

**FABRICATION AND CHARACTERIZATION OF
HYBRID POLYMER SOLAR CELL**

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ABSTRACT

The easy fabrication method, tunable physical and chemical properties and cost-effective fabrication process, makes organic solar cells (OSC) very attractive in photovoltaic application. Nonetheless, the device performance is limited due to the low charge mobility of the organic semiconductors that results in a less efficient of charge transport to the respective electrodes. In order to address such problems, hybrid polymer solar cells based on bulk heterojunction (BHJ) structure, which composed of a combination of both organic and inorganic semiconductors are employed. However, the BHJ device performances are strongly dependent on good processing conditions, especially enhancement of photons absorption as well as the improvement of charge transport properties. Hence, the involved parameters and properties should be well optimized.

This dissertation describes the study of effects of blend composition and types of acceptor materials used on the optical, structural, morphological as well as the electrical properties of the three different hybrid BHJ systems. The hybrid materials consist of a blend of p-type conjugated polymer of poly(3-hexylthiophene) (P3HT) and n-type inorganic metal oxide nanoparticles, namely, zinc oxide (ZnO), titanium dioxide (TiO₂) and yttrium oxide (Y₂O₃). The optical, structural and morphological characterizations of the blend thin films using UV-Visible absorption spectroscopy, X-ray diffraction (XRD) spectroscopy, Atomic Force Microscopy (AFM) and Field-effect Scanning Electron Microscopy (FESEM) are discussed. Furthermore, the co-relation of the thin film property with the device performance is presented. The results show that the device performance has been improved by optimizing the blend composition. This is due to an enhancement in light absorption in broader wavelength regime and improved charge transport through the formation of interpenetrating bicontinuous pathway for the holes and electrons to reach the respective electrodes. These results are supported by the observation of the AFM and FESEM images of the increment in RMS roughness and formation of phase separation features in the blends. Besides, the well dispersion of inorganic nanoparticles over P3HT yields a larger interfacial area for charge carrier generation. Among the three hybrid systems investigated, P3HT:ZnO device performs the best with an optimal blend composition of 3% of ZnO nanoparticles in blend.

In order to further improve the device performances, ZnO sol-gel synthesis route has been utilized to produce a better mixing blend of P3HT and ZnO. Additionally, several approaches have been employed, namely modifying the sol content in blends, varying the annealing temperature, and inserting an additional ZnO buffer layer between the active layer and cathode. An optimal annealing treatment offers improved optical absorption properties and more uniform film surface morphology with eliminated redundant large pores and grain agglomerations. The role of the ZnO buffer layer in the blend system can be seen as an agent in facilitating the electron collection from the active layer to the cathode. The results indicate that the device efficiency has been improved by about 5 times for P3HT:ZnO sol gel device with optimized sol content (0.1ml sol), annealed at an optimized temperature of 100°C with additional ZnO buffer layer, compared to the P3HT:ZnO nanoparticles-based device.

ABSTRAK

Fabrikasi yang mudah, ciri-ciri fizikal dan kimia bolehlaras dan kos efektif proses fabrikasi, telah menyebabkan sel suria organik (OSC) amat menarik dalam bidang penggunaan fotovoltaiik. Walau bagaimanapun, prestasi peranti menjadi terbatas disebabkan oleh kelincahan pembawa cas yang rendah bagi semikonduktor organik yang mengakibatkan angkutan cas ke elektrod menjadi kurang cekap. Dalam usaha untuk menangani masalah tersebut, sel suria polimer hibrid berasaskan struktur simpang-hetero pukal (BHJ) yang terdiri daripada kombinasi semikonduktor organik dan bukan organik telah digunapakai. Namun demikian, prestasi peranti amat bergantung kepada keadaan pemprosesan yang baik, terutamanya peningkatan serapan foton serta penambah-baikkan sifat angkutan. Oleh yang demikian, parameter dan sifat yang terlibat perlu dioptimumkan dengan sebaiknya.

