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APPLICATION OF METAL OXIDE MICROSTRUCTURES IN ORGANIC PHOTOVOLTAICS

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Table of contents

Acknowledgments.....	i
Table of contents.....	ii
Summary	vi
List of Figures	viii
List of Tables	xv
Common Abbreviations	xviii
 Chapter 1: Introduction.....	 1
1.1 Necessity for solar energy harvesting.....	1
1.2 Lure of organic photovoltaics.....	5
1.3 Scope and organization of the thesis.....	8
 Chapter 2: Background.....	 11
2.1 Organic photovoltaics (OPV) through the years.....	11
2.1.1 Bilayer OPV devices.....	12
2.1.2 Bulk heterojunction OPV devices.....	14
2.1.3 Advances in OPV materials and architecture.....	16
2.2 Operation of organic photovoltaics.....	17
2.3 Regular vs. inverted OPV.....	22
2.4 Metal oxides in OPV.....	24
2.4.1 Hole transport layers.....	26
2.4.2 Electron selective layers.....	26
2.5 Nanostructures in OPV.....	27

Chapter 3: Porous zinc oxide in electron selective layer of inverted organic photovoltaic devices.....	31
3.1 Introduction	31
3.2 Experiments.....	34
3.2.1 ZnO sol-gel preparation	34
3.2.2 OPV device fabrication	37
3.2.3 OPV device characterization	39
3.3 Results and discussion	41
3.3.1 Device structures	41
3.3.2 Effect of annealing temperature of porous ZnO layer	42
3.3.3 Impact of spinning speed of active layer.....	44
3.3.4 Effect of PEG concentration.....	48
3.3.5 Haze factor studies on porous ZnO layer.....	57
3.4. Summary.....	63

Chapter 4: Doped porous zinc oxide in electron selective layer of inverted organic photovoltaic devices.....	64
4.1 Introduction	64
4.2 Porous indium-doped ZnO (IZO) electron selective layer for OPV	67
4.2.1 IZO sol-gel preparation	67
4.2.2 IZO OPV device fabrication	70
4.2.3 Results and discussion.....	71
4.3 Porous aluminum-doped ZnO (AZO) electron selective layer for OPV.....	81
4.3.1 AZO sol-gel preparation	81

4.3.2 AZO OPV device fabrication	83
4.3.3 Results and discussion.....	84
4.4 Comparison between IZO and AZO porous ZnO electron selective layer for inverted OPV devices.....	89
4.5 Summary.....	94
Chapter 5: Zinc oxide photonic crystal in electron selective layer of inverted organic photovoltaics.....	95
5.1 Introduction	95
5.2 Experiments.....	99
5.2.1 Photonic crystal structure formation.....	99
5.2.2 OPV device fabrication	102
5.3 Results and Discussion	103
5.3.1 Effect of annealing on ZnO photonic crystal formation.....	103
5.3.2 Effect of the underlying ZnO layer thickness.....	109
5.3.3 Effect of spinning speed of the active layer.....	112
5.4 Numerical simulation studies.....	120
5.5 Summary.....	128
Chapter 6: Conclusion and future direction.....	129
6.1 Concluding remarks	129
6.2 Future work.....	131
6.2.1 Porous structures in OPV.....	131
6.2.2 Photonic crystals in OPV.....	132

List of publications.....	134
Bibliography.....	135

Summary

With the emerging issues of climate change and depleting fossil fuel energy, solar cells are gaining widespread interest in both research labs and industry. Most of today's commercially available solar cells, are however, based on inorganic materials, mainly silicon. Organic photovoltaic (OPVs), though lagging behind its inorganic counterpart in efficiency, has the potential for low cost, ease of fabrication and compatibility with flexible substrates to its advantage. The inverted OPV, with high work function metal electrode and exclusion of the acidic PEDOT:PSS (poly (3,4-ethylene dioxythiophene):(polystyrene sulfonic acid)) interlayer, is the preferred architecture because of its improved air stability and lifetime and enhanced device performance. A number of options such as novel structures and substrates, low bandgap polymers and mixed metal oxides are being currently explored to improve the power conversion efficiency of these OPVs. In this thesis the application of nanostructures on the critical layer of zinc oxide (ZnO) that forms the electron selective inter-film in inverted OPVs to enhance performance was investigated.

In the thesis work, porous ZnO was demonstrated to serve as a nanostructured electron selective layer enhancing light scattering in inverted organic photovoltaics. Porosity was induced and controlled in the ZnO layer with the addition of polyethylene glycol (PEG) organic template. Scanning electron microscopy, contact angle and absorption measurements proved that the ZnO:PEG ratio of 4:1 is optimal for the best performance. Ensuring sufficient pore-filling, the use of porous ZnO structure led to a marked improvement in the device performance when compared to non-porous ZnO, with a 35% increase in the current density and a 30% increase in the efficiency.

The use of porous structure was extended to doped zinc oxide electron selective layers, namely indium-doped and aluminum-doped ZnO layers. The enhanced performance of OPV employing porous structure was observed for these devices also by virtue of the efficient light scattering property of the porous layer. Thus, the

proposed porous nanostructured metal oxides proved to be a portable efficient method of power conversion efficiency enhancement.

Finally, photonic crystal was employed on the zinc oxide electron selective layer of inverted OPVs. By optimizing various process parameters, efficiency enhancement was observed for the OPV devices with photonic crystal ZnO layer compared to planar ZnO electron selective layer. The highly ordered periodic structures of the photonic crystals provided effective light trapping, which resulted in increased absorption in the active layer and subsequent current density improvement.

The findings of this thesis indicate that it is highly beneficial to apply nanostructure or photonic crystal structure as the electron selective layer in OPVs.

List of Figures

Figure 1-1: Predicted potential of renewable energy sources.....	3
Figure 1-2: Energy band diagram of a typical silicon solar cell	4
Figure 1-3: Worldwide annual production and annual average cost of PV modules (MW _p – Megawatt-peak; W _p - Watt-peak	5
Figure 1-4: Energy band diagram of OPV.....	6
Figure 1-5: Best research cell efficiencies (source : NREL).....	8
Figure 2-1: (a) Device schematic and (b) current density-voltage characteristics of a single-layer OPV. (c) Schematic illustrating the exciton generation process in single layer device (η_A , η_D and η_{CC} are the absorption, exciton diffusion and charge collection efficiencies, respectively).....	12
Figure 2-2: Current density-voltage characteristics of the first bilayer layer OPV and its device schematic in the inset.....	13
Figure 2-3: (a) Bulk heterojunction (BHJ) with interface where exciton diffusion takes place. (b) Microscopic illustration of BHJ. The percolation pathways to the two electrodes are indicated with arrows.....	14
Figure 2-4: P3HT and PCBM structures.....	15
Figure 2-5: Molecular structures of (a) PCDTBT, (b) PTB and (c) ICBA.....	17
Figure 2-6: Schematic illustrating the flow of photocurrent generation process in OPVs.....	18
Figure 2-7: Equivalent circuit of a solar cell.....	19
Figure 2-8: Typical J-V curve of an organic solar cell in (a) linear scale and (b) semilog scale. The three regions I to III account for the effects of shunt resistance, recombination currents and series resistance, respectively.....	20
Figure 2-9: Schematic of an OPV employing a BHJ active layer.....	22
Figure 2-10: Schematic representation of a regular OPV device.....	22
Figure 2-11: Schematic representation of an inverted OPV device.....	24
Figure 2-12: Optical electrical field in a typical OPV device (a) without and (b) with the metal oxide interlayer.....	25

