issues that needed further research efforts such as improving power conversion efficiency, device lifetime, large-scale device fabrication and marketing.

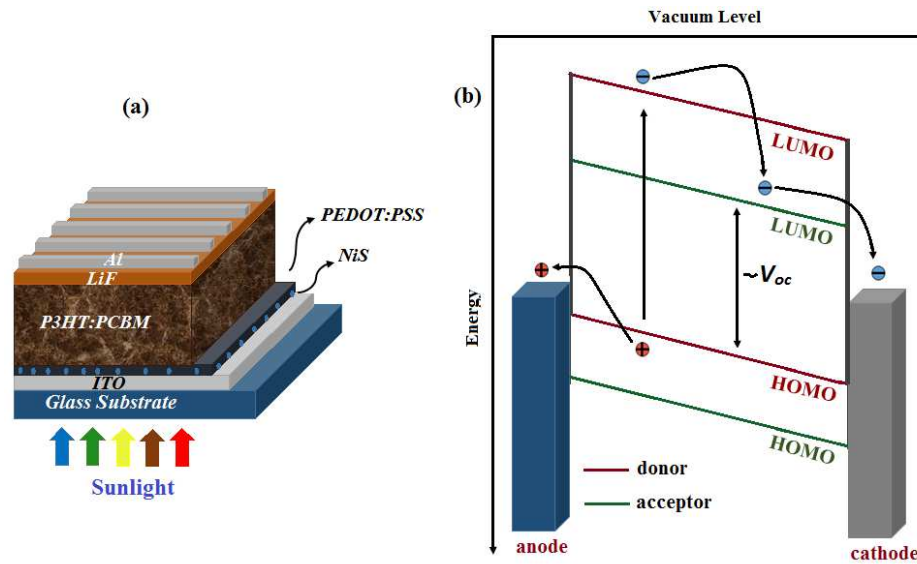


Figure 5.1: (a) Schematic diagram for bulk heterojunction organic solar cell based on NiS nano-particles incorporated into P3HT: PCBM active layer.(b) energy level diagram of the device materials.

One of the area that currently attracted several research attention is the interfacial

charge transport buffer layers. In general, water soluble semiconducting polymer, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) is one of the widely used hole transport buffer layer in the fabrication of solution-processed organic solar cells. This is due to the fact that PEDOT:PSS offers large ionization potential, low electrical resistance, good optical transparency and moderate electrical conductivity. The conventional polymer solar cells based on PEDOT:PSS hole transport layer has benefited from having large open circuit voltage (V_{oc}) and improved charge collection. However, the high acidic and hygroscopic nature of PEDOT:PSS negatively impacted the device stability [18, 19]. In order to exploit the best of PEDOT:PSS as HTL, thermal annealing and chemical doping are often used to improve the conductivity and stability of the film. Nonetheless, the process of chemical doping or thermal annealing of the PEDOT:PSS layers could cause large density of defects, cracks and even reduce optical transmittance. Therefore, a careful optimization of the parameters must be achieved for best device performances [20–23]. Furthermore, the use metal or semiconducting nano-particles has been introduced recently to cater the challenges in the inter-facial layers of organic solar cells.

The incorporation of metal nanoparticles in the PEDOT:PSS hole buffer layer is expected to increase the interfacial roughness between the photo-active and hole transport layers. This leads to a roughened interface enhancement of hole collection which in turn improves the performance of organic photovoltaics. This is due to the fact that metal NPs in PEDOT:PSS exhibits local surface plasmon resonance (LSPR) that can induce intense electromagnetic field at the vicinity of the particles [24–27, 29, 30]. LSPR occurs due to the interaction between surface electrons of the metal and the incident photons electromagnetic fields. The sulphides such as nickel sulphide (NiS) and copper sulfide (CuS) are often used as a p-type hole transport layers in TFOSC as well as a dopant in perovskite solar cells [23, 29]. Moreover, several other inorganic compounds have been extensively used as counter electrode in the dye sensitized solar cell [31–34]. Nickel sulfide, in particular, exhibited properties such as low charge transfer resistance, good stability, superior corrosion resistance, low sheet resistance, good optical transparency. It possesses a wide energy

band gap that makes NiS one of the reliable alternative or dopant for the conventional PEDOT:PSS hole transport layer [35]. In this study, we employed nickel sulphide nano-particles doped PEDOT:PSS as the hole transport interfacial layer for the fabrication of P3HT:PCBM-based organic solar cells. The experimental observations are discussed based on the electrical, optical and morphological characteristics of both the synthesized nano-particles and the photo-active films.

5.3 Experimental Section

5.3.1 Materials

The chemicals used in this study are nickel (II) nitrate hexahydrate (>99% ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ethanol (99.8%) and sodium hydroxide (NaOH) (from Sigma Aldrich). NaOH is used as the reducing agent. The polymers such as poly (3,4-ethylene dioxythiophene):poly (styrenesulfonate) (PEDOT:PSS), Poly (3-hexylthiophene) (P3HT, 95 % regioregular, electronic grade) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM, 95 +%) were all purchased from Ossila Ltd and used without further processing.

Solar Cell Fabrication

Unpatterned ITO coated glass substrate was used in the preparations of thin film solar cells which begins by partially etching the ITO with an acid solution ($\text{HCL}:\text{H}_2\text{O}:\text{HNO}_3$ at 48%:48%:4%). Then, the substrates were thoroughly cleaned using the ultrasonic bath in deionized water, acetone and isopropanol for 10 min each, respectively. They were then dried under a nitrogen flow and then immediately baked in an oven at 120°C for 20 min [26–28]. The thin film polymer solar cell (TFPCs) devices with doped hole-collecting buffer layer were fabricated in the bulk heterojunction architecture containing various layers of materials as glass/ITO/PEDOT: PSS-NiS/P3HT:PCBM/LiF/AL. The schematic diagram for the

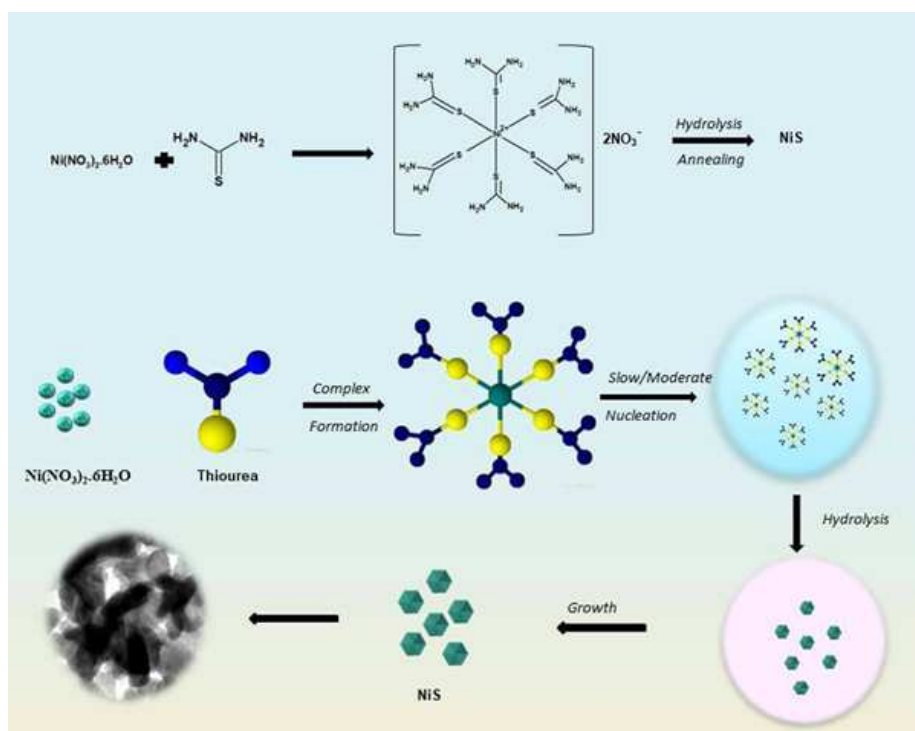


Figure 5.2: Schematic representation of the reaction mechanism in the synthesis of nickel sulphide nano-particles and its possible structure.

device structure is provided in Fig 5.1(a). To obtain the hole-collecting buffer layer a NiS powder was incorporated into the PEDOT:PSS aqueous solution at different concentration (0.1%, 0.2%, and 0.3%). The solution was stirred overnight at 40°C. A thin layer of (PEDOT:PSS/NiS) was deposited by spin-coating at 3500 rpm for the 60s followed by annealing in an oven at 120°C for 20 min under ambient environment. The photo-active layers were prepared, in chloroform solvent, from P3HT:PCBM blend at a 1:1 ratio by weight with a solution concentration of 20 mg/ml. The mixture was stirred for 3 hrs at 40°C to enhance the miscibility of the molecules. The active layer mixture was then spin-coated on top of the dried PEDOT:PSS/NiS at the rate of 1200 rpm for 40 seconds and dried in the furnace at 100°C for 5 min under nitrogen atmosphere. Finally, using a thermal vacuum deposition chamber (Edward auto 306), the electron transport layer and top electrode (LiF(0.4nm)/ AL(60nm)) were deposited on the dried active layers under a vacuum at 10^{-6} mbar.

The electrical properties of the devices were measured using a computer interfaced

Keithley (HP2420) source meter and a solar simulator (model SS50AAA) under a AM 1.5 illumination and operating at a light intensity of 100 mW/cm^2 . The photovoltaic parameters presented in Table II were calculated using 0.05 cm^2 effective area of the diodes.

5.3.2 Synthesis of NiS Nanoparticles

Nickel sulphide nanoparticles were synthesized through the wet chemical route with the following fundamental steps. Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and thiourea ($\text{CH}_4\text{N}_2\text{S}$) were used as precursor in deionized water solvent. Initially, two separate solutions are prepared using 0.2 molar from ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and ($\text{CH}_4\text{N}_2\text{S}$) each and dissolved in deionized water in a separate flasks and, stirred for two hours to attain a complete mixing. Thiourea solution was then added into nitrate hexahydrate solution in drop-wise while continuous stirring. The resulting mixture is a deep green solution turned into black colour after adding drop-wise 0.1 M of NaOH which was dissolved in 50 mL deionized water. The solution was further stirred continuously with a magnetic stirrer for 2 hours. Then, the precipitated particles were centrifuged and washed with distilled water and ethanol, respectively, to remove sodium ions. The filtered precipitate was dried at 80°C for 24 h and was annealed at 300°C for 30 min which resulted in the formation of nickel sulphide nanoparticles [34]. The resultant (NiS) nanoparticles were characterized by scanning electron microscope (SEM: JEOL JSM 6100), transmission electron microscope (TEM: JEOL JEM 1010), and X-ray powder diffractometer. The optical absorption spectra were measured using (T80-PG) UV-Vis spectrometer.

The overall reaction and 3-dimensional representation of the product are given in Figure 5.2 to assist the understanding of the synthesis of nickel sulphide nanoparticles from nickel nitrate precursor. The size, homogeneity and proportional growth depends on concentration of S^{2-} , complex formation and type of counter anion. Here an octahedral complex is formed between Ni^{2+} ions and thiourea with NO_3^- as counter anion as can be seen in the schematic diagram (Fig 5.2). The release of S^{2-} is

slow from thiourea so that a slow nucleation can be achieved [36]. The counter NO_3^- ions lead to a moderate nucleation process because of their polarisation effect. Thus, there is no much growth in size of nanoparticles as is inferred from XRD and TEM data (approx. 30 nm). However, the effect of slow nucleation process is exhibited on morphology as elongation in shape as can be seen slightly irregular hexagonal Ni_2S nanoparticles in TEM images. However, the size is quite uniform and no abnormal changes in shape are also observed. The presence of NO_3^- as counter anions as seen in structure of complex $[\text{Ni}(\text{CH}_4\text{N}_2\text{S})_6](\text{NO}_3)_2$ i.e hexakis(thiourea-s) nickel(II)nitrate) show high polarizability leading to more symmetrical shape of final nanoparticles. Furthermore, the symmetrical hexagonal complex leads to better breakage of bonds via hydrolysis to form symmetrical nanoparticles. Note also that no mixed phases of nickel sulphide are observed in the measured XRD pattern.

5.4 Results and discussion

5.4.1 NiS Characterization

X-ray diffraction

The XRD spectra taken from nickel sulphide nano-particles is provided in Figure 5.3 at the diffraction angles between 20° and 80° . The data provided in Fig 5.3 showed diffraction peaks at 29.36° , 33.37° , 34.60° , 45.65° , 53.57° , 60.88° , 62.73° , 70.79° , 79.10° . The diffractions corresponds to the reflections of the X-ray beam from planes (100), (002), (101), (102), (110), (103), (200), (202) and (104), respectively. The planes are suggestive of the hexagonal NiS phase (JCPDS No. 750613). The average crystallites size was determined through full-width at half maximum (FWHM) of X-Ray diffraction peak by using the Debye-Scherers equation given as

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (5.1)$$

where, λ is the wavelength of the X-ray($1.5405\text{\AA}$), k is the Scherrer constant ($k = 0.89$), β is the full width at half maximum (FWHM) of the diffraction peak in radians and θ is the Bragg angle corresponding to the maximum of the diffraction peak in degrees. The average of crystallite size obtained is $D = 31.37\text{ nm}$ (Table I) which is consistent with the sizes measured from TEM images that will be discussed in the next section. The crystallite sizes distribution ranges from 20 nm to 42 nm (see Table I), which are the desired particle sizes for efficient light scattering in TFOSC. In fact, the influence of the newly synthesised NiS is evident in the improved performance of the doped devices especially at low dopant concentration.