Disertasi ini menerangkan kesan komposisi campuran dan jenis bahan penerima yang digunakan terhadap ciri-ciri optik, struktur, morfologi serta sifat elektrik bagi tiga sistem hybrid BHJ berbeza. Bahan hybrid terdiri daripada campuran bahan jenis-p polimer berkonjugat (3-hexylthiophene) (P3HT) dan bahan jenis-n nanopartikel oksida logam bukan organik, iaitu zink oksida (ZnO), titanium dioksida (TiO₂) dan yttrium oksida (Y₂O₃). Pencirian optik, struktur dan morfologi dibincangkan bagi filem nipis campuran yang menggunakan spektroskopi serapan ultraungu-cahaya-nampak (UV-Vis), spektroskopi belauan sinar-X (XRD), mikroskop daya atom (AFM) dan mikroskop electron daya imbasan (FESEM). Malahan, hubung-kait antara sifat filem nipis dengan prestasi peranti juga dibentangkan. Dapatan kajian menunjukkan bahawa prestasi peranti telah ditingkatkan dengan mengoptimumkan komposisi campuran. Ini disebabkan oleh peningkatan dalam penyerapan cahaya di rantau gelombang yang lebih luas dan meningkatnya angkutan cas melalui pembentukan laluan dwi-berterusan saling-menyusup untuk pergerakan lohong dan electron sampai ke elektrod. Hasil ini disokong oleh pemerhatian terhadap imej AFM and FESEM yang mana terdapat kenaikan dalam nilai kekasaran RMS dan pembentukan pemisahan fasa dalam filem campuran. Selain itu, penyerakan nanopartikel bukan organik yang seragam dalam P3HT menghasilkan kawasan sempadan antara-fasa yang lebih luas untuk menjana pembawa cas. Antara tiga jenis sistem hybrid yang dikaji, peranti P3HT:ZnO memberikan prestasi terbaik dengan 3% nanopartikel ZnO ke dalam komposisi campuran optimum.

Selanjutnya, sintesis sol-jel ZnO telah dijalankan bagi menghasilkan suatu campuran P3HT and ZnO yang lebih baik. Tambahan pula, beberapa pendekatan telah diambil, iaitu dengan mengubah isi kandungan sol dalam campuran, mempelbagaikan suhu pemanasan, dan memasukkan satu lapisan penampam ZnO di antara lapisan aktif dan katod. Rawatan pemanasan yang optimum menawarkan ciri-ciri penyerapan optik yang lebih baik dan permukaan morfologi filem yang lebih seragam dengan menghapuskan liang dan gumpalan besar. Peranan lapisan penampam ZnO dalam sistem campuran tersebut boleh dilihat sebagai suatu ejen yang memudahkan kutipan elektron dari lapisan aktif ke katod. Dapatan kajian ini menunjukkan bahawa prestasi bagi peranti berasaskan P3HT:sol-jel ZnO yang disediakan pada komposisi campuran (0.1 ml sol) dan suhu pemanasan optimum pada 100°C dan mengandungi satu lapisan penampam ZnO, telah meningkat sebanyak 5 kali ganda berbanding dengan peranti berasaskan P3HT:nanopartikel ZnO.

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RESEARCH PAPERS AND CONFERENCES

A. Published Full Papers (ISI-cited)

1. Yusli, M. N., Toong, W. Y., & Sulaiman, K. (2009). Solvent Effect on the thin film formation of polymeric solar cells. *Material Letters*, 63(30), 2691-2694.
2. Toong, W. Y., & Sulaiman, K. (2011). Fabrication and morphological characterization of hybrid polymeric solar cells based on P3HT and inorganic nanocrystal blends. *Sains Malaysiana*, 40(1), 43-47.

B. Conference Papers (Non-ISI cited)

1. Sulaiman, K., & Toong, W. Y., "Studies of optical and morphological properties on the ZnPc/Ga₃ mixture thin films". Paper presented at 24th Regional Conference on Solid State Science & Technology (RCSSST 2008) in Port Dickson, Malaysia.
2. Toong, W. Y., & Sulaiman, K., "Fabrication and morphological characterization of hybrid polymeric solar cells based on P3HT and inorganic nanocrystal blends". Paper presented at National Physics Conference (PERFIK 2009) in Malacca, Malaysia.
3. Toong, W. Y., & Sulaiman, K., "The fabrication and properties characterization of hybrid polymeric solar cells based on conjugated polymer/inorganic nanoparticles". Paper presented at 3rd International Conference on Functional Materials and Devices (ICFMD 2010) in Kuala Terengganu, Malaysia.
4. Toong, W. Y., & Sulaiman, K., "The fabrication and properties characterization of hybrid solar cells based on conjugated polymer/inorganic compound". Paper presented at 5th International Conference on Technological Advances of Thin Films & Surface Coatings (Thin films and COMPO 2010) in Harbin, China.