Figure 2-13: (a) Schematic of the an inverted OPV device with ZnO electron selective layer and (b) the energy level diagram.....	27
Figure 2-14: (a) Schematic representation and (b) cross-sectional SEM image of P3HT/ZnO hybrid OPV (the scale bar is 200nm) and (C) J-V characteristics of the hybrid device with and without nanopillars.....	29
Figure 2-15: (a) Device schematic, SEM of (b) nanostructured ZnO and (c) OPV device employing the ZnO nanostructured layer.....	30
Figure 2-16: J-V characteristics of BHJ OPV with/without nanostructured ZnO electron selective layer.....	30
Figure 3-1: Schematic of device structure, energy level diagram and the SEM image of the porous structure.....	32
Figure 3-2: AFM image of (a) ZnO, (b) ZnO-PEG(2.5%) and (c) ZnO-PEG (5%).....	33
Figure 3-3: (a) SEM image and (b) surface profiling image of the solvent-treated ZnO film.....	34
Figure 3-4: Flowchart illustrating the sol-gel preparation method for our ZnO sol-gel.....	35
Figure 3-5: Structure of polyethylene glycol (PEG).....	36
Figure 3-6: Flowchart illustrating the preparation method for porous ZnO sol-gel.....	36
Figure 3-7: Process flow of our inverted OPV device fabrication.....	39
Figure 3-8: Schematic representation of OPV devices with (a) porous ZnO layer and (b) non-porous ZnO layer, along with respective SEM images showing the porous and non-porous ZnO layer in the corresponding devices.....	42
Figure 3-9: SEM images of porous ZnO layer with layer annealed at (a) 150°C, (b) 200°C and (c) 250°C.....	43
Figure 3-10: J-V characteristics of OPVs with porous and non-porous ZnO layer.....	45
Figure 3-11: J-V characteristics of OPVs with (a) non-porous ZnO layer and (b) porous ZnO layer, with active layer coated at different spin speeds (at 2000 rpm and 800-1000 rpm).....	47
Figure 3-12: SEM image of porous ZnO layer using ZnO:PEG ratio 2:1.....	49

Figure 3-13: SEM images of porous ZnO layer using ZnO:PEG ratios of (a) 3:1, (b) 4:1 and (c) 5:1.....	50
Figure 3-14: Current density-voltage (J-V) characteristics of OPVs having porous ZnO layer with different ZnO:PEG ratios and active layer spin-coating speed of 2000 rpm.....	51
Figure 3-15: Current density-voltage (J-V) characteristics of OPVs having porous ZnO layer with different ZnO:PEG ratios of 3:1, 4:1 and 5:1, together with the non-porous reference device.....	52
Figure 3-16: (a) Efficiency trend for different ZnO:PEG ratios extracted from 24 devices. (b) Values symbolized in the box plot.....	54
Figure 3-17: IPCE spectra of OPVs having porous ZnO layer with different ZnO:PEG ratios with the active layer coated at slow spinning speed (800-1000 rpm).....	55
Figure 3-18: Absorption spectra of OPVs having porous ZnO layer with different ZnO:PEG ratios with the active layer coated at slow spinning speed (800-1000 rpm).....	57
Figure 3-19: Schematic of micropore acting as scattering centre in porous ZnO OPV.....	58
Figure 3-20: Configuration for (a) the calibration for total transmission studies and (b) the total transmission measurements.....	59
Figure 3-21: Configuration for (a) the calibration for diffused transmission studies and (b) the diffused transmission measurements.....	59
Figure 3-22: (a) Total transmission and (b) diffused transmission of OPVs with porous ZnO layer with different ZnO:PEG ratios and non-porous ZnO (reference device).....	61

Figure 3-23: Haze factor of OPVs with porous ZnO layer using different ZnO:PEG ratios and non-porous ZnO (reference device).....	62
Figure 4-1: SEM image of (a) undoped TiO ₂ layer and (b) Cs-doped TiO ₂ layer. (c) J-V characteristics of OPV devices with and without Cs-doped TiO ₂	66
Figure 4-2: Flowchart illustrating the sol-gel preparation method for (a) non-porous IZO and (b) porous IZO.....	69
Figure 4-3: Schematic representation of OPV devices with (a) porous IZO layer and (b) non-porous porous IZO layer, along with SEM images showing the porous and non-porous IZO layer in the respective devices.....	71
Figure 4-4: Current density-voltage (<i>J-V</i>) characteristics of OPVs using IZO:PEG ratios of 3:1, 4:1 and 5:1 for IZO electron selective layer.....	74
Figure 4-5: Current density-voltage (<i>J-V</i>) characteristics of OPVs with porous IZO, non-porous IZO and non-porous ZnO electron selective layer.....	76
Figure 4-6: SEM images of the porous IZO layers using IZO:PEG ratio of (a) 3:1, (b) 4:1 and (c) 5:1.....	78
Figure 4-7: Normalized IPCE spectra of OPVs with porous IZO and non-porous IZO (IZO ref.) layer.....	78
Figure 4-8: Absorption spectra of OPVs with porous IZO and non-porous IZO (IZO ref.) layer.....	79
Figure 4-9: Haze factor of OPVs with porous IZO layer and non-porous IZO (IZO ref.) layer.....	80
Figure 4-10: Flowchart illustrating the sol-gel preparation method for (a) the non-porous AZO and (b) the porous AZO.....	83
Figure 4-11: Schematic representation of OPV devices with (a) the porous AZO layer and (b) the non-porous porous AZO layer, along with SEM images showing the porous and non-porous AZO layer in the respective devices.....	84