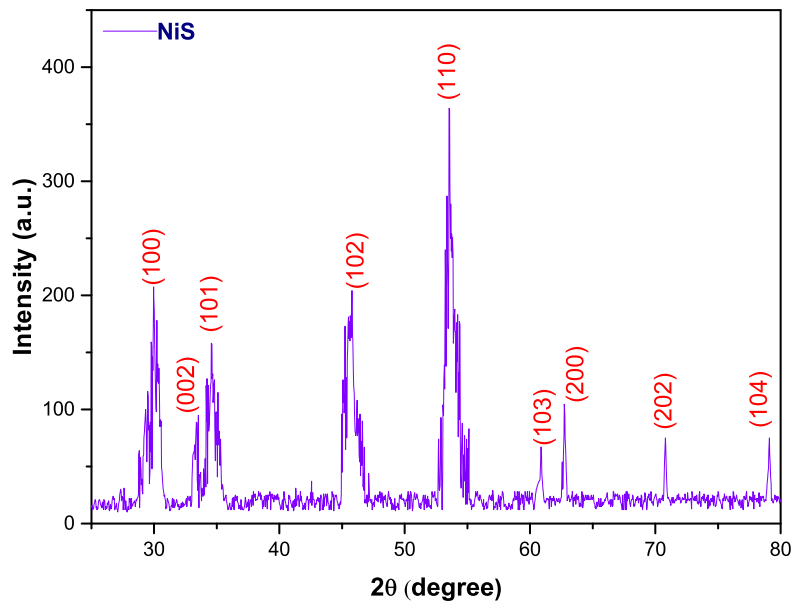


Figure 5.3: X-ray diffraction pattern of NiS nanoparticles

Table 5.1: Analysis of XRD of NiS nanoparticles

Peak No.	$2\theta(\text{degree})$	hkl	FWHM(β)	d(nm)
1	29.96	(100)	0.2386	34.5
2	33.37	(002)	0.40322	20.6
3	34.60	(101)	0.3087	26.9
4	53.57	(110)	0.2401	37.1
5	60.88	(103)	0.44603	20.7
6	62.73	(200)	0.24523	37.9
7	70.79	(202)	0.23256	41.9
8	79.10	(104)	0.32104	32.1

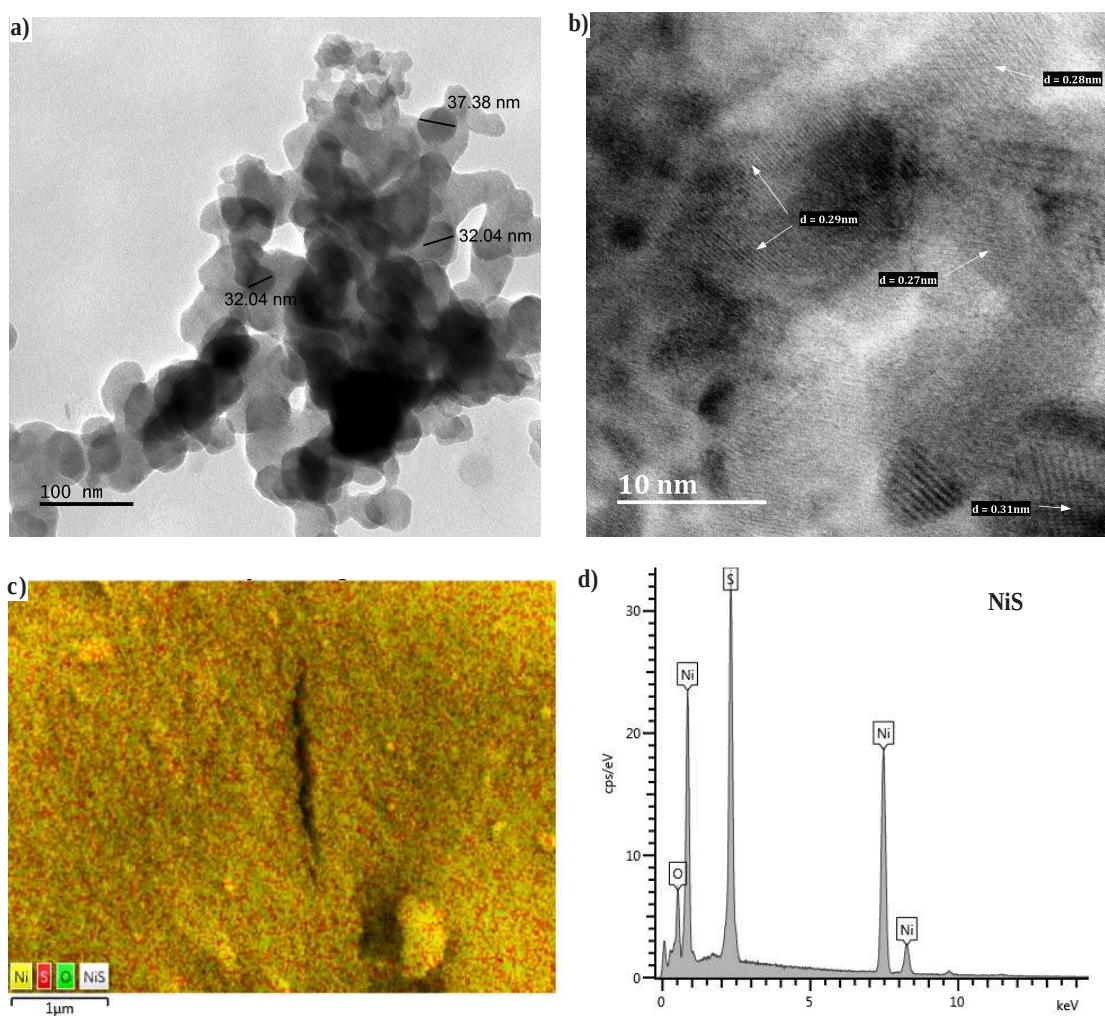


Figure 5.4: Figure (a) and (b) are HRTEM images taken from NiS powder. (c) and (d) are the HRSEM image and an energy dispersive X-ray (EDX) spectrum of NiS nano-particles, respectively.

HRSEM and HRTEM observations

The surface morphology and the structure of nickel sulphide nano-particles were investigated using high resolution scanning and tunneling electron microscopy (HRSEM and HRTEM). The HRTEM images as presented in Figure 5.4(a and b) show that the nano-particles are roughly uniformly distributed in size and shapes. Elliptical and spherical type of geometries are evident on the HRTEM images. The formation of core-shell type structure is expected. The average diameter of the NiS nano-particles was found to be 33.8 nm that is in a good agreement with X-ray diffraction experiments. The elemental mapping of HRSEM image provided in

Fig.5.4c suggests uniform distribution of sulphur and nickel in the medium that support the formation of NiS composite. On the other hand, the EDX data presented in Fig 5.4(d) suggests that mainly nickel and sulphur elements exist in the powder of the synthesised nano-particles. However, a small trace of oxygen has been detected which is either from the target holder or oxidation of the powder from storage in laboratory environment. On the other hand, the crystalline nature of the nano-particles is evident by the observed fringes in the HRTEM image (see Fig 5.4 b) that is consistent with XRD data analysis. The lattice constant determined from the fringes is 0.3 nm which is in agreement with hexagonal structure of NiS.

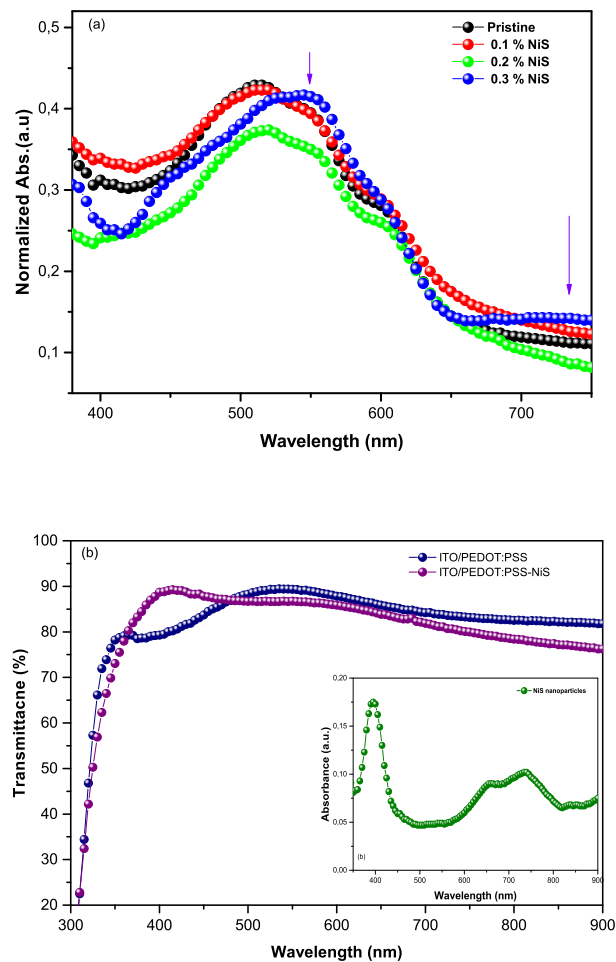


Figure 5.5: Optical absorption of spectra of (a) P3HT:PCBM active layer coated on PEDOT:PSS/NiS hole transport buffer layer at various NiS concentration. (b) NiS nanoparticles powder in a deionized water suspension.

5.4.2 Optical absorption

The optical absorption properties of the hole transport layer (HTL) containing different concentrations of the NiS nano-particles were investigated using UV-Vis spectrometer. The spectra were measured from the films with layers of materials as glass/ITO/PEDOT:PSS-NiS/P3HT:PCBM/, as well as the pristine HTL as provided in Figure 5.5. The pristine film showed a typical absorption pattern for the P3HT:PCBM blend and has a peak maximum centred around 515 nm. While the devices with PEDOT:PSS doped with various concentrations of NiS, in the hole transport layer, demonstrated a relatively stronger absorption in the visible region and infra-red regions. This is due to both light scattering and LSPR effect facilitated by the introduction of the NiS dopant. The spectrum taken at 0.3 % NiS loading particularly showed clear changes in the pattern of the absorption which exhibited red-shift at peak maximum and pronounced absorption beyond 700 nm. The optical transmittance of the PEDOT:PSS films provided in Fig 5.5 (b) clearly showed that NiS doped film exhibits better transmittance in UV region and absorbance in visible and infrared regions. The absorbance is expected from the behaviour of the optical absorption of NiS nano-particles suspension in an ethanol solvent Fig 5.5(b) inset. According to the inset Fig 5.5(b) the spectrum contains three prominent peaks at 400 nm, 650 nm and 740 nm which are typically high-intensity absorption peaks. It is to be noted that there is an extended absorption well above 850 nm into infrared region. The occurrence of the peaks in the UV and visible regions are mainly due to local surface plasmon resonance effect by the presence of nickel. However, the absorption in the infrared regions is attributed to the absorbance by various sized metal nano-particles seated at the HTL of the devices. All of which in turn impacted the total photo-current generation and collection in the NiS doped devices leading to the overall enhanced devices performance. NiS powder exhibited a broad band PL intensity centred at 399 nm peak maximum which is attributed to the electron transition caused by defects [37].

Table 5.2: The solar cell parameters of the best performed devices.

Device	V_{oc} (V)	J_{sc} (mAcm ⁻²)	FF	PCE%	R_s (Ω cm ²)
Pristine	0.57	12.53	43.24	3.09	157
0.1% NiS	0.58	18.65	55.88	6.03	82
0.2% NiS	0.58	16.55	51.15	4.96	170
0.3% NiS	0.58	14.91	51.21	4.47	159

5.4.3 J-V Characteristics

The current-voltage characteristics (J-V) provided in Fig 5.6 describes the electrical properties of the devices prepared with and without the inclusion of NiS in PEDOT:PSS hole transport layer. The concentration of NiS was varied to be able to determine the optimum doping level of the particles in the HTL. Generally, the solar cells fabricated with nickel sulphide nano-particles doped PEDOT:PSS have shown remarkable improvement in power conversion efficiency (PCE) because of enhanced measured photo currents from the devices. Figure 5.6 clearly showed high short circuit current surge due to the presence of metal nano-particles in HTL compared to the pristine type devices (see Table II). The enhanced overall performance of the

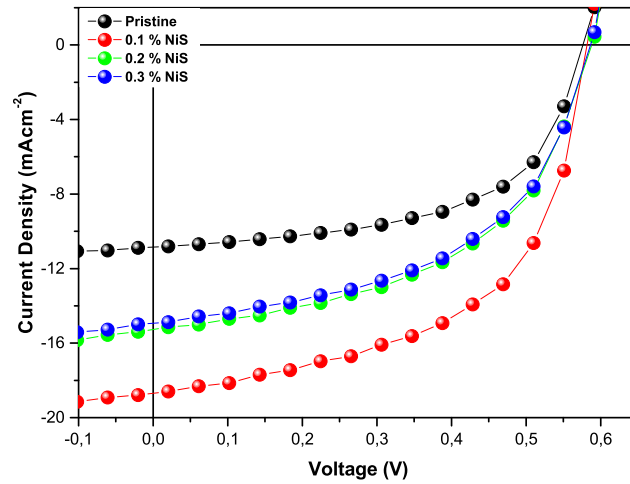


Figure 5.6: The J-V characteristics of the best performing devices.

devices with doped HTL can be attributed to the improved charge selectivity facilitated by the NiS doping. This could result in a possible modification of the work function of the PEDOT:PSS that better match with the ionization potential(IP) of

the P3HT donor molecule. It is to be noted that better alignment of the donor IP with the work function of the HTL facilitates a reduced energy levels offset which in turn not only aid the exciton generation but also the charge transport process. The enhancement of the current density (J_{sc}) is attributed to effective trapping of light through scattering as well as improved charge collections by the electrodes. Besides, an improved optical transparency of the doped PEDOT:PSS layer enhances the internal quantum efficiency via allowing more photons to pass through the films into the active layer in UV and near visible regions. On the other hand, the reduced series resistance especially at the lower concentration of the NiS in the PEDOT:PSS is indicative of an improved conductivity of at the interface between active layer and HTL. This could further assist in reducing non-geminate recombination which is reflected in terms of enhanced value of the fill factor (FF) and photo-current. The device fabricated at 0.1% doping level of NiS is found to be the best performing solar cell in terms of power conversion efficiency followed by 0.2% and 0.3%. The highest PCE recorded in this experiment was 6.03% at 0.1% NiS concentration which is over 95% increment in PCE compared with pristine PEDOT:PSS hole transport layer.