TABLE OF CONTENTS

TABLE OF CONTENTS.....	vii
LIST OF FIGURES.....	xi
LIST OF TABLES.....	xviii
LIST OF SYMBOLS.....	xx
LIST OF ABBREVIATIONS.....	xxi
CHAPTER 1: INTRODUCTION.....	1
1.1 Background of the Research Studies.....	1
1.2 History of Organic Solar Cells (OSCs).....	3
1.3 The Reasons of Investigation on Hybrid Polymer Solar Cells.....	6
1.4 Research Objectives.....	9
1.5 Dissertation Outline.....	10
CHAPTER 2: THEORETICAL BACKGROUND.....	12
2.1 Overview.....	12
2.2 Conjugated Polymers.....	12
2.3 Charge Transport Characteristics of Conjugated Polymers.....	16
2.4 Electronic Properties of Conjugated Polymers.....	17
2.5 Doping.....	20
2.6 Optical Properties of Conjugated Polymers.....	22
2.7 Donor Material.....	24
2.7.1 Poly(thiophene).....	24
I) Regioregularity.....	25
II) Solubility.....	25
III) Regioregular Poly (3-hexylthiophene) (P3HT).....	26
2.8 Acceptor Material.....	27
2.8.1 Inorganic Nanoparticles.....	27
2.8.2 Physical Properties of Inorganic Nanoparticles.....	29
I) Optical Properties.....	29
II) Structural and Morphological Properties.....	30
III) Electrical Properties.....	30
2.8.3. Types of Inorganic Nanoparticles Used in This Research Work.....	31
I) Zinc Oxide.....	31
II) Titanium Dioxide.....	32
III) Yttrium Oxide.....	33

2.9 Sol-Gel Synthesis Route.....	34
2.10 Hybrid Polymer Solar Cells.....	35
2.10.1 Basic Working Principles of Hybrid Solar Cells.....	37
2.10.2 Key Parameters of the Hybrid Solar Cells.....	38
2.10.3 Types of Device Architectures for Organic Solar Cells.....	40
I) Single Layer Organic Solar Cell.....	40
II) Bilayer Solar Cell.....	41
III) Bulk Heteronjunction (BHJ) Solar Cell.....	42
CHAPTER 3: EXPERIMENTAL METHODOLOGY.....	44
3.1 Overview.....	44
3.2 Chemicals and Materials.....	44
3.2.1. Chemicals and Solutions Preparation.....	45
I) P3HT:As-Purchased Inorganic Nanoparticles Blends.....	45
II) P3HT:As-Synthesized Sol-gel ZnO Blend Solutions.....	46
3.2.2 Substrates and Electrodes Preparation.....	48
3.2.3 Substrates Patterning and Cleaning.....	48
3.3 Thin Films Preparation via Spin Coating Technique.....	50
3.3.1 P3HT:ZnO Sol-Gel Film Preparation via Thermal Annealing Treatment.....	52
3.4 Devices Fabrication.....	53
3.4.1 Single Layer and Bulk Heterojunction (BHJ) Structures.....	53
3.4.2 Aluminum (Al) Electrodes Deposition via Thermal Evaporation.....	54
3.5 Characterization Techniques.....	57
3.5.1 Ultraviolet-Visible-Near Infrared (UV-VIS-NIR) Spectrophotometer...	57
3.5.2 X-ray Diffraction (XRD) Technique.....	60
3.5.3 Atomic Force Microscopy (AFM).....	64
3.5.4 Field-Emission Scanning Electron Microscopy (FESEM).....	66
3.5.5 Surface Profilometer.....	69
3.5.6 Photovoltaic (PV) Measurement.....	71
CHAPTER 4: CHARACTERIZATION OF P3HT:ZNO HYBRID THIN FILMS AND SOLAR CELL DEVICES.....	74
4.1 Overview.....	74
4.2 Optical Characterization: Ultraviolet-Visible-Near Infrared (UV-Vis-NIR) Spectra Analysis.....	74
4.3 Structural Characterization: X-ray Diffraction (XRD) Spectra Analysis.....	84

4.4 Morphological Characterization: Atomic Force Microscopy (AFM) and Field Emission Scanning Electron Microscopy (FESEM) Analysis.....	89
4.4.1 AFM Characterization.....	99
4.4.2 FESEM Imaging.....	102
4.5 Electrical Characterization: Current Density-Voltage (J-V) Curve Analysis.	
CHAPTER 5: HYBRID SOLAR CELLS BASED ON INORGANIC NANOPARTICLES AND P3HT:ZNO ACTIVE LAYERS PREPARED BY SOL-GEL SYNTHESIS ROUTE.....	111
5.1 Overview.....	111
5.2 Part I: Investigation of Hybrid Solar Cells Based on Various Inorganic Nanoparticles.....	111
5.2.1. Results on P3HT:TiO ₂ Blend Films and Their Based Solar Cell Devices.....	111
A. Optical Characterization.....	111
B. Structural Characterization.....	113
C. Morphological Characterization.....	115
D. Electrical Characterization.....	117
5.2.2. Results on P3HT:Y ₂ O ₃ Blend Films and Solar Cell Devices.....	119
A. Optical Characterization.....	119
B. Structural Characterization.....	120
C. Morphological Characterization.....	122
D. Electrical Characterization.....	124
5.2.3 Comparison of Hybrid Systems Based on Three Different Types of Inorganic Metal Oxide Nanoparticles.....	126
A. Optical Characterization.....	126
B. Structural Characterization.....	128
C. Morphological Characterization.....	129
D. Electrical Characterization.....	133
5.3 Part II: The Improvement of P3HT:ZnO Devices by Sol-gel Synthesis Route.....	136
5.3.1 First Approach: Effects of Different Sol Content.....	137
A. Optical Characterization.....	137
B. Structural Characterization.....	140
C. Morphological Characterization.....	144