Figure 4-12: Current density-voltage (J-V) characteristics of OPVs with the porous AZO, non-porous AZO and non-porous ZnO electron selective layer in OPV.....	85
Figure 4-13: SEM images of porous AZO layer with AZO:PEG ratio of 4:1.....	86
Figure 4-14: Normalized IPCE spectra of OPVs with the porous AZO and non-porous AZO (AZO ref.) layer.....	87
Figure 4-15: Absorption spectra of OPVs with the porous AZO and non-porous AZO (AZO ref) layer.....	88
Figure 4-16: Haze factor of OPVs with the porous AZO and non-porous AZO (AZO ref.) layer.....	89
Figure 4-17: Current density-voltage (J-V) characteristics of OPVs with the porous IZO and porous AZO electron selective.....	90
Figure 4-18: SEM images of (a) the porous IZO layer and (b) the porous AZO layer, both with a doped ZnO:PEG ratio of 4:1.....	91
Figure 4-19: Haze factor of OPVs with the porous IZO and the porous AZO layer.....	91
Figure 4-20: Absorption spectra of OPVs with the porous IZO and AZO layers.....	92
Figure 5-1: (a) Active layer structure and (b) absorption and mode density of P3HT/PCBM blend vs. P3HT PC in PCBM.....	96
Figure 5-2: (a) Device structure, photograph and (b) SEM and cross-sectional images of OPV devices with planar and photonic crystal embossed BHJ.....	97
Figure 5-3: Cross-sectional SEM images of (a) TiO ₂ PC on ITO and (b) SEM inverted OPV device with TiO ₂ PC electron selective layer.....	98
Figure 5-4: Flowchart of the method used for preparation of the photonic crystal structure on ZnO.....	100

Figure 5-5: Photographs of ZnO photonic crystal structure formed on ITO coated glass.....	101
Figure 5-6: SEM image of ZnO photonic crystal structure fabricated (scale bar is 1 μ m).....	101
Figure 5-7: Schematic representation of OPV devices with (a) ZnO photonic crystal layer and (b) planar ZnO layer, along with illustrations of the photonic crystal and planar layer in the respective devices.....	103
Figure 5-8: J-V characteristics of OPV with the ZnO photonic crystal layer.....	104
Figure 5-9: SEM image of the initial ZnO photonic crystal layer on ITO substrate.....	105
Figure 5-10: SEM image of the annealed ZnO photonic crystal layer on ITO substrate.....	106
Figure 5-11: J-V characteristics of OPVs with the un-annealed and annealed ZnO photonic crystal layer.....	107
Figure 5-12: J-V characteristics of the OPV using the annealed ZnO photonic crystal layer and the reference OPV device with planar ZnO layer.....	108
Figure 5-13: J-V characteristics of the ZnO photonic crystal OPV with an underlying ZnO layer and the reference OPV with planar ZnO layer.....	110
Figure 5-14: J-V characteristics of photonic crystal OPVs with one and two underlying ZnO layers, together with the planar ZnO reference OPV.....	111
Figure 5-15 Schematic illustrating the deposition of active layer material on photonic crystal ZnO.....	113
Figure 5-16: J-V characteristics of ZnO photonic crystal OPVs with active layer spin-coated at 2000 rpm and 800-1000 rpm, together with the planar ZnO reference OPV.....	115

Figure 5-17: J-V characteristics of ZnO photonic crystal OPVs with active layer spin-coated at 2000 and 2500 rpm, together with the planar ZnO reference OPV.....	118
Figure 5-18: Normalized IPCE spectra of the planar ZnO reference OPV and the OPV with ZnO photonic crystal layer.....	119
Figure 5-19: Absorption spectra of the planar ZnO reference OPV and the OPV with ZnO photonic crystal layer.....	120
Figure 5-20: Refractive index of different organic layers in the simulated OPV device at 510 nm	122
Figure 5-21: Simulated absorption in P3HT:PCBM active layer for the photonic crystal OPVs with one and two underlying ZnO layers, together with the planar ZnO reference OPV	123
Figure 5-22: Simulated electric field distribution for (a) the reference OPV with planar ZnO layer, (b) the ZnO PC OPV with 1 underlying ZnO layer and (c) the ZnO PC OPV with 2 underlying ZnO layers	125
Figure 5-23: Simulated electric field distribution for (a) the reference OPV with planar ZnO layer, (b) the ZnO PC OPV with active layer spin-coated at 2000 rpm and (c) the ZnO PC OPV with active layer spin-coated at 2500 rpm.....	127

List of Tables

Table 1-1: The fossil fuel use in 2004 and projected time left for complete depletion (TW- Terawatt (10^{12} Watt); ZJ – Zepto Joule (10^{21} Joule).....	1
Table 1-2: Current and predicted renewable energy use by category.....	2
Table 1-3: Comparison of the cost estimates for OSC to other thin films and mc-Si...7	
Table 2-1: Device parameters of single-junction and tandem OPVs with the highest reported efficiencies.....	17
Table 3-1: Comparison of the device parameters for reference and porous ZnO OPVs	32
Table 3-2: Device parameters of non-porous and porous ZnO OPV	44
Table 3-3: Device parameters of non-porous and porous ZnO OPV with active layer spin-coated at different spinning speeds (at 2000 rpm and 800-1000 rpm).....	48
Table 3-4: Device parameters of porous ZnO OPV with different ZnO:PEG ratios and active layer coated at spinning speed of 2000 rpm.....	51
Table 3-5: Device parameters of the best porous ZnO OPV with different ZnO:PEG ratios and non-porous reference device fabricated.....	53
Table 3-6: Current densities of porous ZnO PV, non-porous ZnO PV and porous ZnO PV with pure P3HT.....	55
Table 3-7: Contact angle measurements of ZnO layer with different ZnO:PEG ratios.....	56
Table 4-1: Device parameters of OPV devices with different spin-coating speeds for IZO electron selective layer.....	72
Table 4-2: Device parameters of OPV devices with different annealing temperature for IZO electron selective layer.	72
Table 4-3: Device parameters of OPV devices with different spin-coating speeds for active layer.....	73

Table 4-4: Device parameters of OPV devices using IZO:PEG ratios of 3:1, 4:1 and 5:1 for IZO electron selective layer.....	74
Table 4-5: Device parameters of OPVs with porous IZO, non-porous IZO and non-porous ZnO electron selective layer.....	76
Table 4-6: Device parameters of OPV devices using AZO:PEG ratios of 3:1, 4:1 and 5:1 for AZO electron selective layer.....	82
Table 4-7: Device parameters of the porous AZO, non-porous AZO and non-porous ZnO electron selective layer in OPV.....	86
Table 4-8: Device parameters of the porous IZO and porous AZO electron selective layer in OPV.....	90
Table 4-9: Contact angle measurements of IZO and AZO layer using doped-ZnO:PEG ratio of 4:1.....	93
Table 5-1: Device parameters of OPV with the ZnO photonic crystal layer and reference OPV with planar ZnO layer.....	104
Table 5-2: Device parameters of OPVs with un-annealed and annealed ZnO photonic crystal layer.....	107
Table 5-3: Device parameters of the OPV using the annealed ZnO photonic crystal layer and the reference OPV device with planar ZnO layer.....	109
Table 5-4: Device parameters of the ZnO photonic crystal OPV with an underlying ZnO layer and the reference OPV with planar ZnO layer.....	110
Table 5-5: Device parameters of ZnO photonic crystal OPVs with one and two underlying ZnO layers, together with the planar ZnO reference OPV.....	112
Table 5-6: Device parameters of ZnO photonic crystal OPVs with active layer spin-coated at 2000 rpm and 800-1000 rpm, together with the planar ZnO reference OPV.....	114