5.4.4 Charge Transport Properties Analysis

The charge transport properties has been investigated based on the measured dark current from both types of devices fabricated with and without NiS nano-particles (Fig 5.7). The carrier mobility was derived from the measured space charge limited current (SCLC) as described by Mott Gurney law (Equ. 2). The model assumes constant charge mobilities, the medium is free of traps and Ohmic injection contact [30, 35, 38–40]. The current in the device can be expressed by the equation of the form:

$$J = \frac{9}{8} \epsilon \epsilon_0 \mu_0 \frac{V^2}{L^3} \quad (5.2)$$

where ϵ is the relative permittivity of the medium, ϵ_0 is the permittivity of the vacuum, μ_0 is the mobility, and V is the voltage dropped across the sample which is corrected for built-in potential V_{bi} , which is taken from the knee of the space charge limited region of the dark current in logarithm scale. In this case $V_{bi} = 1.15$ V and

L is the thickness of the photo-active layer.

$$V = V_{ap} - V_{bi} \quad (5.3)$$

where V_{ap} is the applied bias voltage. The Poole-Frenkel field dependent mobility equation can be described by the form;

$$\mu = \mu_0 \exp(\gamma \sqrt{E}) \quad (5.4)$$

where μ_0 is the low-field mobility and γ is the field activation factor

$$J = \frac{9}{8} \epsilon \epsilon_0 \mu_0 \frac{V^2}{L^3} \exp(0.89 \gamma \sqrt{\frac{V}{L}}) \quad (5.5)$$

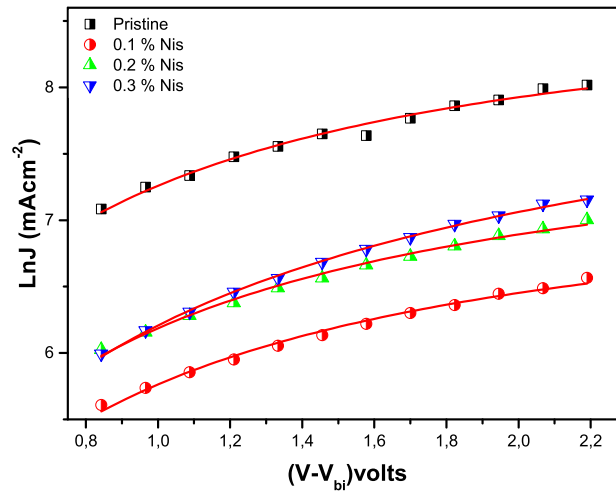


Figure 5.7: (a) J-V dark currents of the best performing devices at various NiS nanoparticles loading in HTL (b) Space charge limited currents of the diodes with solid lines representing computer fits according to equ(5).

The SCLC data taken from the dark J-V curve were fitted with Equ. 5 (Fig 5.7). The zero-field carrier mobility and field activation factor derived from the fit to the SCLC data for the devices are listed in Table III. According to the results, the zero field mobilities derived from the devices that uses NiS exhibit higher mobility compared with HTL without nickel sulphide nano-particles. The mobility slightly dependant on the concentration of NiS in the HTL which decreases with increasing

Table 5.3: The charge carrier transport parameters of the TFPSCs.

HTL material	$\mu_0(\text{cm}^2\text{S}^{-1}\text{V}^{-1})$	$\gamma(\text{cmV}^{-1})$
Pristine PEDOT:PSS	5.60×10^{-4}	-5.90×10^{-5}
0.1% NiS	1.45×10^{-2}	-1.06×10^{-3}
0.2% NiS	5.10×10^{-3}	-3.72×10^{-4}
0.3% NiS	3.62×10^{-3}	-2.65×10^{-4}

concentration from 0.1% to 0.3%. In fact, the mobilities at the optimum concentration of 0.1% by weight are two orders of magnitude greater than the device with pristine HTL. This is clear indications of the influence of NiS nano-particles in HTL that improved the charge transport in the medium. The results seem to suggest that there is also a reduced geminate and non-geminate recombination processes which assisted better charge carrier dissociation, transport and collection by the electrodes. The betterment of charge transport and extraction processes induced by the addition of NiS boosted the measured photo-currents in the devices.

5.5 Conclusion

Nickel sulphide nano-particles are synthesized and successfully incorporated in the hole transport layer of solution processed thin film organic solar cell. The experimental evidences suggest that significant improvement has been recorded in the power conversion efficiency due to the presence of NiS nano-particles in PEDOT:PSS layer of the devices. The observed changes in the device performance is attributed to the occurrence of local surface plasmon resonance absorption and light scattering process as evidenced by optical measurements. The metal nano-particles are expected to aid the charge transport processes via reduced charge carrier recombination, assist in the collection of photo-generated charges by offering additional and alternative charge percolation channels to the electrodes. The devices with the NiS doped HTL showed high short-circuit current density and power conversion efficiency compared to the devices that used a pristine HTL. Moreover, the solar cell performance appeared to be dependant on the doping level of NiS in PEDOT:PSS layer. The best power conversion efficiency measured in this experiment is 6.03% at

concentration of 0.1% by weight which is a significant increment in the performance compared to pristine HTL used device. The use of NiS nano-particles is compatible with roll to roll solar cell fabrication which is an important progress for mass and cheap device fabrication.

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CHAPTER 6

Silver-sulphide nano-composite assisted photons capture in thin film polymer solar absorber

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Silver sulphide nano-particles enhanced photo-current in polymer solar cells

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Abstract

Silver sulphide nano-particles (NPs) have been employed as light trapping mechanism in the solar absorber layer of thin film inverted organic solar cell. The synthesized nano-particle has been characterized using high-resolution scanning and transmission electron microscopy (HRSEM and HRTEM), X-Ray diffraction (XRD). The effects of Ag₂S NPs in the newly fabricated inverted polymer solar cell with architecture ITO/ZnO/P3HT:PC₆₁BM-Ag₂S/MoO₃/AL were characterized using optical and electrical properties of the solar absorber film. The optimized NPs in the photoactive layers are designed to improve photons harvesting, charge transport and reduced charge recombination, which resulted in the collection of high short circuit current density, as large as 16.50 mAcm⁻². The measured high photocurrent and better device rectification has lead to improved power conversion efficiencies (PCEs) and device stability. The best power conversion efficiency recorded in this investigations was 5.15 % at the concentration of 1 % Ag₂S by weight. Furthermore, the solar cells exhibited extraordinary environmental stability stored in ambient environment which is attributed to the inverted device architecture.

Keywords Silver sulphide · Nano-particles · Charge transport

6.1 Abstract

Silver sulphide nano-particles (NPs) have been employed as light trapping mechanism in the solar absorber layer of thin film inverted organic solar cell. The synthesized nano-particle has been characterized using high-resolution scanning and transmission electron microscopy (HRSEM and HRTEM), X-Ray diffraction

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6.2 Introduction

Polymer molecules based solar cells (PSCs) have increasingly attracted a lot attention due to their several advantageous over the traditional silicon based solar cells. PSC offers low cost device production, the ease of processability, low weight, and mechanical flexibility [1–6]. Recently, power conversion efficiency of polymer solar cells has reached to 16% which is very close to other types of solar cell technologies but at lower cost. The PCE has showed better progress even in an inverted and tandem device structures which rose to as high as 17.3% [7–11]. The polymers blend composed of poly(3-hexylthiophene) (P3HT) and the C₆₀ derivative (6,6)-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM), in bulk heterojunction (BHJ), are the most popular polymer blend in the fabrication of thin film organic solar cell (TFOSC)[12–14]. In a conventional device architecture, the active layer is sandwiched between high work function metals and transparent conducting anode such as indium tin oxide (ITO). This arrangement is expected to improve hole collection of free charge carriers at the electrodes with the assistance of PEDOT:PSS and LiF buffer layers [8, 15]. However, the PEDOT:PSS hole transport buffer layer has acidic character and easily absorbs moisture due to its hygroscopic nature that the influences the

performance of the photoactive film as well as severely influence device stability [16, 17]. There are several efforts are in progress to cope the challenges with device

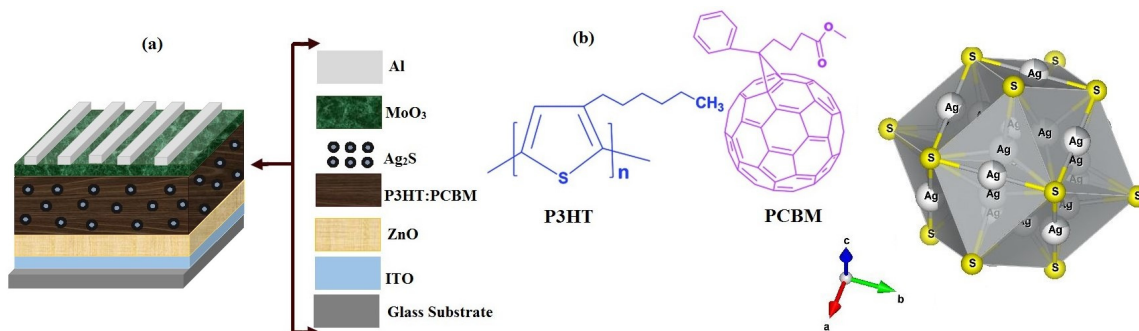


Figure 6.1: (a) Schematic diagram for bulk heterojunction organic solar cell based on P3HT:PC₆₁BM active layer doped with Ag₂S nanoparticles. (b) The molecular structure of P3HT and PCBM.

stability and improve the power conversion efficiency using new device architecture that entirely replacing PEDOT:PSS with inorganic semiconductors. So far, the inverted device architecture shows superior environmental stability and higher power conversion efficiency compared to the conventional device architecture.

Metal oxides such as zinc oxide (ZnO), titanium oxide (TiO₂), and caesium carbonate (Cs₂CO₃) have been used as n-type electron buffer layer which are deposited on indium tin oxide (ITO) film to form the inverted device structure. Similarly, transition metal oxides with a large work function such as molybdenum oxide (MoO₃), vanadium pentoxide (V₂O₅), tungsten trioxide (WO₃), and nickel oxide (NiO) have been used for efficient hole extraction replacing, poly(3,4 ethylene dioxothiophene):poly(styrene sulfonate) (PEDOT:PSS), to improve the stability of devices under ambient environment[18–22]. The n-type semiconductor zinc oxide (ZnO) has been considered as an appropriate electron buffer layer material due to its relatively high electron mobility, large band gap, which blocks ultraviolet light from entering into active layer to prevent the polymer material from photo-degradation [23–25].

Furthermore, the incorporations of metal nano particles (NPs), in various layers of thin-film organic solar cells (TFOSC), has shown significant contribution in mitigat-

ing the challenges of effective photons harvesting and the charge transport process in the polymer medium. The metal nano-particles that utilizes the local surface plasmon resonances (LSPR) effect to trap light in the photoactive medium expected to improve the optical absorption of the polymer blend film [26–30]. Jay Guo et al have successfully incorporated silver nano-wire electrode in the preparation of improved organic solar cell [31, 32]. In light of this, the n-type semiconductor silver sulfide (Ag_2S) is employed in the current investigations. Silver sulfide has several interesting properties such as monoclinic crystal structure, a narrow band gap (0.9–1.05) eV, a large absorption coefficient and good chemical stability. It has an excellent electronic and photo-conductivity that are suitable for photovoltaic application [33–36]. In this study, silver sulphide nano-particles were synthesized and incorporated into the photoactive layer of P3HT:PC₆₁BM blend at different concentrations of 1%, 3%, 5%, and 7% by weight. The power conversion efficiency measured in this investigations are far better than those reported in literature [36]. The details of the synthesis of the nano-particles as well as device characterization are presented in the following sections.

6.3 Experimental details

6.3.1 Materials

Chemicals used in this study were silver nitrate hexahydrate (> 99.5% $\text{AgNO}_3 \cdot 6\text{H}_2\text{O}$), sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), 98.0%), Polyvinyl Pyrrolidone (PVP) molecular weight 25000–30000 (from Merck, Germany). Poly (3,4-ethylene dioxythiophene):poly (styrenesulfonate) (PEDOT:PSS), Poly (3-hexylthiophene) (P3HT, 95 +% regioregular, electronic grade) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM, 95 +%) were purchased from Ossila. Sodium hydroxide (NaOH) was used as the reducing agents.

6.3.2 Synthesis of Ag₂S Nanoparticles

The synthesis of silver sulfide nano-particles begins with the preparation of various solutions of the precursors. First, 1.698g (0.1M) of silver nitrate hexahydrate (AgNO₃.6H₂O), 0.4g (0.1M) of sodium sulphide Na₂S.6H₂O and 3.0g of PVP were dissolved in 50mL of deionized water solvent, separately. The solutions of sodium sulphide and PVP were mixed into silver nitrate solution by drop-wise while stirring using magnetic stirrer. The solutions mixture was then stirred continuously under magnetic stirrer for 3 hours. The precipitate was centrifuged twice at 4500 rpm for 5 min followed by washing successively with deionized water and ethanol, respectively. This precipitate was dried in an oven at 80°C for 2-3 hours. The resultant silver sulphide nano-particles Ag₂S structure and morphology were characterized by scanning electron microscope (SEM: JEOL JSM 6100), transmission electron microscope (TEM: JEOL JEM 1010), X-ray powder diffractometer and the optical absorption UV-visible absorption spectra measured on a spectrometer (Rayleigh1601).

6.3.3 Organic Solar Cells Fabrication

The thin-film organic solar cells were fabricated using sol gel process on ITO coated glass substrate. The preparation methods are extensively discussed in number of articles from our research groups [37, 38]. The inverted device architecture constitute a different layers of materials, such as: glass/ITO/ZnO/P3HT:PC₆₁BM-Ag₂S/MoO₃/AL. The schematic diagram for the device structure is provided in Fig 6.1. A thin layer of ZnO electron transport layer (ETL) was spin-coated on the substrate at 3500 rpm for 60 s. The ZnO film was dried at 100°C on a hotplate for 20 min under ambient conditions. The solution of the photoactive layer was prepared in chloroform solvent using P3HT and PC₆₁BM blend at 1:1 ratio by weight at a concentration of 20 mg/mL. The Ag₂S nanoparticles were added in P3HT:PC₆₁BM blend solution at the concentration of 1%, 3%, 5%, and 7% by weight. The mixture was stirred for 4 hrs at 40°C to enhance the miscibility of the molecules. The photoactive films were spin-coated at 1200 rpm for 40 s and annealed at 90°C for 5 min

in a N₂ gas filled furnace. Finally, the hole transport layer (MoO₃) and aluminium electrodes were deposited at thickness of 8 nm and 85 nm, respectively. The current density-voltage (J-V) data were collected using HP2420 Keithley source meter and a solar simulator (model SS50AAA) operating at AM1.5 and 100 mW/cm². The photo-active films characteristics was studied by optical absorption measurement using UV-Vis spectrometer (Rayleigh 1601).