D. Electrical Characterization.....	149
5.3.2 Second Approach: Effects of Different Annealing Temperature.....	152
A. Optical Characterization.....	152
B. Morphological Characterization.....	154
C. Electrical Characterization.....	156
5.3.3 Third Approach: Effects of Additional ZnO Buffer Layer.....	158
A. Morphological Characterization.....	158
B. Electrical Characterization.....	160
CHAPTER 6: CONCLUSIONS AND FUTURE WORKS.....	163
6.1 Conclusions.....	163
6.2 Future Works.....	168

LIST OF FIGURES

	Page
Figure 1.01: Block diagram of research methodology used in this study.....	11
Figure 2.01: The examples of 1) non-conjugated polymers: (i) Polypropylene, (ii) Poly(vinyl alcohol); 2) conjugated polymers: (i) Polyacetylene, (ii) Polythiophene (Skotheim, et al., 1998).....	14
Figure 2.02: (a) The structure of ethylene comprises of σ bonds which formed from the three sp^2 -hybridized orbitals on each carbon atom. (b) The formation of π bond due to the overlap of the unhybridized p_z orbital. (c) A cutaway view of the whole σ and π system within the ethylene molecule (Hari Singh Nalwa, 2002).....	15
Figure 2.03: The schematic diagram of HOMO and LUMO bands.....	15
Figure 2.04: Schematic representation of intrachain charge diffusion (left) and interchain charge diffusion (right) in polyacetylene.....	16
Figure 2.05: Potential energy as a function of bond length alternation for the two categories of conjugated polymers are exhibited for (a) a degenerate ground state conjugated polymer, <i>trans</i> -polyacetylene; (b) a non-degenerate ground state conjugated polymer (in the given example is poly-para-phenylene (PPP)).....	18
Figure 2.06: Schematic structure and energy diagram for solitons in conjugated polymer is shown.....	19
Figure 2.07: Schematic structure and band diagrams for excitations in non-degenerate ground state conjugated polymers. Allowed optical transitions are exhibited by the blue-colored dashed arrows.....	20
Figure 2.08: Removal of two electrons (p-type doping) from a polyacetylene chain produces two radical cations. The combination of both radicals forms a spinless di-cation.....	21
Figure 2.09: Removal of two electrons (p-type doping) from a polythiophene chain produces bipolaron. Bipolaron moves as a unit up and down the polymer chain, which is responsible to the electrical properties of conjugated polymers.....	22
Figure 2.10: A coplanar π -orbitals polythiophene (top); a twisted substituted polythiophene (bottom) (Skotheim, et al., 1998).....	23
Figure 2.11: The chemical structure of monomer repeating unit of PTs.....	24
Figure 2.12: The differences between regiorandom and regioregular PTs in aspect of chain structure and charge transport characteristics.....	25

Figure 2.13:	The chemical structure of P3HT.....	27
Figure 2.14:	The structures and shapes of the inorganic nanoparticles that are widely used in hybrid polymer solar cells.....	29
Figure 2.15:	Energy dispersion for the (a) bulk semiconductor compared with that of (b) the nanoparticles (Dhlamini, et al., 2008).....	31
Figure 2.16:	The chemical structure of ZnO.....	32
Figure 2.17:	The chemical structure of TiO ₂	33
Figure 2.18:	The chemical structure of Y ₂ O ₃	34
Figure 2.19:	Schematic structure of hybrid solar cell.....	36
Figure 2.20:	The working principle of hybrid polymer solar cell consisting of an electron donor and acceptor pair.....	38
Figure 2.21:	The current density-voltage curve (J-V curve) of a hybrid solar cell under illuminated condition (dash line).....	39
Figure 2.22:	(a) The basic structure of a single layer solar cell. (b) Schematic of a single layer solar cell with a Schottky contact at the lower function electrode B contact. Photogenerated excitons can only be dissociated within a narrow depletion layer, and thus the device is exciton diffusion limited.....	41
Figure 2.23:	The basic structure of a bilayer solar cell. (b) Schematic of a bilayer heterojunction solar cell. The donor (D) contacts the higher work function electrode A and the acceptor (A) contacts the lower work function electrode B, in order to achieve charge carrier collection, respectively. Excitons can only be dissociated within the region at the D/A interface.....	42
Figure 2.24:	(a) The basic structure of a bulk heterojunction solar cell. (b) Schematic of a bulk heterojunction solar cell device. The excitons can be dissociated throughout the volume of material as the D is well blended with A.....	43
Figure 3.01:	Pristine solutions and the P3HT:inorganic nanoparticles blend solutions.....	46
Figure 3.02:	P3HT:sol-gel ZnO blend solutions.....	47
Figure 3.03:	ITO substrates patterning.....	49
Figure 3.04:	The spin coating machine which is used for thin films deposition.....	51