Table 5-7: Device parameters of ZnO photonic crystal OPVs with active layer spin-coated at 2000 and 2500 rpm, together with the planar ZnO reference OPV.....	117
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Common Abbreviations

Abbreviations	Full expression
Ag	Silver
Al	Aluminum
AM1.5G	Air Mass 1.5 Global
AM2	Air Mass 2 Global
AZO	Aluminum doped zinc oxide
BHJ	Bulk heterojunction
CdTe	Cadmium telluride
CIGS	Copper indium gallium selenide
Cs	Cesium
Cs ₂ CO ₃	Cesium carbonate
CuPC	Copper phthalocyanine
D-A	Donor-acceptor
EQE	External quantum efficiency
FF	Fill factor
FTO	Fluorine doped tin oxide
HOMO	Highest occupied molecular orbital
ICBA	Indene-C60 bisadduct
IPA	Isopropyl alcohol
IPCE	Incident photon-to-electron conversion efficiency
IQE	Internal quantum efficiency
ITO	Indium tin oxide
IZO	Indium doped zinc oxide
J _{sc}	Short-circuit current density
J-V	Current density-voltage
L _D	Diffusion length
LiF	Lithium fluoride
LUMO	Lowest unoccupied molecular orbital

MEH-PPV	Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]
MoO ₃	Molybdenum oxide
Ni	Nickel
NiO	Nickel oxide
OPV	Organic photovoltaics
OSC	Organic solar cell
PC	Photonic crystal
P3HT	Poly(3-hexylthiophene)
PCBM	6,6-phenyl C61-butyric acid methyl ester
PCDTBT	N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole))
PCE	Power conversion efficiency
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)
PEG	Polyethylene glycol
PTB	Benzodithiophene polymer
PV	Photovoltaic
R _s	Series resistance
R _{sh}	Shunt resistance
SEM	Scanning electron microscopy
Si	Silicon
TCO	Transparent conductive oxide
TDPTD	Poly(3-(2-methyl-2-hexylcarboxylate)
TiO ₂	Titanium oxide
WO ₃	Tungsten oxide
V ₂ O ₅	Vanadium oxide
V _{oc}	Open-circuit voltage
ZnO	Zinc oxide

Chapter 1: Introduction

1.1 Necessity for solar energy harvesting

To date the world energy demands have been predominantly met with the use of fossil fuels such as coal and petroleum. However, these energy sources are limited and are being rapidly depleted with extensive use. Although at the time of preparation of this thesis the world fuel prices are low due to geo-political reasons, it is foreseen that in the near future, with the ever increasing demand and limited supply, the prices are expected to increase. Another more important issue is the toxic gases, which are created as a byproduct of the refinement and use of these sources. The use of fossil fuels has a major role in the critical environmental concerns including climate change and global warming [1-3]. Table 1-1 lists the fossil fuel use in 2004, with a projection of the number of years until complete depletion if used at the same rate. However, with the rapid industrialization and increase in human population, the rate of use per year is bound to surge, thereby hastening the exhaustion of these resources [4].

Table 1-1: The fossil fuel use in 2004 and projected time left for complete depletion (TW- Terawatt (10^{12} Watt); ZJ – Zepto Joule (10^{21} Joule) [4].

	Form	Consumption (TW)	Annual consumption (ZJ year ⁻¹)	Energy Reserve (ZJ)	Time left (years)
Coal	Solid	3.8	0.12	290	2400
Oil	Liquid	5.6	0.18	57	316
Natural gas	Gaseous	3.5	0.11	30	272

Therefore, in the context of emerging issues of climate change and depleting fossil fuel energy, the research on utilization of renewable energy sources is gaining widespread interest in both research and industry. Renewable energy sources are theoretically boundless and mainly include hydropower, wind, solar, tidal, biomass and geothermal. In addition, they are environmentally friendly. Table 1-2 lists the current and predicted renewable energy use. From Table 1-2 it is clear that hydropower is the most extensively used renewable energy. Fig. 1-1 shows the potential of various renewable energy sources to meet the global energy demand. Although solar energy has immense potential, it is not being exploited to a significant extent when compared to other sources.

Table 1-2: Current and predicted renewable energy use by category [5].

	2010	2020	2035
Electricity generation (TW h)	4206	6999	11342
Hydropower	3431	4513	5677
Bioenergy	331	696	1487
Solar PV	32	332	846
Wind energy	342	1272	2681
Geothermal energy	68	131	315
Marine	1	5	57

Figure 1-1: Predicted potential of renewable energy sources [5].

Of the many renewable energy sources available, solar energy is the most promising one. Solar energy as renewable energy source is not only carbon-neutral but also abundant; the amount of solar energy that earth receives is approximately 10,000 times the energy that is consumed per year [6, 7]. It is in fact, directly or indirectly, the source of all other renewable and non-renewable energy resources. Thus, if efficient energy conversion can be achieved by solar cells, the looming energy crisis can be curbed to a large extent.

Although the photovoltaic effect was first discovered as early as 1839 by Alexandre-Edmond Becquerel, the first successful silicon solar cell was not demonstrated until later in 1954 at Bell. At the heart of the conventional solar cell is the p-n junction [8]. The p-type layer absorbs the incident photon and the minority carrier diffuses to the junction, where the electrons are swept to the n-type layer and the holes to the p-type layer, due to the built-in electric field (Fig. 1-2). These carriers are then collected at the respective electrodes.

Figure 1-2: Energy band diagram of a typical silicon solar cell [9].

Since their inception, research on silicon solar cells has been incessant and led to efficiency levels of above 25%. This is the first generation of solar cells and they boast >86% of the market share [10]. Although monocrystalline silicon solar cells have higher efficiencies, industrial viability is an issue because of the high cost of production and complex processing. Hence, they are being rapidly displaced by thin film solar cells dubbed as the second generation of solar cells. They mainly comprise of amorphous silicon, CdTe (cadmium telluride) and CIGS (copper indium gallium selenide). They provide lower cost of manufacturing but with lower efficiencies compared to the first generation devices. Fig. 1-3 shows the annual production and annual average costs of photovoltaic modules till 2010. Market research reports have indicated that the photovoltaic module prices have dropped from \$3.8/W in 2006 to \$0.91/W in 2012 [11].