X-ray diffraction

The XRD data measured from silver sulfide powdered nanoparticles was investigate in terms of crystallographic structure (see in Fig 6.2). The diffraction pattern was scanned from 20° upto 70°, which resulted in the appearance of several prominent peaks in the chosen range. The prominent peaks are located at angles 2θ 26.00°, 28.95°, 31.49°, 33.90°, 34.47°, 36.8°, 37.71°, 40.78°, 43.41°, 45.44°, 46.04°, 47.75°, 48.73°, 53.25°, 58.28°, 63.73°. These peaks correspond to the reflection of the X-ray beam from lattice planes (-101), (111), (-112), (120), (-121), (121), (-103), (031), (200), (023), (113), (311), (21-2), (22-2), (042), (034), respectively. The diffraction patterns seem to indicate the existence of monoclinic Ag₂S phase with lattice parameters a = 4.22900 Å and c = 7.86200 Å as compared to the data from (JCPDS Card File: 00-014-0072). The average crystallites size of silver sulphide nanoparticles Ag₂S were determined through Full-Width at Half Maximum (FWHM) of X-Ray diffraction peaks by using the Debye-Scherers [41] equation given as

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

where λ is the wavelength of the X-ray (1.5405 Å), k is the Scherrer constant (k = 0.89), β is the full width at half maximum (FWHM) of the diffraction peak in radians and θ is the Bragg angle corresponding to the maximum of the diffraction peak in degrees. The average of crystallite size obtained is D = 31.37 nm. This is consistent with the sizes determined from HRTEM images which are found to be in the range of 20 nm to 80 nm. Such particle size are favourable to the effective light scattering and LSPR effects in polymer medium which are evident in the improved performance of

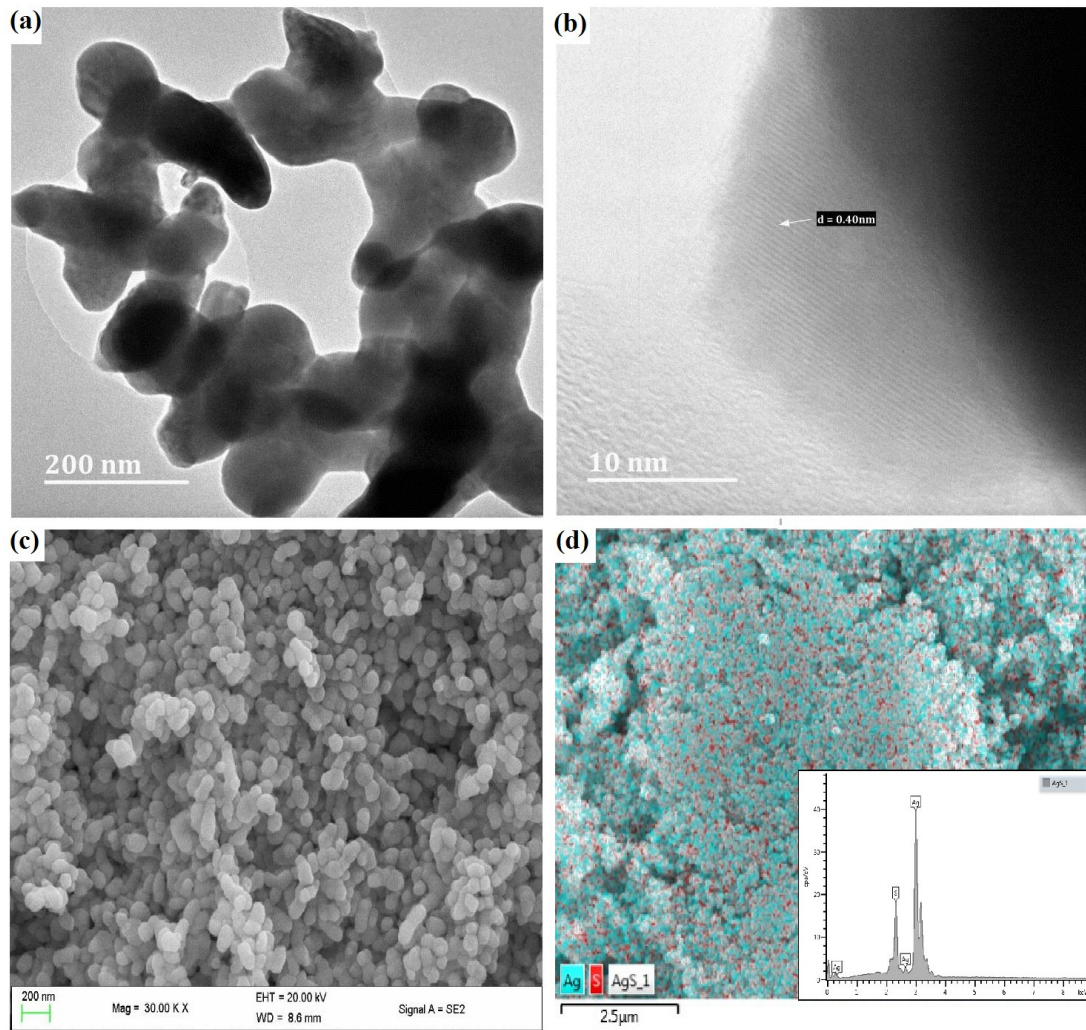


Figure 6.2: X-ray diffraction pattern of Ag_2S nano-particles powder

the doped devices especially at low dopant concentration.

6.4 Results and discussion

6.4.1 Characterizations of Silver sulfide

SEM and TEM electron microscopy

The nano-morphology of the synthesized silver sulphide (Ag_2S) nano-particles were investigated using high-resolution scanning and transmission electron microscopy

Table 6.1: Analysis of XRD of Ag₂S nanoparticles

Peak No.	2 θ (degree)	hkl	FWHM(β)	d(nm)
1	26.00	($\bar{1}$ 01)	0.35943	22.7
2	28.95	(111)	0.26494	30.9
3	31.49	($\bar{1}$ 12)	0.25767	32.0
4	33.90	(120)	0.31242	26.5
5	34.47	($\bar{1}$ 21)	0.26496	31.3
6	36.80	(121)	0.34300	24.4
7	37.71	($\bar{1}$ 03)	0.24985	33.5
8	40.78	(031)	0.28266	30.0
9	43.41	(200)	0.45434	18.8
10	45.44	(023)	0.56564	15.2
11	46.04	(113)	0.36434	23.7
12	47.75	(311)	0.73323	11.8
13	48.73	(21 $\bar{2}$)	0.33684	25.9
14	53.24	(22 $\bar{2}$)	0.40229	22.1
15	58.28	(023)	0.77081	11.8
16	63.73	(034)	0.9334	10.0

(HRSEM and HRTEM). The HRSEM image provided in Fig 6.3(c,d) clearly shows the presence of various forms of clusters which appeared to be composed of the same interconnected bud like structure (Fig 6.3c). The elemental mapping taken from the same powder showed uniformly distributed elements of silver and sulfur in the medium. Furthermore, the elemental analysis carried out based on EDX data are presented in Fig 6.3d (inset) that indicate clearly two dominant peaks associated with the existence of silver and sulphur in the synthesized nano-particles. Hence, the powder consists of 88 % silver while the remaining 12 % was found to be sulphur. No other impurities were detected by the analysis. On the other hand, the high-resolution transmission electron microscopy provided in Fig 6.3(a) shows interconnected ring-like structure and different spherical shapes. The sizes of the NPs measured from HR-TEM images ranged from 20 nm to 80 nm that is in agreement with X-ray diffraction experiments and existence of (Ag₂S) which exhibited the core-shell structure. Fig 6.3(b), the HRTEM image, clearly showed well aligned crystallite with crystal spacing 0.40 nm which is consistent to the ($\bar{1}$ 01) atomic planes of (Ag₂S). This is found to be similar to those reported in the literature[39, 40]. These particle sizes were suitable to improve light-scattering processes in polymer absorber medium that traps incident photons, and consequently, enhances the short circuit current density (J_{sc}).

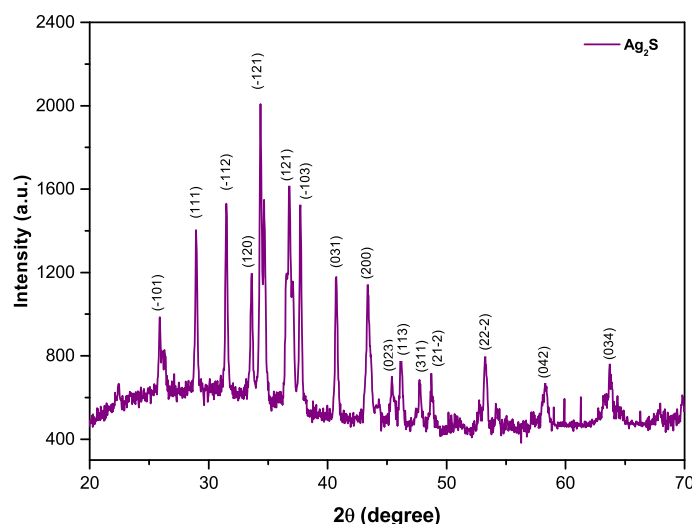


Figure 6.3: (a) and (b)HRTEM images; (c) and (d) HRSEM images with energy dispersive X-ray (EDX) spectrum of Ag₂S nanoparticles.

6.4.2 Optical absorption

UV-Vis spectra were measured from Ag₂S nano-particles doped various media as provided in Fig 6.4. There are two main absorption mechanisms for the proposed thin film solar cells. The first one is the occurrence of local surface plasmon resonance absorptions by the presence of metal nano-particles. The second absorption mechanism, induced by the metal NPs, is light scattering. By way of changing the direction of the incident light (elastic and inelastic scattering) more light can be trapped in the solar absorber medium which enhances absorption. Figure 6.4b stands for the optical absorption of silver sulfide nanoparticles in deionized water, which exhibited a broad absorption peak centered around 550 nm. The wide absorption band width must have been the result of scattering of light by the particles in the water medium. On the otherhand, the spectra taken from Ag₂S doped photoactive films showed two new and distinct regions of optical absorption, in addition to the absorbance of P3HT:PCBM blend. The first one is at the ultraviolet windows (380-440 nm) and the second one in the near infrared regions (700-900) nm. These two new absorption ranges are the consequence of the incorporation of Ag₂S in the photoactive films of the solar cell. The first absorption range is attributed to the

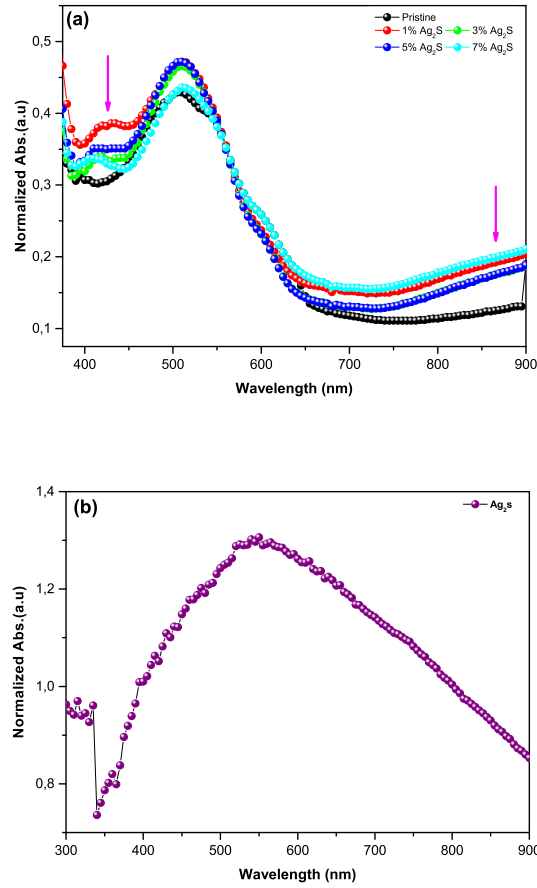


Figure 6.4: (a) Optical absorption spectra of P3HT:PC₆₁BM films prepared at different Ag₂S concentration. (b) Optical absorption spectrum of the Ag₂S powder in a deionized water suspension

surface plasmon polariton resonance (SPPR) which arises from the collective oscillations of conduction electrons on the surface of the metal nanoparticles [42, 43]. The second broadband absorption (above 700) is originated from size distribution of NPs, the increase in the surface states and scattering. According to the optical absorption peak provided in Fig 6.4a, the pristine film showed a typical P3HT:PCBM blend absorbency while those photoactive layers prepared with various concentration of silver sulphide nano-particles have a slightly red-shifted compared to the un-doped films. However, the absorption width is also slightly enhanced in devices containing silver sulphide nano-particles. It is to be noted that the enhancement of optical absorption above 700 nm in Ag₂S nano-particles doped films can also be attributed to the light trapping mechanisms through scattering. This involves indeed

multiple reflections of light within the photoactive layer that lead to trapping and improve light harvesting.

6.4.3 J-V Characteristics

The current-voltage characteristics (J-V) of the polymer solar cells (PSCs) doped with silver sulphide nano-particles have been taken under 1 Sun illumination using solar simulator operating at AM1.5. Fig 6.5 shows the different J-V data taken from devices fabricated using P3HT:PC₆₁BM containing Ag₂S nanoparticles at various concentrations. One can clearly see the current surge as the result of doping the nano-particles into the photoactive layer of the PSC compared to un-doped devices. Because of such current surge the performance of the solar cells are also varied with concentration as summarised in Table I. It is to be noted here that the main contribu-

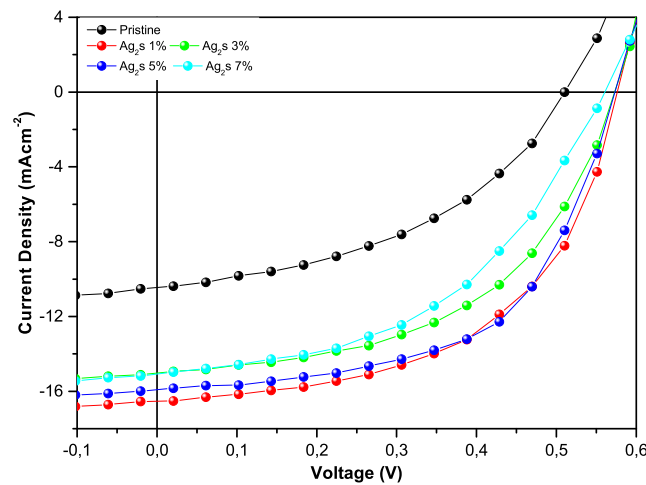


Figure 6.5: The J-V characteristics of the solar cells fabricated with/without nickel sulphide nano-particles.

tor for improved device performance is the large photo-current collected from Ag₂S nano-particles doped photoactive layer. However, there is also changes in the open circuit voltages (V_{oc}) compared to the reference cell which has increased by about 15 % from 0.51 V to 0.59 V at 3 % wt concentration of Ag₂S. The change in the V_{oc} can be attributed to the improved interface condition between the active layer and

Table 6.2: The solar cell parameters of the best performed devices.