Figure 3.05:	Schematic representation of the spin coating technique.....	51
Figure 3.06:	The flow chart for the preparation of the P3HT:sol-gel ZnO films.....	52
Figure 3.07:	The device construction of solar cells based on different devices geometry and hybrid systems.....	54
Figure 3.08:	Thermal evaporation system for Al electrode deposition. The inset shows the designed shadow mask used in this work.....	55
Figure 3.09:	The schematic diagram of the evaporation system arrangement within the vacuum chamber.....	55
Figure 3.10:	Possible electronic transitions of π , σ or n electrons.....	58
Figure 3.11:	Photograph of Jasco V-570 UV-VIS-NIR Spectrophotometer.....	59
Figure 3.12:	Schematic diagram of the components of a UV-VIS-NIR spectrophotometer.....	60
Figure 3.13:	The diffraction pattern of X-rays by planes of atoms.....	61
Figure 3.14:	(a) Photograph of the XRD instrument (Bruker AXS). (b) The basic components of a X-ray diffractometer.....	62
Figure 3.15:	Schematic diagram of an atomic force microscope.....	64
Figure 3.16:	Photograph of Veeco Dimension 3000 AFM instrument.....	66
Figure 3.17:	Field-emission scanning electron microscope (FESEM).....	67
Figure 3.18:	Principle features of a SEM instrument.....	68
Figure 3.19:	(a) The schematic diagram of a contact profilometer. (b) Resultant surface profile that is generated based on the tip deflection.....	70
Figure 3.20:	KLA Tensor P-6 surface profilometer for film thickness measurement.....	70
Figure 3.21:	(a) An Oriel 67005 solar simulator. (b) The internal structure of the Oriel solar simulator.....	72
Figure 3.22:	(a) A Keithley 236 SMU instrument. (b) A solar cell device connected to its appropriate terminals under I-V measurement....	73
Figure 4.01:	Absorption coefficient of pristine P3HT, ZnO and P3HT:ZnO blend films with different contents of ZnO nanoparticles. The inset shows the variation of maximum absorption coefficient peak values, α_{\max} and film thickness, t as a function of blend composition.....	74

Figure 4.02:	The pre-estimated E_g of the pristine (a) P3HT film and (b) ZnO nanoparticles film using plots of $d\ln(\alpha hv)/dhv$ versus hv	79
Figure 4.03:	Plots of $\ln(\alpha hv)$ versus $\ln(hv - E_g)$ to determine the n value for (a) P3HT and (b) ZnO nanoparticles films, respectively.....	80
Figure 4.04:	Plots of $(\alpha hv)^2$ against hv for (a) P3HT and (b) ZnO films.....	81
Figure 4.05:	The typical energy band diagram of (a) P3HT and (b) ZnO nanoparticles films where the conduction band of ZnO is tunable due to the variation in nanoparticles size.....	82
Figure 4.06:	Plots of $d\ln(\alpha hv)/dhv$ versus hv to pre-estimate the E_g of the P3HT:ZnO blend films with different contents of ZnO.....	83
Figure 4.07:	Plots of $(\alpha hv)^2$ against hv for P3HT:ZnO blend films with different contents of ZnO.....	84
Figure 4.08:	The XRD pattern of ZnO nanoparticles in powder form.....	85
Figure 4.09:	Williamson-Hall plots to determine the microstrain of ZnO.....	87
Figure 4.10:	The XRD spectra of pristine P3HT and P3HT:ZnO blend films. The inset illustrates the orientation of P3HT crystallites with respect to the substrate.....	87
Figure 4.11:	Three-dimensional AFM images by $10 \times 10 \mu m^2$ scan for (a) pristine P3HT and the blend films in different compositions with (b) 1%, (c) 2%, (d) 3%, (e) 4%, (f) 5%, and (g) 10% ZnO.....	93
Figure 4.12:	2-dimensional AFM images of the (a) pristine P3HT and its blends with (b) 1%, (c) 2%, (d) 3%, (e) 4%, (f) 5%, and (g) 10% ZnO.....	97
Figure 4.13:	The schematic illustration of some possible morphologies that most likely have been achieved for the P3HT:ZnO blends incorporated with different amount of ZnO contents.....	99
Figure 4.14:	FESEM images of (a) P3HT and its blends with (b) 1%, (c) 3%, (d) 5% and (e) 10% ZnO ((e(ii) shows the focused zone area of image (e))......	101
Figure 4.15:	The FESEM images of pristine ZnO nanoparticles film.....	101
Figure 4.16:	The current density–voltage (J-V) characteristics of solar cell devices based on pristine P3HT and P3HT:ZnO blends in different blend compositions under dark condition.....	102
Figure 4.17:	Current density-voltage (J-V) characteristic curves of the solar cell devices under light illumination. The inset displays an equivalent circuit diagram of solar cells which consists of series	