Figure 1-3: Worldwide annual production and annual average cost of PV modules (MW_p – Megawatt-peak; W_p – Watt-peak) [12].

1.2 Lure of organic photovoltaics

Inorganic solar cells are still the front runners in this field. They provide efficiencies in the range of 10-20%, which is sufficient for on-grid or local use [13]. In spite of the high efficiencies offered by these devices, manufacturing and installation costs are still high and the process involved in fabrication of these high-efficiency devices is complex.

Organic photovoltaics, especially polymer-based OPVs, promise an alternative approach to harvest the renewable solar energy. Semiconducting polymer, with its ease of fabrication and semiconducting electrical properties, is the core of OPVs [14]. For this landmark discovery, the Nobel Prize for Chemistry in 2000 was jointly awarded to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa. Ultrafast charge transfer between semiconducting polymer, which acts as a donor, together with fullerene derivative acceptors, forms the basis of the working of OPVs [15, 16].

With the advantages of solution processing, ease of fabrication and capability to be deposited on flexible substrates, it is possible to adopt large-scale and low-cost inkjet or roll-to-roll manufacturing for OPV fabrication [17-26]. With a low cost of production compared to inorganic solar cells, OPVs with an efficiency of $\sim 10\%$ and a lifetime of 8-10 years may be used for commercial applications [27, 28]. Thus, provided that sufficient power conversion efficiency and lifetime can be achieved, the possibility of cheap, large-area, printable, flexible solar panels for widespread deployment becomes a reality [29-32].

Since the first demonstration of organic donor/acceptor heterojunction by Tang in 1986 [33], there has been tremendous research effort invested in the OPVs [2, 27]. The operation of OPVs is very different from conventional solar cells. By virtue of the low dielectric constant of the semiconducting polymers used, light absorption does not lead to the generation of free carriers, but instead leads to the formation of excitons in the semiconducting polymer [34]. The donor-acceptor (D-A) interface is the dissociation site of these excitons (note that the working principle of OPVs is further elaborated in Chapter 2). Fig. 1-4 gives an illustration of the exciton formation and dissociation. This limits the efficiency attainable by OPVs when compared to conventional solar cells.

Figure 1-4: Energy band diagram of OPV [8].

Table 1-3 lists the reported projected cost estimates for materials, process and module for manufacturing organic solar cells, CdTe based and multicrystalline (MC) silicon solar cell. From the table it is evident that organic solar cells offer cost benefit. Though CdTe shows comparable cost benefits, it has to be noted that cadmium is toxic, and a known carcinogen, which will be a major concern during the disposal of CdTe solar cells while the OPV is environmentally friendly technology.

Table 1-3: Comparison of the cost estimates for OSC to other thin films and mc-Si [35].

Tech.	Materials			Process Costs (\$/m ²)
	Active (\$/m ²)	Inactive (\$/m ²)	Total (%)	
OSC	6.7–10.0	16.70–27.48	(27–48)	9.30–69.60
CdTe [†]	6.84	58.86	(53)	30.11
mc-Si [‡]	150.57	57.49	(57)	95.81

Tech.	Overhead Costs (\$/m ²)	Module Manuf. Costs ^a (\$/m ²)	Module Cost ^b (\$/Wp)
OSC	13.78–25.21	48.80–138.80	1.0–2.83
CdTe [†]	27.38	129.33	1.65
mc-Si [‡]	23.27	343.50	2.34

[†] Estimates by Zweibel (1999).

[‡] Estimates by Little and Nowlan (1997).

^a Takes into account 95% cell yield.

^b Representative efficiencies used : 5% for OSC ; 8% for CdTe; and 15% for mc-Si; 98% module yield for all.

The highest efficiency reported for single-junction OPV is ~9.94% [36] and ~10.6 % for tandem OPV [37]. However, the efficiency is still low compared to inorganic solar cells. For low-cost large-scale deployment of organic photovoltaics, an efficiency level of at least >10% should be achieved [19].

Fig. 1-5 shows the best research cell efficiencies collated by the NREL (National Renewable Energy Laboratory). From the figure it is clear that, though organic photovoltaics lags behind its inorganic counterpart, the performance is fast improving and it will not be long before OPVs reach the efficiency needed for the OPV technology to be a strong candidate to replace silicon solar cells.

With numerous benefits, polymer based OPVs are apt candidates for clean, environmentally friendly low-cost renewable energy harvesting. However, due to their low efficiency, commercialization of this technology is still in its early stage. The research effort to enhance efficiency of OPVs has been multipronged including optimizing morphology, solvent and thermal annealing, tandem cells, novel active materials and electrodes, plasmonics, and device architectures [38-59]. Apart from these, the modification and optimization of metal oxides, which form the electrode inter-layers in OPVs, also provide a means to enhance performance. The main objective of the research project was to study the affect of employing microstructures on the electron selective metal oxide interlayer of OPV. Focus was on the ZnO electron selective layer of inverted OPV and the investigations were divided into

three sub-projects which were (a) to employ porous microstructures on the ZnO electron selective layer of the organic photovoltaics, and to study the effect of these structures on the device performance, (b) to investigate the possibility of the portability of these porous structures on doped zinc oxide electron selective layers and (c) to study the OPV device performance on the use of photonic crystal structure on the ZnO electron selective layer. This thesis presents and explains motivation behind the choice of project, the analysis of investigations on porous and photonic crystal ZnO microstructures in OPVs and the future direction of the research project.

Chapter 2 gives the background studies on OPVs. This chapter covers the evolution of polymer based OPVs including the recent advances in efficiency enhancement, the working principle of the OPV device and comparison between the regular and inverted architectures. This chapter also describes the role of metal oxides in OPVs and also discusses previous studies reported on the application of nanostructures in active layer. This chapter also further describes the motivation in application of the metal oxide microstructures in OPVs as an efficiency enhancement route.

Chapters 3 presents the marked improvement in device efficiency with use of porous zinc oxide microstructure in the electron selective layer of the inverted OPV. The chapter includes detailed explanations on experimental methods and data analysis. The chapter also discusses the role of ZnO porous layer as an efficient scattering layer and studies the influence of various process parameters on the device performance.

Chapter 4 reports the transfer of porous structure to doped ZnO electron layer. The effect of porous structure on both indium doped and aluminium doped ZnO are examined. The chapter also studies the applicability of porous structure for scattering enhancement in these doped ZnO layers and consequences on the absorption and current density of the devices are analysed.

Chapters 5 shows the use of photonic crystal (PC) on ZnO electron selective layer of OPV. The process of fabricating photonic crystal structure and the optimization of

this process are analysed. Also the effect of device processing parameters on the light trapping, absorption, current density and the resultant OPV performance are investigated.