Device	$V_{oc}(V)$	$J_{sc}(mAcm^{-2})$	FF	PCE%	$R_s(\Omega cm^2)$
Pristine	0.51	10.46	43.72	2.33	139
1% Ag ₂ S	0.58	16.50	54.12	5.15	107
3% Ag ₂ S	0.59	14.99	50.32	4.42	226
5% Ag ₂ S	0.57	15.91	56.25	5.13	123
7% Ag ₂ S	0.57	15.02	46.21	3.97	446

the electrodes. Generally, the performance of solar cells is dependant on the doping level of Ag₂S nanoparticle in the active layers. The best device performances were recorded at the concentrations of 1 % and 5 % by weight which corresponds to the power conversion efficiency of 5.15 % and 5.13 %, respectively. The J_{sc} was increased by 58 % and 52 % for concentration 1 %wt and 5 %wt, respectively. The J_{sc} enhancement is attributed to an improved charge transport processes in addition to improved optical absorbance. Increased photo-generated excitons and improved electron-hole pair dissociation due to near-field enhancement around the plasmonic Ag₂S nano-particles are responsible for better solar cell performances. Furthermore, the rectification of the diodes is very good as reflected by the magnitude of the measured fill factor which has grown by 29 % and 24 % for 1 % and 5 %, respectively. The current results could also suggest that reduced geminate recombination might have occurred by the presence of metal Ag₂S nano-particles.

According to the bar diagram given in Fig 6.6 the power conversion efficiency found from P3HT:PC₆₁BM based solar cells varies from 2.33% to 5.15% with increasing concentration of Ag₂S from (0-5)% by weight. However, excess concentration of Ag₂S is unfavourable for solar cell performance because of leakage currents that reduces the rectification of the diodes. For instance, the concentration 7% of Ag₂S the power conversion efficiency of the devices dropped to 3.64%. The current experimental evidences suggest that the optimum NPs concentration for best device performances ranges from (1-5) % by weight.

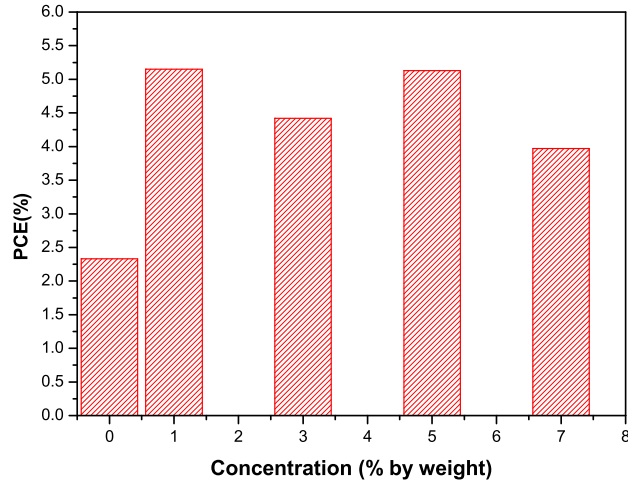


Figure 6.6: The power conversion efficiency of P3HT:PC₆₁BM based solar cells containing various concentration of Ag₂S.

6.4.4 Charge carrier mobility

The charge transport properties of the newly fabricated polymer solar cells were investigated using space charge limited current (SCLC) measured under dark conditions. The effects of Ag₂S nanoparticles on the charge carrier mobility in various solar cell media are compared with Mott-Gurney law. The model assumes that the charge mobilities are constant, the medium is free of traps and the injection contact is Ohmic [44, 45]. The current density in the device can be expressed by the equation:

$$J = \frac{9}{8} \epsilon \epsilon_0 \mu_0 \frac{V^2}{L^3} \exp(0.89\gamma) \sqrt{\frac{V}{L}} \quad (6.2)$$

where ϵ is the relative permittivity, ϵ_0 is the permittivity of free space; μ_0 is the zero-field mobility, γ is the field activation factor, L is the thickness of the active layer and V is the voltage drop across the sample which is corrected for built-in potential V_{bi} . The details of the model is given in published articles [29, 37]

According to Fig.6.7, the measured space charge limited current agree very well

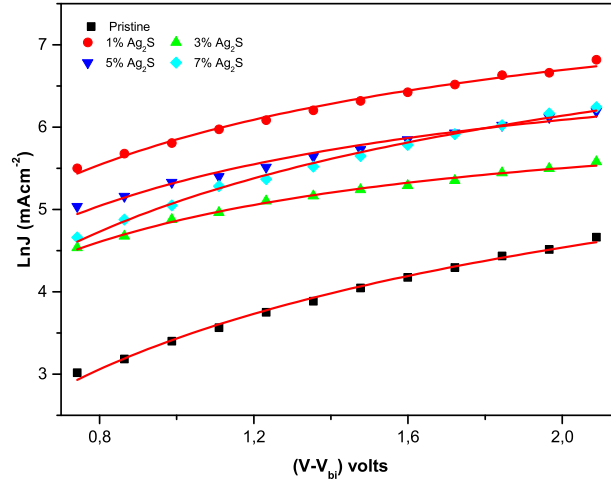


Figure 6.7: Space charge limited currents of the diodes and solid lines representing computer fits according to equation (2).

Table 6.3: The charge carrier transport parameters of the TFPSCs.

Concentration %	$\mu_0(\text{cm}^2\text{S}^{-1}\text{V}^{-1})$	$\gamma(\text{cmV}^{-1})$
0	1.06×10^{-4}	-8.43×10^{-6}
1	2.24×10^{-3}	-1.77×10^{-4}
3	1.36×10^{-3}	-1.08×10^{-4}
5	1.63×10^{-3}	-1.29×10^{-4}
7	4.42×10^{-4}	-5.07×10^{-5}

with equ (2). The zero field mobilities (μ_0) and field activation factor derived from the devices composed of P3HT:PC₆₁BM-Ag₂S (Table 3) exhibit increased carrier mobilities by two orders of magnitude higher than the pristine device. These results suggest improved charge transport process by the presence of Ag₂S nano-particles in the photoactive medium of the solar cells. Furthermore, the incorporation of the metal Ag₂S in the photoactive layer may have created the formation of additional interfacial areas that could assist in carrier transport and collection.

6.5 Device degradation under ambient conditions

The environmental stability of the inverted thin-film organic solar cells was studied by keeping the devices under ambient environments without device encapsu-

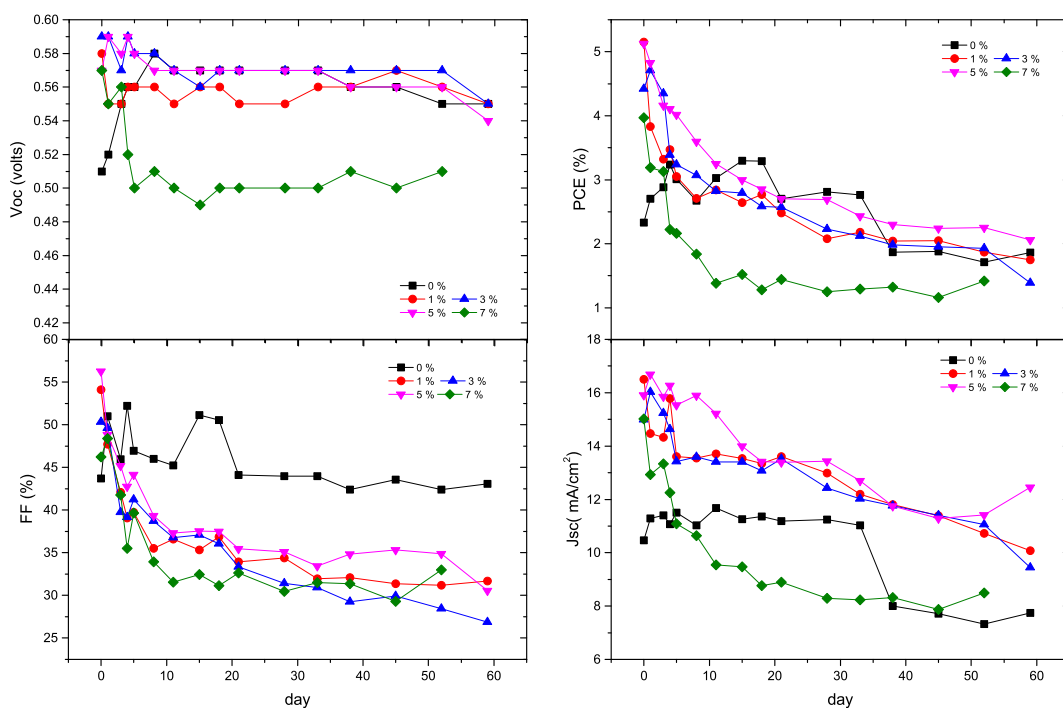


Figure 6.8: Lifetime tests for devices fabricated with/without Ag_2S nanoparticles. The percentages in the panel refers to the concentration of the particles in the solar absorber layer of the devices.

lation. The solar cell parameters was measured at a regular time interval under 1 Sun from the devices stored in ambient condition (see Fig 6.8). The measured main solar cell parameters such as open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor(FF) and power conversion efficiency (PCE) were plotted as function of time as depicted in Fig 6.8. The parameters clearly show changes in magnitudes, particularly, J_{sc} , FF and PCE decreases monotonically with time. The open circuit voltage appears to be decreasing very slowly compared to the other parameters of the devices except to the highly doped solar cell (7% wt). It is to be noted that the fill factor of the pristine film remains higher than NP doped devices which is attributed to a close and vertically graduated structure of bulk heterojunction P3HT:PC₆₁BM blend. The device doped with Ag_2S nano-particle at concentrations 1 % and 5 %wt, retained about 57% of its highest PCE value for about 20 days. The PCE of the

pristine devices appears to be improving with time and reaching nearly 3.2% in the first 15 days test. After that the values are decreasing monotonically with time. The initial improvement of PCE can be due to improved crystallinity of the polymer chain by storing the solar cell in dark condition. Furthermore, the rate at which the parameters of the doped device changes with time is found to be different for the various concentrations metal NPs in the active layers. For instance, the initial values of the fill factor (FF) of device 1 %, 3 %, 5 % and 7 %wt, have reduced by 69%, 85%, 80%, and 44% respectively, after two months. After the initial reduction of values in the first 10 days storage, the device parameters remained relatively stable in air for over two months. The relative stability of V_{oc} and FF in undoped devices could be attributed to the better tight inter-facial condition between the electrodes and the active layers that prevents the infiltration of oxygen and moisture into the active layer.

6.6 Conclusion

In summary, we synthesized metallic silver sulphide nano-particles by a wet chemistry process and incorporated successfully in inverted organic solar cells, using bulk heterojunction (BHJ) P3HT:PCBM blend solar absorber. The results are clearly showed improved optical and electrical properties of the solar absorber films by the presence of the metal nano-particles, which in turn enhanced the photovoltaics parameters such as J_{sc} , FF, and PCE. The improved device performances are attributed to the occurrence of surface plasmon polariton resonance (SPPR) and light scattering effect of the incorporated metallic nano-particles. The best device performance determined from this investigation was 5.15 % at doping level 1% by weight. The storage life time of the solar cells is found to be significant and lasted over two months this is mainly due to sealing mechanism of the inverted structure that prevented oxygen and humidity from entering into the photoactive layer. However, the inclusion of the metal nano-particles has improved the initial power conversion efficiency of the solar cells by 120 % compared to the pristine devices. This suggest that the devices needs to be encapsulated right after fabrication to maintain the de-

vice performance for a longer period of time. However, the Ag₂S nano-particles are environmentally stable and compatible with sol gel device fabrication using roll to roll methods. This will assist in cheap solar cell fabrication and reduce the cost for energy.

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CHAPTER 7

Highly stable thin film organic solar cells using poly crystallized silver doped LaPO_4

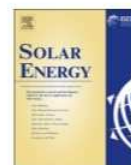
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Highly stable thin film organic solar cells using poly crystallized silver doped LaPO_4



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ABSTRACT

Silver doped lanthanum phosphate (LaPO_4 :Ag) nano-composite was successfully synthesized at various concentrations of silver using wet chemistry. The newly synthesized particles were used in the solar absorber medium of thin-film organic solar cells to assist in photons harvesting. The photoactive layer of the solar cell was composed of poly-3-hexylthiophene (P3HT) and (6–6) phenyl-C61-butyric acid methyl ester (PCBM) molecules blend with a small concentration of LaPO_4 :Ag by weight. The solar cells were fabricated in an inverted device architecture consisting of layers of materials as ITO/ZnO/P3HT:PC61BM- LaPO_4 :Ag/ MoO_3 /AL. As a result, significant power conversion efficiency was recorded as high as 5.23% using the newly synthesized nano-composite at a silver concentration of 0.05 mol. This is an excellent achievement for ambient device preparations conditions which is over 124% growth in PCE compared to undoped devices. The incorporation of LaPO_4 :Ag into the polymers blend absorber layer is expected to broaden optical absorption and enhance photons harvesting. The inclusion of silver in the composite could also be expected to trigger surface plasmon resonance effect. Moreover, LaPO_4 :Ag doped solar cells appeared to be highly stable under ambient environment. The optical and morphological properties of the nano-composite are well presented and discussed.

7.1 Abstract

Silver doped lanthanum phosphate (LaPO_4 :Ag) nano-composite was successfully synthesized at various concentrations of silver using wet chemistry. The newly syn-

thesized particles were used in the solar absorber medium of thin-film organic solar cells to assist in photons harvesting. The photoactive layer of the solar cell was composed of (poly-3-hexylthiophene (P3HT) and (6-6) phenyl-C61-butyric acid methyl ester (PCBM) molecules blend with a small concentration of $\text{LaPO}_4\text{:Ag}$ by weight. The solar cells were fabricated in an inverted device architecture consisting of layers of materials as ITO/ZnO/P3HT:PC61BM- $\text{LaPO}_4\text{:Ag}$ / MoO_3 /AL. As a result, significant power conversion efficiency was recorded as high as 5.23% using the newly synthesized nano-composite at a silver concentration of 0.05 mol. This is an excellent achievement for ambient device preparations conditions which is over 124% growth in PCE compared to undoped devices. It is to be noted that the incorporated $\text{LaPO}_4\text{:Ag}$ into the polymers blend absorber layer is expected to broaden optical absorption band since Lanthanide (Ln) has the properties to enhance photons harvesting, charge carrier transport and increase exciton dissociation. The inclusion of silver in the composite could also be expected to trigger surface plasmon resonance effect. Moreover, $\text{LaPO}_4\text{:Ag}$ doped solar cells appeared to be highly stable under ambient environment. The optical and morphological properties of the nano-composite are well presented and discussed.