	resistance, R_s and shunt resistance, R_{sh}	103
Figure 4.18:	The schematic energy band diagram of ITO/PEDOT:PSS/P3HT:ZnO/Al devices.....	105
Figure 4.19:	The variation of (i) J_{sc} and V_{oc} , (ii) FF and η with the blend composition.....	106
Figure 4.20:	The variation of R_{sh} and R_s with the blend composition.....	109
Figure 5.01:	Absorption coefficient of P3HT:TiO ₂ blend films with different contents of TiO ₂ nanoparticles. The inset shows the variation of maximum absorption coefficient peak values, α_{max} and film thickness, t as a function of TiO ₂ contents.....	112
Figure 5.02:	The XRD patterns of (i) TiO ₂ in powder form; (ii) pristine P3HT and P3HT:TiO ₂ blend films.....	113
Figure 5.03:	AFM images in 2D and 3D views for (a) pristine P3HT and P3HT:TiO ₂ blend films with (b) 1%, (c) 2%, (d) 3%, (e) 4%, (f) 5%, and (g) 10% TiO ₂	116
Figure 5.04:	The J-V plots for P3HT:TiO ₂ solar cells with different blend compositions under light illumination.....	117
Figure 5.05:	Variations in the device parameters for (i) J_{sc} and V_{oc} , (ii) R_s and R_{sh} , (iii) FF and η as a function of blend composition.....	118
Figure 5.06:	The optical spectra for the P3HT:Y ₂ O ₃ blend films. The inset indicates the variation of α_{max} and film thickness as a function of Y ₂ O ₃ content in P3HT:Y ₂ O ₃ blends.....	119
Figure 5.07:	The XRD spectra of (i) Y ₂ O ₃ nanopowder; (ii) P3HT:Y ₂ O ₃ blend films.....	120
Figure 5.08:	The AFM images for (a) pristine P3HT and the blend films with (b) 1%, (c) 2%, (d) 3%, (e) 4%, (f) 5%, and (g) 10% Y ₂ O ₃	123
Figure 5.09:	The J-V plots for pristine P3HT and P3HT:Y ₂ O ₃ blend devices....	124
Figure 5.10:	Variations in the device parameters for (i) J_{sc} and V_{oc} , (ii) R_s and R_{sh} , (iii) FF and η as a function of blend composition.....	125
Figure 5.11:	(i) Plots of $(\alpha hv)^2$ against hv for ZnO, TiO ₂ and Y ₂ O ₃ films, the inset shows the plots of $\ln(\alpha hv)$ versus $\ln(hv - E_g)$ to determine the type of electronic transition for the nanoparticles. (ii) Absorption coefficient spectra of the P3HT:nanoparticles blends; the inset shows the estimated E_g of the blends.....	126
Figure 5.12:	The XRD spectra of P3HT:nanoparticles blend films.....	128

Figure 5.13:	The AFM images of P3HT:nanoparticles blend films in 3D and 2D views for (i) P3HT:ZnO, (ii) P3HT:TiO ₂ , and (iii) P3HT:Y ₂ O ₃ film.....	129
Figure 5.14:	FESEM images of the (a) pristine inorganic metal oxide nanoparticles, and (b) P3HT:nanoparticles blend films with ZnO (I), TiO ₂ (II) and Y ₂ O ₃ (III).....	131
Figure 5.15:	Comparison of the J-V characteristics of the solar cells based on three different types of P3HT:metal oxide nanoparticles hybrid systems under white light illumination.....	133
Figure 5.16:	An inferred schematic energy band diagram for the P3HT:inorganic nanoparticles hybrid systems, placed between anode ITO and cathode Al.....	135
Figure 5.17:	Absorption coefficient spectra of pristine P3HT, sol-gel derived ZnO and P3HT:sol gel ZnO blend films with different sol contents. The inset indicates the variation of α_{\max} and film thickness as a function of sol content. Also, the comparison between P3HT:ZnO NPs and P3HT:sol-gel ZnO films is shown.....	137
Figure 5.18:	The plots of $(\alpha h\nu)^2$ against $h\nu$ for P3HT:sol gel ZnO blend films with different sol contents.....	138
Figure 5.19:	The XRD patterns of P3HT:sol-gel ZnO blend films with different sol contents as well as XRD patterns of bared ZnO NPs deposited film and sol-gel derived ZnO films.....	140
Figure 5.20:	XRD parameters of blend films as a function of different sol contents, namely: (i) FWHM, (ii) crystallite size and (iii) dislocation density corresponding to (100), (002), and (110) planes.....	141
Figure 5.21:	The AFM images of P3HT:sol-gel ZnO blend films with (a) 0.05 ml, (b) 0.1 ml, (c) 0.2 ml, and (d) 0.3 ml sol content.....	144
Figure 5.22:	AFM images by $10 \times 10 \mu\text{m}^2$ scan in both 2D and 3D views of (i) P3HT:ZnO NPs and (ii) P3HT:sol gel ZnO blend films.....	144
Figure 5.23:	The FESEM images of P3HT:sol-gel ZnO films with (a) 0.05 ml, (b) 0.1 ml, (c) 0.2 ml, and (d) 0.3 ml sol.....	144
Figure 5.24:	The comparison of FESEM images between (i) P3HT:ZnO NPs film and (ii) P3HT:sol-gel ZnO film. The inset shows the surface micrograph of (i) bare ZnO NPs film and (ii) bare sol-gel derived ZnO film.....	147
Figure 5.25:	The J-V plots for P3HT:sol-gel ZnO solar cells with different sol contents in blends.....	147