The final chapter draws relevant conclusions and provides recommendations for future direction.

Chapter 2: Background

2.1 Organic photovoltaics (OPV) through the years

Organic photovoltaics can be broadly classified into two types of devices with different light absorbing materials: small molecules and conjugated polymers [60, 61]. This thesis concentrates on the applications of metal oxide microstructures on OPVs based on polymers (popularly known as polymer solar cells). Hence, all further discussions will be for such polymer-based OPVs.

Application of organic semiconductor to achieve photovoltaic response was first demonstrated as an organic layer (PPV) sandwiched between a transparent conductive electrode and a metal electrode [62]. This device showed extremely low efficiency ($< 1\%$). Due to its inherently high binding energy, light absorption in such organic semiconductor materials leads to exciton formation. Upon incident light absorption, electron is excited from the HOMO (highest occupied molecular orbital) of the material to its LUMO (lowest unoccupied molecular orbital) and results in the generation of exciton (bound carrier) (Fig. 2-1(c)). In single-layer OPV devices, such excitons can only be dissociated at the electrodes, which create difficulty in charge collection. In addition, the charge mobility is very low in such materials ($\sim 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$).

(a)

Figure 2-1: (a) Device schematic and (b) current density-voltage characteristics of a single-layer OPV [62] . (c) Schematic illustrating the exciton generation process in single layer device (η_A , η_D and η_{CC} are the absorption, exciton diffusion and charge collection efficiencies, respectively).

It is possible to work around these issues by using a device structure that consists of two organic layers with different ionization potentials and LUMO offsets, which helps in dissociation of exciton before reaching the electrodes. Such OPV devices are known as bilayer OPV devices.

2.1.1 Bilayer OPV devices

Tang et al. reported the first bilayer OPV device in 1986 [33]. Copper phthalocyanine (CuPc) and perylene tetracarboxylic derivative were the organic materials used for the bilayer device. Efficiency of 1% was achieved under AM2 (air mass 2) illumination conditions.

Figure 2-2: Current density-voltage characteristics of the first bilayer layer OPV and its device schematic in the inset [33].

Although the bilayer device showed considerable improvement in efficiency compared to its predecessor, the internal quantum efficiency was still severely limited. The exciton diffusion length was intrinsically short in organic devices (few tens of nanometers) and, hence, the OPV required a compromise in the active layer thickness, which in turn reduces the absorption. Replacing these semiconductors with other more suitable organic materials emerged as a viable option. PCBM (6,6-phenyl C61-butyric acid methyl ester), a fullerene derivative, as acceptor replacement, and conjugated polymers such as MEH-PPV (Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]), as donor replacement, were subsequently reported [63, 64]. PCBM, by virtue of its structure, is highly conductive and provides favorable orbital overlap, which results in excellent electron and exciton diffusion efficiencies [17]. In addition, it has high solubility in most common organic solvents and shows the best performance amongst the commonly used acceptor materials evaluated [65]. Although different architectures such as double heterostructures were implemented

to improve the OPV device performance, the major breakthrough came by the application of bulk heterojunction to form the active layer of OPV.

2.1.2 Bulk heterojunction OPV devices

Bulk heterojunction was first demonstrated in 1995 [15, 66]. The short exciton diffusion length in polymers curbs the active layer thickness of the OPV. This bottleneck imposes a compromise between the possible light absorption and charge dissociation. The dilemma was overcome by employing bulk heterojunction (BHJ) as the active layer in the OPV. In BHJ, the donor and acceptor materials are mixed to form an interpenetrating network with nanoscale phase separation [27, 67-72]. This increases the donor acceptor interfacial area for excitonic dissociation with donor acceptor junctions available within the exciton diffusion lengths [Fig. 2-3(a)]. These donor acceptor interfaces distributed throughout the BHJ active layer are sites for ultrafast photoinduced charge transfer between these materials leading to efficient charge separation [15]. BHJ also provides transport pathways for the dissociated carriers to move to their respective electrodes. Fig. 2-3(b) shows the pathways provided by the phase segregation of donors and acceptors in the BHJ architecture. BHJ is also compatible with large-scale manufacturing such as inkjet printing and roll-to-roll processing [73].

Figure 2-3: (a) Bulk heterojunction (BHJ) with interface where exciton diffusion takes place. (b) Microscopic illustration of BHJ. The percolation pathways to the two electrodes are indicated with arrows [17].

The introduction of P3HT (poly(3-hexylthiophene)) as donor material in BHJ was another significant milestone in the OPV history. With the use of P3HT:PCBM BHJ active layer, the highest efficiency reported to that date (~4.4%) was obtained [74]. P3HT is a semi-crystalline polymer and its absorption is compatible with the solar spectrum [65, 75]. P3HT was also applied in hybrid OPVs, where the electron donor was replaced with metal nanoparticles/nanostructures [76-79]. By optimizing the process parameters such as organic solvent used, thermal and solvent annealing for active layer, increased regioregularity of P3HT and post fabrication annealing; the use of P3HT:PCBM BHJ active layer for OPV has lead to impressive efficiency enhancement ~5% [18, 80-82]. Depending on the solvent used the segregation of the acceptor and donor in the active layer differs, because the different boiling points of the solvents results in dissimilar solvent evaporation rates during spin-coating. Both solvent and thermal annealing has been shown to improve phase segregation of donor and acceptor molecules. When P3HT of higher degree of regioregularity is used the resultant film has crystallized P3HT which leads to improved charge transport and better light absorption. Hence, the most widely used electron donor is P3HT and electron acceptor is PCBM [[83]. This is the active layer BHJ blend that was used for the experiments in this thesis.

Figure 2-4 : P3HT and PCBM structures [18]

2.1.3 Advances in OPV materials and architecture

A comprehensive review on the novel materials employed so far in OPVs is beyond the scope of this chapter. Hence, a few pertinent structures employed in polymer solar cells are discussed to elaborate on the efforts made to improve the overall performance and power conversion efficiency (PCE) of the devices.

The solar spectrum is broad when compared to the narrow absorption spectra provided by single BHJ OPV devices used extensively. Hence, to maximize the absorption of solar spectrum, a stack of OPVs, each absorbing across a different part of the solar spectrum, was developed. These so-called tandem OPVs have shown significant efficiency enhancement when compared to their single-junction counterparts [84-87].