7.2 Introduction

Solution-processable polymer solar cells (PSCs) have gained tremendous research interest in the past three decades because of their potential in photonic and electronic devices. Thin film polymer solar cells especially offers cheap materials and device fabrication cost, light weight, semitransparency and mechanical flexibility [1–7]. Consequently, there has been significant progress in polymer solar cells today with the best power conversion efficiency (PCE) above 16% [8–10]. Such significant successes in PSC were possible through immense research efforts in the synthesis of conducting polymer, designing various device structures etc. Recently, the incorporation of metal nanoparticles at the various functional layers of the device structure produced important development in the field [11, 12]. It is important to note that

to overcome the challenge of losing more incident photons from the thin film polymers blend a mechanism is sought to trap light by way of metal plasmon resonance. Local surface plasmon resonance (LSPR) effect induced by metal nano-particles in the polymer-fullerene blend solar absorber is reported to have important influence on optical absorptions the films and improved the conductivity of the medium for better charge transport processes.

Near-field enhanced exciton dissociations resulted in the collection of large photocurrent which then improved power conversion efficiency (PCE) of the thin-film organic solar cells [13–18]. The local surface plasmon resonance is highly dependent on the size and shape of the metal nanoparticles. Stratakis et. al have reported that if the diameter of the nano-particles is much smaller than the wavelength of light (5-20 nm diameter) then they can be employed as subwavelength, however, larger diameter NPs (>50 nm) can be used as an effective subwavelength scattering elements into high angles inside the photoactive layer[19]. The noble metals nanoparticles such as gold and silver are an excellent choice for plasmonic since they are excellent light scatterer, good conductors and they can be synthesized using low temperature colloidal chemistry [21, 22]. However, the cost of these precious metals is still the challenge for mass production PSCs. Therefore, the synthesis of alternative metal nano-particles or composite with various elements are still highly sought. Oseni et al. have investigated the bimetallic nano-composites silver:zinc (Ag:Zn) and silver: magnesium (Ag:Mg) in polymer solar absorber and reported improved overall performance of the thin-film organic solar cell (see table 1) [15].

Lanthanum based compound is used in the current investigation which is a well-known transition metal and an important family of inorganic material for PSC. Lanthanide ions have been studied as a possible solar spectral converter for solar energy harvesting [23, 26]. Similarly, phosphors containing lanthanide based molecules can be used as photocatalysis, photovoltaics, heat resistant materials, white light-emitting diodes, and even for nuclear waste disposal[24–27]. Furthermore, lanthanum has a high refractive index, high thermal and chemical stability. They have optical and chemical characteristics resulting from their unique (4f electron) configuration that allow electron transitions from 4f ground state to 5d excited

states [28, 29]. The lanthanum has been extensively synthesized in various forms, for instance, LaPO_4 [28], LaF_3 [30, 31] and $\text{La}_2\text{Sn}_2\text{O}_7$ [32] nano-composites.

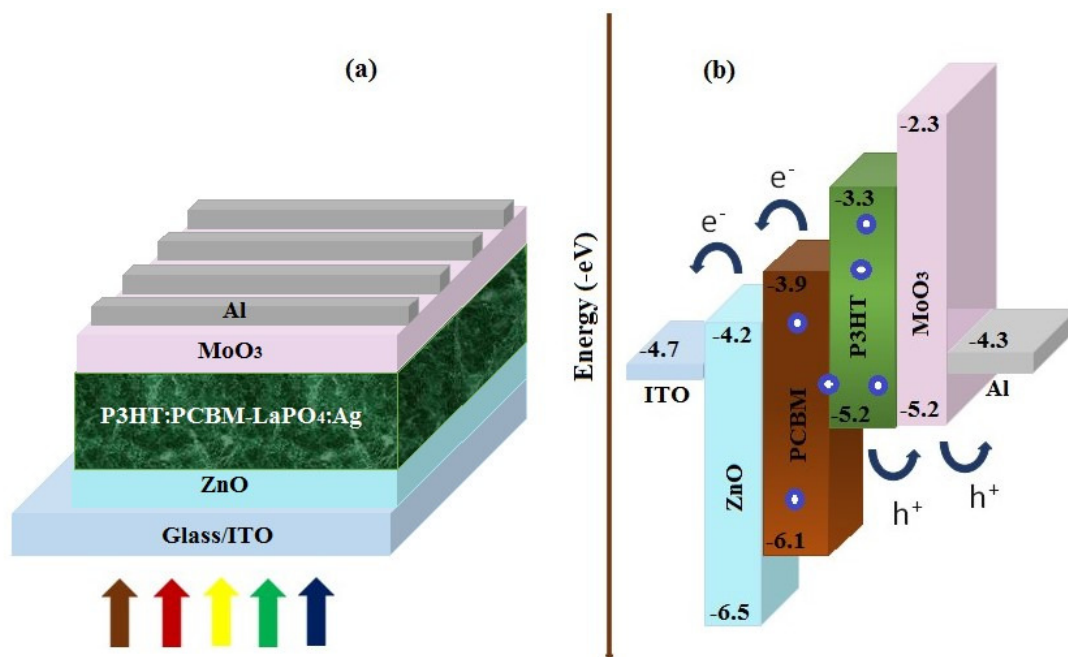


Figure 7.1: (a) Schematic diagram for bulk heterojunction organic solar cell based on $\text{LaPO}_4\text{:Ag}$ nano-composite incorporated into P3HT: PCBM active layer.(b) energy level diagram of the device materials.

In this work, silver doped lanthanum phosphate ($\text{LaPO}_4\text{:Ag}$) nano-composite was successfully synthesized at different concentration of silver, and introduced into the poly (3-hexylthiophene)(P3HT): [6,6]-phenyl C61 butyric acid methyl ester(PC61BM) solar absorber medium of the thin-film organic solar cell to assist in the photons harvesting. By adding 1% by weight of the synthesized of $\text{LaPO}_4\text{:Ag}$ in the solar absorber medium, the performance of the devices has improved, and achieved a power conversion efficiency (PCE) as high as 5.23 %. This is an increase by 124 % compared to the pristine type photoactive medium. The improvement of PCE is attributed to enhanced photo-current as the results of improvement in charge carrier mobility, light-harvesting, and exciton dissociation. The experimental results are well presented and discussed at the different sections of the manuscript.

Table 7.1: Summary of the plasmon effect

Device structure	matels	plasmon effect	$V_{oc}(V)$	J_{sc} (mAcm ⁻²)	FF	PCE	Year	Ref
ITO/ZnO/PTB7:PCBM-Ag:Zn:Ni/MoO3/Al	Ag:Zn:Ni	LSPR	0.73	14.76	46.93	5.06	2019	[33]
ITO/ZnO/PTB7:PCBM-Ag:Mg/MoO3/Al	Ag:Mg	LSPR, and scattering	0.76	14.13	45.43	4.96	2019	[15]
ITO/PEDOT:PSS/P3HT:PCBM-Ag@Cu /LiF/Al	Ag@Cu	LSPR	0.60	11.90	54.40	3.87	2018	[14]
ITO/PEDOT:PSS/P3HT:PCBM-Ag:Zn:Ni /LiF/Al	Ag:Zn:Ni	LSPR	0.56	12.36	47.70	3.33	2019	[20]
ITO/Au@SiO-WO3/P3HT:PCBM/LiF/Al	Au@SiO	LSPR	0.61	4.72	54	1.58	2019	[22]
ITO/Au-PEDOT:PSS/P3HT:PCBM/Al	Au-NW	LSPR	0.65	9.02	46	2.72	2012	[21]
ITO/NiS-PEDOT:PSS/P3HT:PCBM/LiF/Al	NiS	LSPR	0.58	18.65	55.88	6.03	2019	[18]
ITO/PEDOT:PSS/P3HT:PCBM-Au@SiO ₂ /Al	Au@SiO ₂	LSPR	0.62	10.6	57.00	3.80	2013	[49]
ITO/ZnO-Ag@SiO ₂ /P3HT:PCBM/PEDOT:PSS/Ag	Ag@SiO ₂	LSPR	0.54	13.44	53.00	3.97	2019	[50]

7.3 Experimental details

7.3.1 Materials

Chemicals used in this study were silver nitrate hexahydrate (> 99.5% AgNO₃·6H₂O), lanthanum(III) nitrate hexahydrate ((La(NO₃)₃·6H₂O), 99.99%), orthophosphoric acid (H₃PO₄, 85 wt. % in H₂O, 99.99%) which are purchased from Capital lab. The polymers used in device preparations were poly (3,4-ethylene dioxythiophene):poly (styrenesulfonate) (PEDOT:PSS), Poly (3-hexylthiophene) (P3HT, 95 +% regioregular, electronic grade) and [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM, 95 +% (MoO₃ Aldrich, 99.9%), (ZnO nanograde, 2.5 wt% in IPA), all purchased from Ossila Ltd.

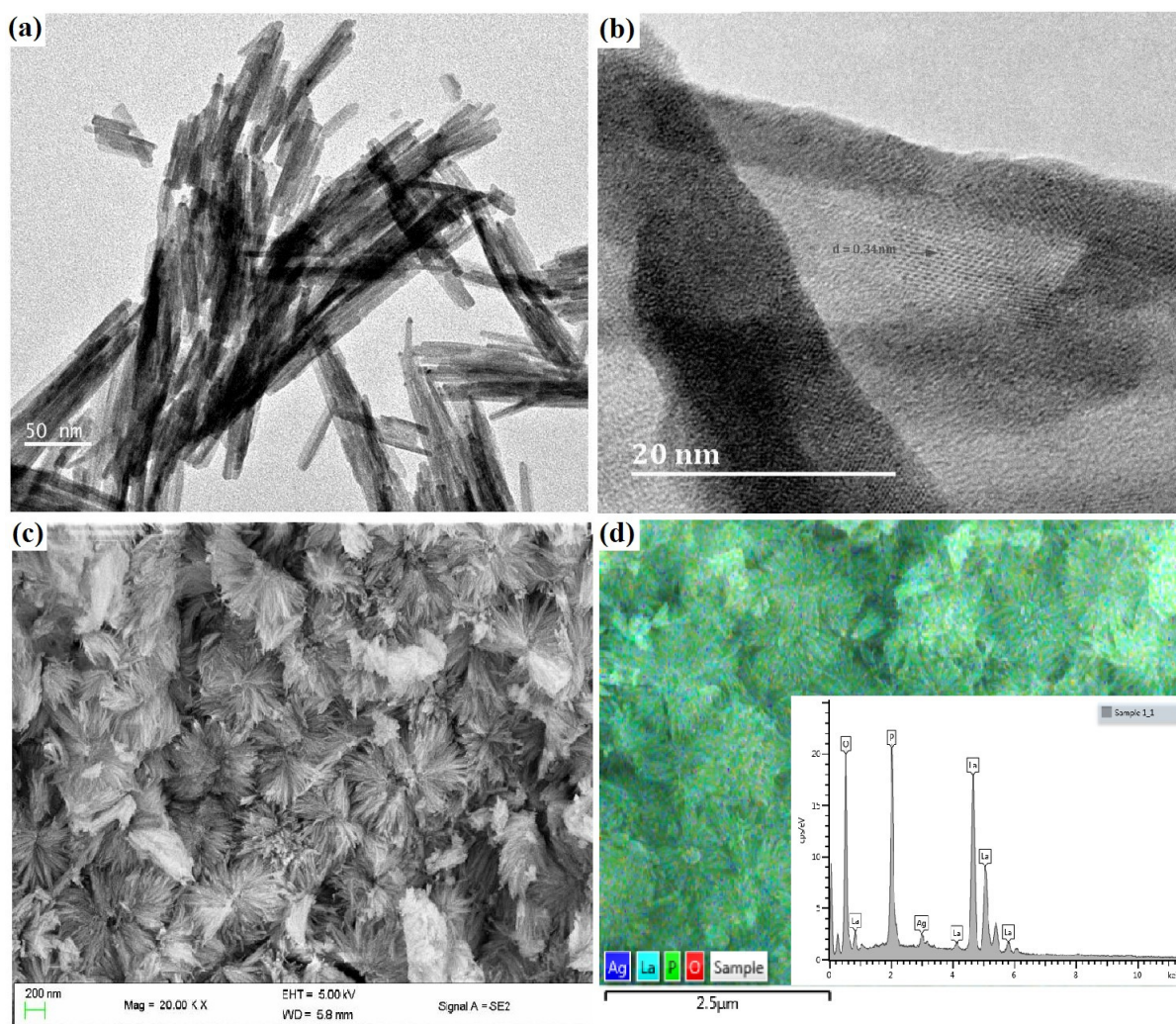


Figure 7.2: HRSEM images of lanthanum phosphate doped silver ($\text{LaPO}_4\text{:Ag}$) nano-composite

7.3.2 Synthesis of ($\text{LaPO}_4\text{:Ag}$) nano-composite

The silver doped lanthanum phosphate ($\text{LaPO}_4\text{:Ag}$) nano-composite was synthesized through the wet chemical route with the following fundamental steps. Initially, 0.1 mol of lanthanum nitrate $\text{La}(\text{NO}_3)_3$ was dissolved in 25mL of deionized water, and 0.05 mol of silver nitrate AgNO_3 was dissolved in 25mL of deionized water. The silver nitrate was then added into lanthanum nitrate solution in drop-wise while continuous stirring. Furthermore, the third solution was prepared from 0.1 mol of orthophosphoric acid H_3PO_4 dissolved in 48 mL of deionized water, which is then slowly added by drop-wise into the above mixture. The solution was further

stirred continuously with a magnetic stirrer for 2 hours. The resulting mixture was then filtered, washed several times with deionized water. Finally, the precipitate was dried under vacuum at 70°C for 2 hours which resulted in the formation of silver doped lanthanum phosphate (LaPO₄:Ag). The structure and morphology of the synthesised composite were characterized by various spectrometer such as scanning electron microscope (SEM: JEOL JSM 6100), transmission electron microscope (TEM: JEOL JEM 1010), X-ray powder diffractometer and UV-visible spectrometer (Rayleigh1601).