Figure 5.26:	Variations in the device parameters for (i) J_{sc} and V_{oc} , (ii) R_s and R_{sh} , (iii) FF and η as a function of sol content in blends.....	149
Figure 5.27:	Photovoltaic comparison for P3HT:sol gel ZnO and P3HT:ZnO NPs films.....	151
Figure 5.28:	The optical spectra of P3HT:sol-gel ZnO films annealed at different temperatures, T_a . The inset indicates the variation of α_{max} and film thickness as a function of T_a	153
Figure 5.29:	The plots of $(\alpha hv)^2$ against $h\nu$ for P3HT:sol gel ZnO blend films annealed at different T_a	153
Figure 5.30:	The AFM images in 2D and 3D of P3HT:sol gel ZnO films annealed at different T_a of (a) 75 °C, (b) 100 °C, (c) 150 °C, (d) 175 °C.....	155
Figure 5.31:	The J-V plots for P3HT:sol gel ZnO solar cells fabricated from active layers annealed at different T_a	156
Figure 5.32:	Variation in the device parameters for (i) J_{sc} and V_{oc} , (ii) R_s and R_{sh} , (iii) FF and η as a function of annealing temperature.....	157
Figure 5.33:	Morphological characteristics of the P3HT:sol-gel ZnO film (i) without and (ii) with an additional ZnO buffer layer (BL) via AFM imaging.....	159
Figure 5.34:	The comparison of the J-V characteristics of the solar cell devices without and with an additional ZnO buffer layer.....	160

LIST OF TABLES

	Page
Table 1.1:	A list of development in the organic solar cells..... 5
Table 3.1:	Blend compositions and the respectively masses of P3HT:inorganic nanoparticles blends..... 45
Table 3.2:	Blend compositions of P3HT:sol-gel ZnO..... 47
Table 3.3:	The deposition parameters of Al electrodes..... 56
Table 3.4:	Parameters of UV-VIS-NIR spectrum..... 60
Table 3.5:	Scanning parameters of XRD measurement..... 63
Table 3.6:	Parameters of the AFM measurement..... 66
Table 3.7:	Scanning parameters of film thickness measurement..... 71
Table 4.1:	The comparison of the absorption coefficient peak values and the corresponding wavelength positions for pristine P3HT and P3HT:ZnO blends..... 76
Table 4.2:	The values of average thickness for pristine P3HT, ZnO and P3HT:ZnO blend films..... 76
Table 4.3:	The values of E_g for pristine P3HT, ZnO and P3HT:ZnO blend films based on two different types of functions, in which the later one gives a more precise estimation value of E_g 84
Table 4.4:	Summary of the XRD properties of the P3HT:ZnO nanoparticles blend films with different ZnO content..... 89
Table 4.5:	The mean surface roughness and root-mean-square roughness of the films obtained from AFM for Figure 4.11..... 94
Table 4.6:	The comparison of device characteristics parameters for pristine P3HT and P3HT:ZnO solar cells with different ZnO concentration..... 104
Table 4.7:	The variation of R_{sh} and R_s with the blend composition..... 109
Table 5.1:	Summaries of the α_{max} values together with the corresponding wavelength positions, λ , film thickness, t and estimated E_g for pristine P3HT and P3HT:TiO ₂ blends..... 112
Table 5.2:	Summaries of the Bragg diffraction angles and film roughnesses (obtained from AFM images) of pristine P3HT and P3HT:TiO ₂ blends..... 113
Table 5.3:	The comparison of device characteristics parameters for P3HT:TiO ₂ solar cells..... 117