Another approach to increase OPV efficiency has been to find replacements for the extensively used P3HT and PCBM [42, 73, 88-90]. Low bandgap conjugated polymers with low HOMO levels are the main class of organic semiconductors being studied. The low bandgap also enables absorption in the hitherto unused region of solar spectrum ~ 700 nm [7]. The photon flux of the solar spectra is the highest in this region, which could not be exploited by P3HT. These low bandgap polymers such as poly (N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)) (PCDTBT) have the push-pull architecture with electron-rich and electron-deficient moieties, which provide enhanced charge carrier mobility [73, 91, 92]. Benzodithiophene polymers (PTBs) such as PTB4 and PTB7 in OPVs have also been reported to exhibit efficiency of $\sim 7.4\%$ [7]. The low LUMO level of PCBM limits the open circuit voltage of OPVs. To increase the LUMO level, replacement acceptors such as indene-C₆₀ bisadduct (ICBA) and other fullerene derivatives as well as non-fullerene acceptors have been suggested and successfully applied to improve the device efficiency [57, 90, 93, 94]. The molecular structure of PCDTBT, PTB and ICBA is shown in Fig. 2-5. In addition, mixed solvents and additives such as alkanethiols have also been used for efficiency enhancement by inducing favourable nanoscale morphology in the active layer [39, 95-97].

Figure 2-5 : Molecular structures of (a) PCDTBT, (b) PTB and (c) ICBA [7, 90, 92].

Efforts have also been made to modify the architecture of the OPVs. These include metallic nanocrystals, plasmonic nanostructures, metal substrates and substrate texturing [21, 48-50, 59, 98] In addition, metal oxide nanostructures have also been utilized for efficiency enhancement in OPVs. This has been discussed in detail in a later section (2.5).

The highest efficiencies reported to date in publications for both single junction and tandem architecture for OPVs are listed in Table 2-1.

Table 2-1: Device parameters of single-junction and tandem OPVs with the highest reported efficiencies [36, 99].

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
Single-junction	0.794	17.420	0.72	9.94%
Tandem	2.28	7.63	0.66	11.55%

2.2 Operation of organic photovoltaics

The key component of organic photovoltaics is the conjugated polymers, which form the active layers of these devices[100]. The polymers can generate charge carriers and the delocalized π -bonds can transport these charge carriers.

The photocurrent generation process in the OPV is illustrated in Fig. 2-6.

Figure 2-6: Schematic illustrating the flow of photocurrent generation process in OPVs [17].

The process begins with the absorption of the incident light by the photon absorbing conjugated polymer. The polymer used in OPVs have inherently large exciton binding energy of the order of 0.1-0.4 eV because of the low dielectric constant of these materials [18]. As a result, the absorbed light is unable to produce free carriers; instead, it leads to the formation of excitons. These excitons then diffuse through this material to the dissociation site, i.e. the boundary where donor and the acceptor material unite. The LUMO offset and the difference in ionization potential at this site ensures the dissociation of the exciton (charge separation) [101]. These separated carriers are then collected by the respective electrodes. The efficiency of this process is determined by the efficiency at these individual steps, namely η_A (light absorption efficiency), η_{ED} (exciton diffusion efficiency), η_{CT} (charge transfer efficiency), and η_{CC} (charge collection efficiency).

The product of these efficiencies is the internal quantum efficiency (η_{IQE}).

$$\eta_{IQE} = \eta_A \eta_{ED} \eta_{CT} \eta_{CC} \quad (1)$$

The absorption efficiency is given by,

$$\eta_A = (1 - e^{-\alpha d}) \quad (2)$$

And the exciton diffusion efficiency is given by

$$\eta_{ED} = e^{-d/L_D} \quad (3)$$

where α is absorption coefficient, d is the thickness of active layer and L_D is the diffusion lengths.

From Equations (2) and (3) it is clear that these competing efficiencies are the limiting factor for IQE. Absorption cannot be increased by the active layer thickness as this will adversely affect the diffusion efficiency due to the inherently low diffusion length of excitons ($\sim 3\text{-}10$ nm) in the organic layer [65].

A typical solar cell is depicted by the equivalent circuit shown in Fig. 2-7. The photocurrent source represents the photocurrent generation and the diode represents the recombination at the junction of donor and acceptor layers. The internal resistance created by the material resistance, contact resistance, etc. is represented by the series resistor while the leakage current is represented by the shunt resistor.

Figure 2-7: Equivalent circuit of a solar cell [19].

It can be modelled by the following equation:

$$J = J_o \left[\exp \left(\frac{e(V - JR_s)}{nk_B T} \right) - 1 \right] + \frac{V - JR_s}{R_{sh}} - J_{ph} \quad (4)$$

where J_0 is the reverse bias saturation current density, e is the elementary charge, R_s and R_{sh} is the series and shunt resistance respectively, n is the diode ideality factor, k is Boltzmann's constant and T is temperature while J_0 represents the reverse bias saturation current density.

This model for conventional solar cell is generally applicable to organic photovoltaics. However, it is necessary to bear in mind that the BHJ morphology in the active layer and the excitonic dissociation limitation can lead to new photocurrent loss mechanisms which are not included in the conventional model [19].

The resultant current density-voltage (J - V) curve is shown in Fig. 2-8 [19]. The J - V characteristics for both dark and illuminated conditions are shown. J_{ph} is the generated photocurrent. Three regions are demarcated in the graph and they represent how the J - V curve is influenced by different components of the equivalent circuit. In Region I, the J - V curve is influenced by the shunt resistance, which is a measure of the leakage current in the device. In Region II, J_0 and n affect the device and in Region III, the effect of series resistance, which is a measure of the resistance to current flow in the device, is dominant.

Figure 2-8: Typical J - V curve of an organic solar cell in (a) linear scale and (b) semilog scale. The three regions I to III account for the effects of shunt resistance, recombination currents and series resistance, respectively[19].

To quantify the OPV behaviour or circuit, important device parameters are extracted. These are the short circuit current density (at $V=0$), the open circuit voltage (at $J=0$) and fill factor. The fill factor is given by

$$FF = \frac{J_m V_m}{J_{sc} V_{oc}} \quad (5)$$

where J_m and V_m are the current and voltage at a point where the power is maximum in the curve. This is the operating point of the solar cell. The fill factor is an important measure of the quality of the solar cell.

From these parameters, the power conversion efficiency can be calculated as:

$$\text{Power} = \frac{P_{out}}{P_{in}} = \frac{J_m V_m}{P_{in}} = \frac{FF J_{sc} V_{oc}}{P_{in}} \quad (6)$$

where P_{out} and P_{in} is the output power and input power respectively.

Fig. 2-9 illustrates the schematic of typical OPV employing a BHJ. The most popularly used electron donor is P3HT [poly(3-hexylthiophene)] and the electron acceptor is PCBM [6,6-phenyl C61-butyric acid methyl ester]. A blend of the acceptor and donor forms the active layer of the OPV. Transparent conductive oxide (TCO) coated substrate forms one of the electrodes; low work function metals such as aluminium forms the opposite electrode. The interfacial layers (e.g, metal oxides, LiF, etc. for the cathode and PEDOT:PSS for the anode) perform the important role of easing the carrier collection of one type of carriers while blocking the other (depending on the polarity of the adjacent electrode).