7.3.3 Solar Cells Fabrication

The inverted polymer solar cells were fabricated on ITO coated glass substrate according to procedures followed in references [31, 32]. The solar cell is composed of different layers of materials which are arranged in device architecture as glass/ITO/ZnO/P3HT:PC₆₁BM-LaPO₄: Ag /MoO₃/AL. The schematic diagram for the device structure is provided in Fig 7.1. A thin layer of ZnO electron transport layer (ETL) was spin-coated on the ITO substrate at 3500 rpm for 60 s which then annealed at 100°C on a hotplate for 20 min. The photo-active layer was spin coated on ETL from the solution of P3HT and PC₆₁BM blend 1:1 ratio by weight at a concentration of 20 mg/mL. The synthesized particles of LaPO₄:Ag nano-composite were incorporated into the blend P3HT:PCBM blend solution at the concentration of 1% by weight. The mixture was stirred for 4 hrs at 40°C to enhance the miscibility of the molecules. The photoactive films were spin-coated at 1200 rpm for 40 s and annealed at 90°C for 5 min in an N₂ filled furnace. Finally, the hole transport layer (MoO₃) and aluminum electrodes were deposited on the active layer under a vacuum pressure lower than 4.0×10⁻⁶ Pa at a thickness of 8 nm and 85 nm, respectively. The current density-voltage (J-V) data were collected using Keithley HP2420 source meter and a solar simulator (model SS50AAA) operating at AM1.5 and 100 mW/cm². The absorber films optical characteristics were studied using UV-Vis absorption spectra obtained with an absorption photo spectrometer (Rayleigh 1601).

7.4 Results and discussion

SEM and TEM electron microscopy

The surface morphology and microstructure of silver doped lanthanum phosphate ($\text{LaPO}_4\text{:Ag}$) nano-composite were investigated using scanning electron microscopy SEM and high-resolution transmission electron microscopy HRTEM. The TEM image provided in Fig 7.2(a) clearly shows rod-like structure with various sizes. The high-resolution transmission electron microscopy HRTEM image provided in Fig 7.2(b) clearly showed nanorod which exhibited crystalline nature as clearly visible fringes with an interplanar spacing of about 0.34 nm. The lattice constant is consistent with the (110) lattice spacing of hexagonal LaPO_4 reported in literature [33]. Moreover, the SEM image given in Fig 7.2(c,d) showed flower like micro-structures and urchin-like shape architectures. These micro-structures are the micro nanorods observed in HRTEM. The elemental mapping taken from the same powder sample showed uniform distribution of the elements of lanthanum, silver, phosphorus, and oxygen. This is supported by the elemental analysis of the EDX data provided in Fig 7.2 d(inset) which are evident on the intensity peaks corresponding to La, Ag, P, and O. These elements are found in the powder with the proportion of 54.58% lanthanum, 2.28% silver, 12.89% Phosphorus, while the remaining 30.25 oxygen. This confirms the absence of any impurity in the nano-composite.

X-ray diffraction

The X-ray diffraction experiment were conducted in an effort to get more understanding on the crystal structure of the ($\text{LaPO}_4\text{:Ag}$) nano-composite. The powder sample was used to conducted XRD experiment and data was taken in the diffraction angle (2θ) interval between 15° and 70° as depicted in Fig 7.3. The resulting XRD spectrum consist of varipous differaction peaks at 19.90° , 25.20° , 29.10° , 31.26° , 37.53° , 41.64° , 48.23° , 51.62° , 53.26° , and 58.93° . These peaks corresponds to the X-ray reflections from lattice planes (121), (110), (200), (120), (112), (211),

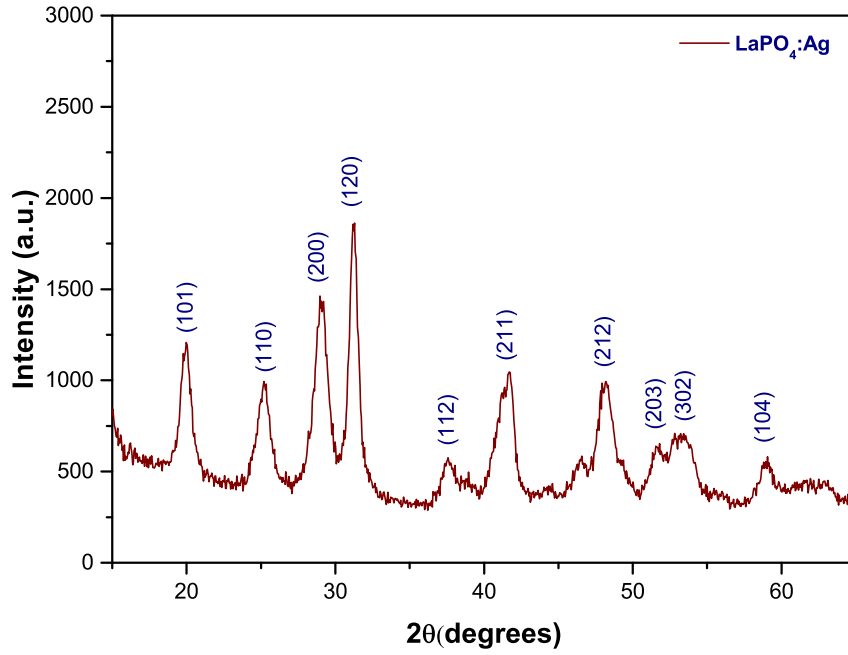


Figure 7.3: X-ray diffraction pattern of LaPO₄:Ag nanocomposite.

(212), (203), (302) and (241), respectively. The planes are representing a hexagonal and monoclinic of LaPO₄: Ag with lattice parameters are $a = 7.08100\text{\AA}$ and $c = 6.468\text{\AA}$ which are in agreement with the standard data of literature (JCPDs card no. 32-0493) confirmed the existence of LaPO₄ due to their similar ionic [34, 35]. We can observe there are no more diffraction peaks beyond LaPO₄, and silver Ag ion might have introduced into the LaPO₄ lattices. Therefore, the average crystallite sizes of the synthesized (LaPO₄:Ag) nano-composite were calculated using the Debye Scherrer formula (equ. 1)

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (7.1)$$

Where, λ is the wavelength of the X-ray ($1.5405\text{\AA}$), k is the Scherrer constant ($k = 0.89$), β is the full width at half maximum (FWHM) of the diffraction peak in radians and θ is the Bragg angle corresponding to the maximum of the diffraction peak in degrees. The higher three intensity peak (101) at (20.00°), (200) at (29.08°), and (120) at (31.26°) to estimate the crystallite size. The average size is between 5-9 nm was obtained of (LaPO₄:Ag) nanocomposite.

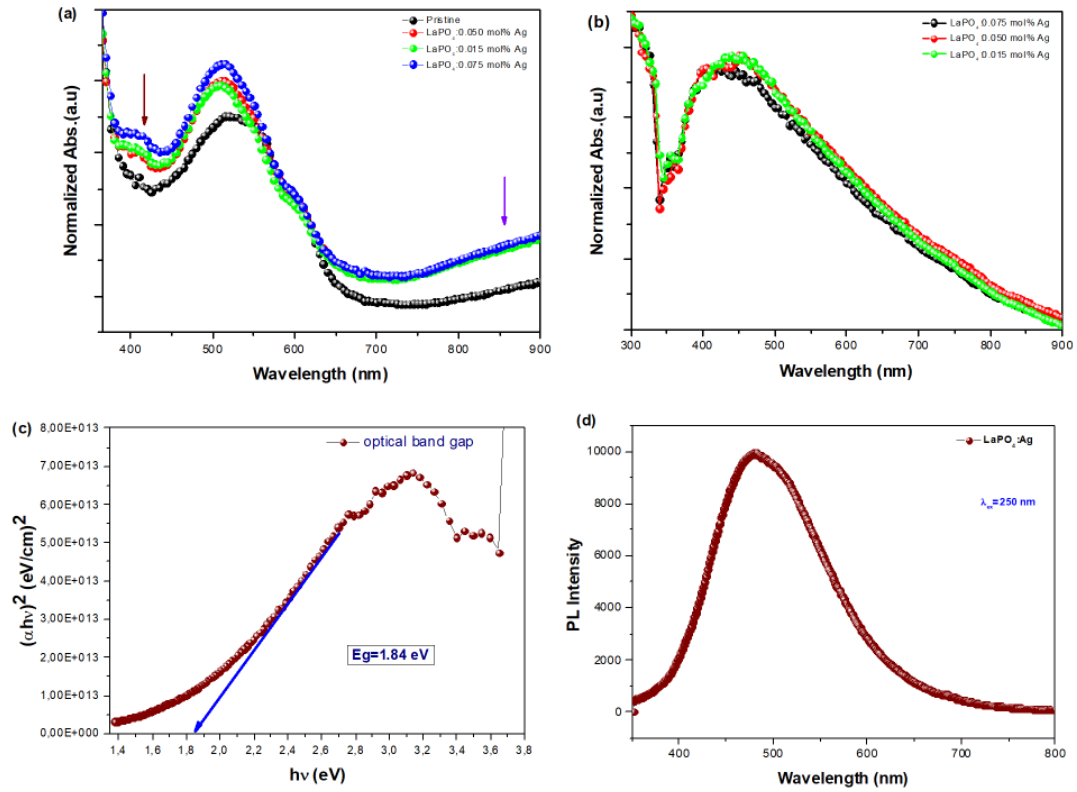


Figure 7.4: (a) Optical absorption spectra of the films (b) Optical absorption of the LaAgPO₄ suspension in deionized water. (c) Optical bandgap of the LaAgPO₄ nano-composite (d) Photoluminescence spectrum of the LaAgPO₄ powder.

7.4.1 Optical absorption

Normalized optical absorption properties of LaPO₄:Ag doped photo-active films and the synthesised nano-composite in deionized water suspension are provided in Fig 7.4(a) and Fig. 7.4 (b), respectively. The LaPO₄:Ag nano-composite in deionized water exhibits a broadband absorption from 350-800 nm with an absorption peak centred around 420 nm. This absorbance is presumably is due to the charge transfer

Table 7.2: The solar cell parameters of the best performed devices.

Device	V_{oc} (V)	J_{sc} (mAcm ⁻²)	FF	PCE%	R_s (Ω cm ²)
Pristine	0.51	10.46	43.72	2.33	139
LaPO ₄ :0.015mol%Ag	0.55	15.94	53.52	4.72	72
LaPO ₄ :0.050mol%Ag	0.56	16.47	56.40	5.23	73
LaPO ₄ :0.075mol%Ag	0.54	14.21	54.41	4.23	179

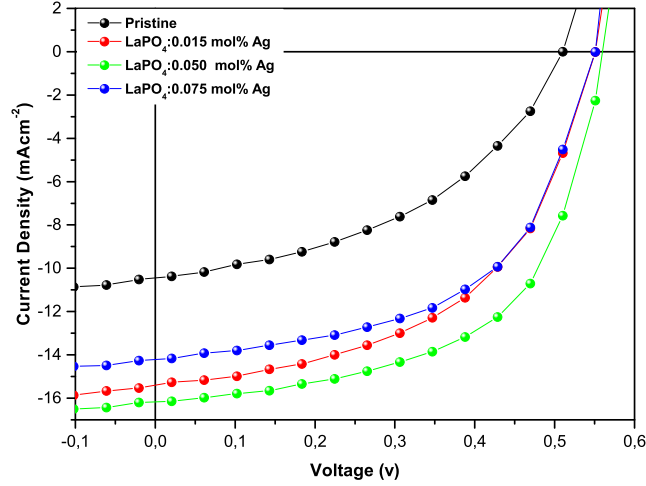


Figure 7.5: (a) The J-V characteristics of the best performing devices at various LaPO₄:Ag nano-composite loading in active layer.

between silver and the oxygen anion. Such broad absorbency is expected to enhance photons harvesting in the absorber layer of the solar cell. The optical absorption of the doped photo-active films exhibited two prominent regions of interest in addition to the absorbency of the polymer blend. The absorption peak around bump around 420 nm coincided with the absorbance peak of the nano-composite discussed earlier. Another new region of interest is the absorbance above 720 nm which mainly attributed to the long wavelength scattered waves due to the presence of silver in the composite. The optical absorption of the P3HT:PCBM blend centred around 520 nm have been blue-shifted to 510 nm by the incorporation of nano-composite in the absorber medium. Moreover, the width of absorption of have been grown compared to the absorbency of the pristine layer absorber(see Fig. 7.4a). The optical band gap were calculated by Tauc's equation and plotted in Fig 7.4(c) together with absorbances taken from the onset of absorption.

$$(\alpha h\nu)^2 = \beta(h\nu - E_g) \quad (7.2)$$

where β is a constant, E_g is the optical energy gap, h is Plank's constant, α is the absorption coefficient. The plot of $(\alpha h\nu)$ vs. $(h\nu)$ is the direct allowed transition [36, 37]. The straight line to intercept the energy axis and when $(\alpha h\nu)^2 = 0$, It is

observed that the band gap approximately 1.84 eV

Fig 7.4(d) showed the photoluminescence spectrum of the nano-composite $\text{LaPO}_4\text{:Ag}$ powder suspension in deionized water. A broad emission peak ranging from 370 to 690 nm nearly covering the most of ultraviolet and visible regions was measured under excitation 250 nm laser beam. Strong emission peak observed centred around 480 nm which corresponds to a lower recombination rate of photo-induced charge carriers due to the presence of silver. The excitation wavelength of 250 nm is the energy required for electronic charge transition to take place from silver orbitals configuration of $4d^{10}$ to $4d^9 5s^1$ orbitals. This transition is in fact parity forbidden but allowed in solid due vibrational coupling [40]. However, the presence of silver in the composite/polymer matrix could enhance the effect of near-field that improves exciton dissociation and photons harvesting in the solar cells.