Table 5.4:	Summaries of the α_{\max} values together with the corresponding wavelength positions, λ , film thickness, t and estimated E_g for pristine P3HT and P3HT:Y ₂ O ₃ blends.....	119
Table 5.5:	Summaries of the Bragg diffraction angles and film roughnesses of pristine P3HT and P3HT:Y ₂ O ₃ blends.....	121
Table 5.6:	The comparison of device characteristics parameters for P3HT and P3HT:Y ₂ O ₃ solar cells.....	124
Table 5.7:	Variation in the J-V characteristics of P3HT: metal oxide nanoparticles hybrid solar cells.....	133
Table 5.8:	The comparison of α_{\max} values, the corresponding wavelength positions, average film thicknesses and estimated E_g for P3HT:sol gel ZnO blends with different sol contents.....	139
Table 5.9 (i) & (ii):	Summaries of the XRD parameters of P3HT:sol gel ZnO blend films with different sol contents.....	140
Table 5.10:	Surface roughness values of the blend films obtained from AFM.....	145
Table 5.11:	The comparison of device characteristics parameters for P3HT:sol-gel ZnO solar cells.....	149
Table 5.12:	The comparison of the α_{\max} values, the corresponding wavelength positions, average film thicknesses and estimated E_g for the P3HT:sol gel ZnO films annealed at different T_a	153
Table 5.13:	Surface roughness values of P3HT:sol gel ZnO films annealed at different T_a	156
Table 5.14:	The comparison of device characteristics parameters for P3HT:sol gel ZnO solar cells.....	156
Table 5.15:	Surface roughness values of the films obtained from AFM.....	160
Table 5.16:	Device characteristics parameters of P3HT:sol gel ZnO solar cells with ZnO buffer layer spun at different spin speed.....	160
Table 5.17:	Device characteristics parameters of P3HT:sol gel ZnO solar cells.....	161

LIST OF SYMBOLS

$>$	Less than
$<$	More than
π	Pi
σ	Sigma
T	Transmittance
A	Absorbance
I_0	Light intensities
E	Energy
λ	Wavelength
d	Interatomic spacing distance
θ	Diffraction angle
E_g	Energy gap
Δr	Bond length alternation
I_{SC}	Short-circuit current
V_{OC}	Open circuit voltage
P_{max}	Maximum power
P_{out}	Output power
V_{max}	Voltage at maximum power
I_{max}	Current at maximum power
P_{in}	Input power
FF	Fill factor
η	Power conversion efficiency
α	Absorption coefficient
t	Film thickness
B	Full width at half maximum
t_c	Crystallite size
C	Scherrer constant
ε	Strain
Λ_E	Exciton diffusion length
D_E	Exciton diffusion coefficient
τ_E	Exciton lifetime
R_a	Mean surface roughness
V_{on}	Turn-on voltage
J_{sc}	Short-circuit current density
R_{sh}	Shunt resistance
R_s	Series resistance
D/A	Donor/Acceptor
J-V	Current density-voltage
δ	Dislocation density
T_a	Annealing temperature

LISTS OF ABBREVIATIONS

BHJ	Bulk heterojunction
1-D	One dimensional
AFM	Atomic force microscopy
Ag	Silver
Al	Aluminum
AM 1.5	Air mass 1.5
Au	Gold
BL	Buffer layer
C ₆₀	Buckminsterfullerene
Ca	Calcium
CB	Conduction band
CdSe	Cadmium selenide
CHCl ₃	Chloroform
Cu	Copper
DEA	Diethanolamine
EDX	X-ray spectroscopy
FESEM	Field-effect scanning electron microscopy
FWHM	Full width at half maximum
HCl	Hydrochloric acid
HE	High energy
HOMO	Highest occupied molecular orbital
ITO	Indium tin oxide
JCPDS	Joint committee on powder diffraction standards
LE	Low energy
LUMO	Lowest unoccupied molecular orbital
MEH-PPV	Poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene]
MgPh	Magnesium phthalocyanine
NPs	Nanoparticles
OSCs	Organic solar cells
P3HT	Poly(3-hexylthiophene)
PbS	Plumbum sulfide
PCBM.	[6,6]-phenyl-C ₆₁ -butyric acid methyl ester
PCE	Power conversion efficiency
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)
PPP	Poly-para-phenylene
PT	Poly(thiophene)
PV	Photovoltaic
RMS	Root-mean-square
rpm	Rotations per minute
SMU	Source measuring unit
STC	Standard test condition
TiO ₂	Titanium dioxide
UV-VIS-NIR	Ultraviolet-visible-near-infrared
VB	valence band
XRD	X-ray diffraction
ZnO	Zinc oxide