7.4.2 J-V Characteristics

The current-voltage (J-V) characteristics of the thin-film solar cells doped with $\text{LaPO}_4\text{:Ag}$ nano-composite have been taken under one Sun illumination using solar simulator operating at AM1.5. Fig 7.5(a) shows the different performances of the device fabricated using P3HT:PCBM containing the composite $\text{LaPO}_4\text{:Ag}$ at a concentration of 1 % by weight. However, the synthesised nano-particle contains various concentration of silver as 0.05M, 0.015M, 0.075M. The solar cell performance parameters are summarized in Table I. The pristine device has shown a relatively low power conversion efficiency (PCE) of 2.33% with relatively low fill factor 43.72%. The device performance has significantly improved when the $\text{LaPO}_4\text{:Ag}$ nano-composite is introduced into the photo-active layer of thin-film solar cells. For instance, the performance of the device doped with nano-composite $\text{LaPO}_4\text{:Ag}$ synthesized at silver concentration of 0.050 mol exhibit the best performance with PCE of 5.23%, which is the result of measured high photocurrent and better device rectification expressed in terms of the values of $J_{sc} = 16.47 \text{ mA cm}^{-2}$, and FF = 56.40%, respectively. The growth in terms of power conversion efficiency is 124%

compared to the pristine type photo-active medium. Subsequently, as the concentration of silver increases in synthesis of the composite, the device performance has reduced. Lowering the silver concentration even further is also counter productive which decrease device performance to the PCE 4.72% at 0.015M. The best device performance in this investigations was on the synthesis of the composite at silver concentration of 0.05M. In addition to the enhanced optical absorption that lead to high photo-current the reduced geminate recombination and improved charge transport processes have attributed to high current collections. Moreover, the fill factors have grown by nearly 29% in all the devices doped with $\text{LaPO}_4\text{:Ag}$, which suggests better device rectification was possible with nano-composite compared to pristine active layer. The conductivity of the absorber layer would have improved as expressed by low serieis resistance (R_s), which could prevent the leakage and improve the J_{sc} and FF[40–42].

7.4.3 Charge carrier mobility

The effects of $\text{LaPO}_4\text{:Ag}$ nano-composite on the charge transport properties of polymers blend photo-active layer was investgated based on the measured space charge limited current (SCLC). The space charge limited current can be described by Mott Gurney law considering that the charge mobilities are constant, the insulator is free of traps, and the injection contacts are Ohmic. The SCLC data was taken from the flanks of J-V characteristics in the dark condition taken from forward bias voltage. The zero filed charge mobility can be derived from equation (3). The current density in the device can be expressed by the equation:

$$J = \frac{9}{8} \epsilon \epsilon_0 \mu \frac{V^2}{L^3} \quad (7.3)$$

where ϵ is the relative permittivity, ϵ_0 is the permittivity of free space $\epsilon_0 = 8.85 \times 10^{-12}$ F/cm; μ_0 is the zero-field mobility, is the field activation factor, L is the thickness of the photoactive layer $L = 100$ nm and V is the voltage drop across the sample which

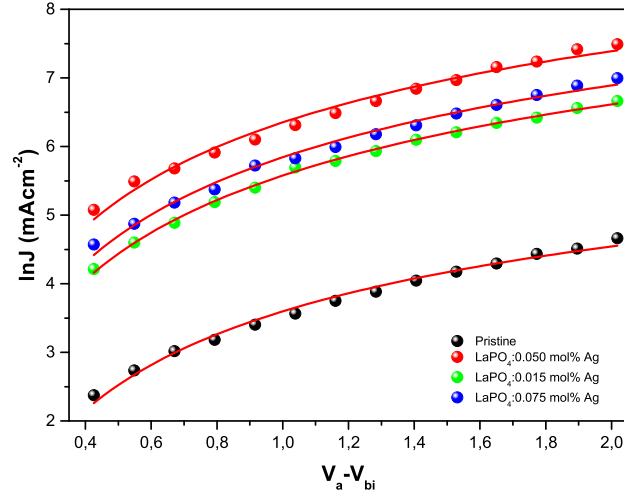


Figure 7.6: Space charge limited currents of the diodes with solid lines at various LaPO₄:Ag.

is corrected for built-in potential V_{bi} as: [44, 44–46].

$$V = V_{ap} - V_{bi} \quad (7.4)$$

where V_{ap} is the applied bias voltage. The mobility μ is dependent on the electric field and can be described by the Poole-Frenkel (PF) equation as;

$$\mu = \mu_0 \exp(\gamma \sqrt{E}) \quad (7.5)$$

where μ_0 is the low-field mobility and γ is the field activation factor. From the combination of Eqs. (2) and (4), the field-dependent SCLC can be expressed by

$$J = \frac{9}{8} \epsilon \epsilon_0 \mu_0 \frac{V^2}{L^3} \exp(0.89 \gamma \sqrt{\frac{V}{L}}) \quad (7.6)$$

According to Fig 7.6, the measured space charge limited current agree very well with the model expressed according to equ (5). The zero field mobilities (μ_0) and field activation factor derived from the devices composed of functional layers as ITO/ZnO/P3HT:PC₆₁BM-LaPO₄:Ag /MoO₃/AL, are summarized in Table 3. The P3HT:PCBM blend solar cells containing composite which are synthesized at dif-

Table 7.3: The charge carrier transport parameters of the TFPSCs.

Concentration %	$\mu_0(\text{cm}^2\text{S}^{-1}\text{V}^{-1})$	$\gamma(\text{cmV}^{-1})$
Pristine	1.84×10^{-4}	-1.66×10^{-5}
LaPO ₄ :0.050mol%Ag	2.31×10^{-3}	-2.09×10^{-4}
LaPO ₄ :0.015mol%Ag	1.07×10^{-3}	-9.62×10^{-5}
LaPO ₄ :0.075mol%Ag	1.36×10^{-3}	-1.22×10^{-4}

ferent concentration of silver as LaPO:0.050 mol Ag, LaPO:0.015 mol Ag, and LaPO:0.075 mol Ag exhibited the highest charge mobilities compared to pristine layer. The highest charge mobility recorded in this investigation correlated with the best device performance , that is ($2.31 \times 10^{-3} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) (see Table 3). The values are increased by 92%, 82%, and 86% respectively compared with pristine device with mobility ($1.84 \times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$). The enhancement in hole mobility by introducing LaPO₄: Ag within the photo-active layer effectively improved charge transport processes in the medium as well as collection by the electrode.

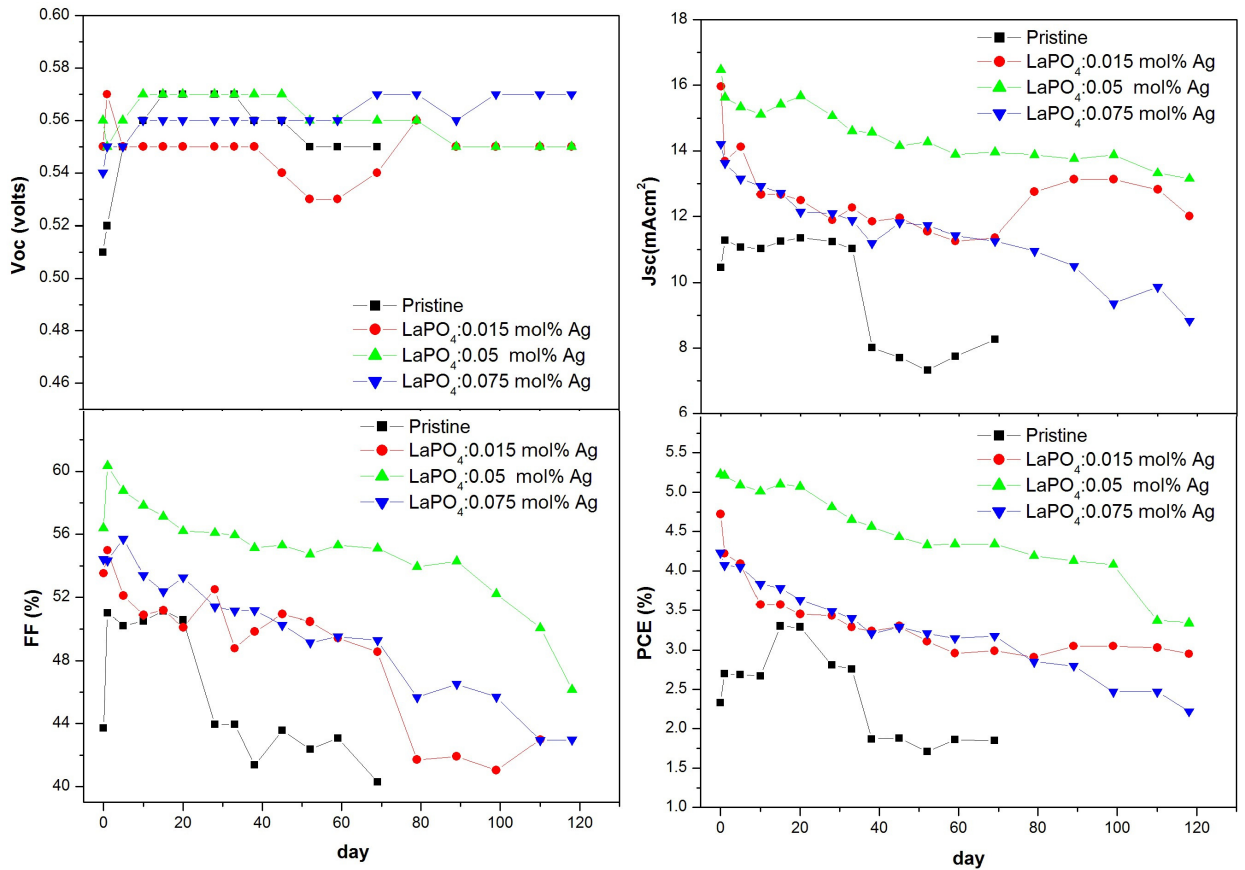


Figure 7.7: Lifetime tests for devices at various LaPO₄:Ag nano-composite loading in active layer.

7.5 Device degradation under ambient conditions

One of most important issues in organic solar cells research is device stabilities. It is one of the main factor that hinders the commercial use of polymer-based solar cells in the energy market [31, 47]. However, the inverted thin-film organic solar cells structure is a promising route to address device stability, but, the requirement for high vacuum deposition of buffer layers and electrodes is still remain a challenge. We studied here the life time of the devices by storing in an ambient environments without device encapsulation. Generally, the photovoltaic parameters decreases monotonically with time except the open circuit voltage which remains almost unaffected for much of the measurement time (see Fig 7.7). The data were taken at a regular time under 1 Sun from the devices stored in the ambient condition. The V_{oc} values determined for the devices initially increased steadily until they stabilized at a constant value on the seven days after device fabrication. Significant loss in V_{oc} has been observed after storage time between 55-60 days which is attributed very good inter-facial condition between electrodes and active layer. The PCE of the device doped with LaPO_4 :0.050 mol Ag nano-composite lasted for over 100 days while others lasted for about 80 days. The PCE of the pristine devices shows to be improving with time and reaching nearly 3.3% in the first 20 days test due to improve the crystallinity polymer in dark condition and room temperature. Subsequently, the values are decreasing monotonically with time and ceased to exist after 60 days. Generally, the all parameters for the device doped with LaPO_4 Ag nano-composite relatively stable in the test period due to the improvement of crystallinity of P3HT.

7.6 Conclusion

In the study, we have successfully synthesized silver doped lanthanum phosphate (LaPO_4 :Ag) nano-composite at varying concentration of silver using the wet chemistry method. The newly synthesized nano-composite was introduced into bulk

hete-rojunction (BHJ) P3HT:PCBM blends solar absorber with the aim to enhance photons harvesting and the charge carrier mobility in the devices. The results are clearly showed that composite doped solar absorber indeed improved optical absorption as well as the overall device performances. The best power conversion efficiency of the solar cell in this investigations was 5.23%. This growth in PCE counts over 124% compared to the pristine absorber layer device with a PCE of 2.33%. The improvement of the photo-voltaic parameters of the doped $\text{LaPO}_4\text{:Ag}$ nano-composite device is mainly attributed to the enhanced photon harvesting due to electron transitions from the ground state 4f to the different components of the excited electrons in a 5d orbital. In addition, the incorporate $\text{LaPO}_4\text{:Ag}$ into the photo-active layer enhanced the charge transport process by making more conducting compared to the P3HT:PCBM blend. The crystallinity for P3HT and near field enhancement at Ag improved charge carrier transport, increase exciton dissociation. The storage lifetime of the devices of solar cells studied under ambient environments without device encapsulation are found to be significant and lasted over four months.

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CHAPTER 8

Conclusion

Metal nano-composites have been chosen in this investigation to improve the power conversion efficiency of solution processed thin film organic solar cells. The metals under this study are known to exhibit local surface plasmon resonance (LSPR). LSPR on one hand induces strong electromagnetic field in the vicinity of the particles due to the interaction with incident photons and on the other causes scattering phenomena in the solar cell devices. Several nano-composites were employed in the duration of the study and as a consequence a number of exciting and promising research results were measured. Based on the experimental results five research articles have been reported in highly reputable international journals. Nanoparticles such as silver doped lanthanum phosphate ($\text{LaPO}_4\text{:Ag}$) and metallosulfide (CuS , NiS , Ag_2S) were successfully synthesized and employed in various layers of organic solar cell. The nano-composites were mainly incorporated in the solar absorber and the hole buffer layers of the thin-film organic solar cells. The metal nano-particles embedded into solar cells influenced the charge transport processes and hence the solar energy harvesting, which improve the power conversion efficiency (PCE) and stability of the devices.

Copper sulphide nano-particles (CuS-NPS) were used in the photoactive layer TFOSC which resulted in enhanced performance of the devices with power conversion efficiency that grew from 2.98% to 5.04%. The improvement in PCE is due to enhanced optical absorption assisted by local surface plasmon resonances exhibited by the existence of the nanoparticles. The particles are also expected to serve as scattering centres that would cause multiple light scattering in the medium. As for nickel sulphide NiS , the nanoparticles were embedded in PE-

DOT:PSS hole transport layer. We found significant improvement in the power conversion efficiency as high as 6.03% for solar cells fabricated under ambient environment. The silver sulphide nanoparticles Ag_2S (NPS) were incorporated in the photoactive layer of in an inverted organic solar cells using P3HT:PCBM blend solar absorber. Alongside improved optical and electrical properties, the device performances also improved from 2.33% to 5.15%, and were very stable environmentally. The improvements were attributed to the occurrence of surface plasmon polariton resonance (SPPR). The newly synthesized $(\text{LaPO}_4:\text{Ag})$ nanocomposite was also introduced into P3HT:PCBM blends solar absorber in an inverted structure to assist photons harvesting and the charge carrier mobility in the devices. The doped-composite solar absorber indeed demonstrated improved optical absorption and overall device performances, the best power conversion efficiency in this case was measured as high as 5.23%. All the devices in this investigation were fabricated under ambient laboratory condition without encapsulation.

The improvement in device performances are mainly attributed to the enhanced photon harvesting due to the local surface plasmon resonance, light scattering and surface plasmon polariton. Finally, the metals nanocomposite is compatible with roll-to-roll device preparation which expected to reduce the cost of solar panel in the energy market.