Figure 2-9: Schematic of an OPV employing a BHJ active layer [19].

2.3 Regular vs. Inverted OPV

The schematic of OPV structure commonly used for employing BHJ is illustrated in Fig. 2-10. The structure is of the form ITO/hole-selective layer P3HT:PCBM/electrode. Indium-doped tin-oxide coated on glass is used as a substrate for OPV and forms the anode of the BHJ. PEDOT:PSS (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)) spin-coated on the ITO substrate is used as a hole-selective layer. It also acts a blocking layer for electrons. PEDOT:PSS also has the important role of adapting the ITO surface to assist in hole selection [102, 103]. A blended solution of P3HT:PCBM spin-coated on PEDOT:PSS forms the BHJ active layer. The top electrode for this structure requires a low work function metal such as aluminum.

Figure 2-10: Schematic representation of a regular OPV device.

Although these so-called regular OPVs exhibited good performance trends, the stability of these devices was a cause of concern. The main factors plaguing the stability are the detrimental effects of the low work function aluminum electrode and PEDOT:PSS on the active layer of OPV [97, 104]. PEDOT:PSS is acidic and hygroscopic [102, 103, 105]. Given that PEDOT:PSS is in direct contact with the ITO surface and the active layer, the PEDOT:PSS with its hygroscopic nature can lead to degradation of ITO over time and allow indium diffusion into active layer and eventually lead to device degradation [106]. The low work function Al electrode is air sensitive and upon exposure to ambient environment, oxidation occurs [107]. The result is moisture penetration to the active layer through the pin holes and grain boundaries of the oxidized aluminum electrode [102, 104].

The work function of ITO lies midway between the HOMO of the donor and LUMO of the acceptor material. Owing to this, ITO has the ability to act as the anode or cathode depending on the work function of the interfacial layer coated on ITO [97]. This gives the flexibility of switching the electrodes of OPV to form an inverted structure with the transparent ITO electrode acting as a cathode. Consequently, to convert the top electrode to anode, aluminum can be replaced by a higher work function metal such as Ag. Silver has an elevated air stability compared to aluminum and it is resistant to oxidation. Hence, applying silver as the top electrode alleviates the main issue in the use of regular structure [83]. It is also compatible with large-scale manufacturing [108]. Although PEDOT:PSS has been used also as an interlayer in the inverted structure [108, 109], replacement by p-type oxides such as NiO, MoO₃, WO₃, V₂O₅ etc. is gaining popularity [102, 104, 105, 110-117].

The inverted OPV structure is of the form ITO/electron selective layer/P3HT:PCBM/HTL/electrode (Fig. 2-11). Metal oxides such as TiO_x, ZnO and Cs₂CO₃ are commonly used as electron selective layer [102, 104, 105, 109, 110]. When used from a sol-gel source, such an electron selective layer is spin-coated on ITO substrate and helps modify the layer for electron selection. The active layer is a similar blend of P3HT:PCBM as used in the regular structure. Hole selective layers such as PEDOT:PSS and other p-type oxides are used and high work function metals such as silver form the top electrode for this structure.

Figure 2-11: Schematic representation of an inverted OPV device.

Because of the aforementioned benefits the inverted architecture of OPV is the one chosen to be employed in all the experiments for this thesis.

2.4 Metal oxides in OPV

The use of inverted structure for OPV led to the widespread application of metal oxides as interfacial layers in OPVs. Compared to the acidic and hygroscopic PEDOT:PSS, these metal oxides were found to be stable with excellent optical properties. The metal oxides act as interfacial layers in OPVs. The n-type metal oxides, whose energy levels ease the extraction of electrons from active layer to ITO, are used as electron selective layers. ZnO and TiO_2 are the main candidates. Metal oxides as electron selective layer is further discussed in section 2.4.2. The p-type metal oxides, whose energy levels ease the extraction of holes from active layer to metal electrode, are used as hole transport layers. In addition to their use in inverted OPVs, p-type metal oxides are also being used in regular structure OPVs as replacement for PEDOT:PSS. Metal oxides as hole transport layer is further discussed in section 2.4.2.

Metal oxides have dual roles in the functioning of OPVs. They improve charge extraction by lowering the barrier height at the electrode while at the same time restricting the opposite charge from reaching the electrode, thus reducing their recombination [19, 118]. At the anode side, the metal oxide acts as a hole transport

layer and electron blocking layer, while at the cathode the role of the metal oxide is to act as an electron transport layer and a hole blocking layer, thus providing a boost to the device performance.

In addition, the metal oxide under the top electrode has another function in OPVs. This layer acts as an optical spacer [13, 119]. The need for such a layer can be explained as follows. In OPV devices, the active layer thickness is restricted mainly due to the series resistance and carrier charge recombination limits imposed by the conjugated polymer. Hence, the optical field is distributed in the device in such a way that the interference peak does not coincide with the active layer location (Fig. 2-12(a)). The result is partial absorption of light. Upon the addition of the metal oxide layer on the active layer, the optical field redistributes and its maximum is aligned with the active layer position, thus maximizing the optical absorption (Fig. 2-12(b)).

Figure 2-12: Optical electrical field in a typical OPV device (a) without and (b) with the metal oxide interlayer [13].

2.4.1 Hole transport layer

In recent studies, because of the shortcomings in using PEDOT:PSS, thin layers of p-type metal oxides such as MoO_3 , V_2O_5 , WO_3 and NiO are used in its place [104, 111, 120]. This hole transport layer is used to modify the ITO to assist in hole collection in regular OPVs and used as a contact to top electrode in inverted OPV. They exhibit high work function, good hole conductivity and electron blocking capability [104]. In earlier studies these metal oxides needed high vacuum environment for thermal deposition, which is not only more expensive than solution processing but also incompatible with large-area processing [103]. Recent efforts on solution processing of p-type metal oxides such as MoO_3 , V_2O_5 and NiO have proven successful in application to OPVs [113, 121, 122].

2.4.2 Electron selective layer

For electron transfer layer, metal oxides such as TiO_2 , ZnO and Cs_2CO_3 are used [102, 104, 105, 109, 110, 123-132]. This layer is used as a contact to top electrode in regular OPV, providing more air stability and to modify the ITO to assist in electron collection in inverted OPV. In the absence of this layer, ITO is not selective to electrons and can cause recombination losses [108]. Both ZnO and TiO_2 exhibit good electron selectivity and are widely used in both regular and inverted OPVs [103, 104, 109]. TiO_2 has a good hole blocking ability and also a proven ability of efficient electron transfer from conjugated polymer [19, 109]. ZnO with its high electron mobility is also highly transparent in the visible region making it an apt candidate to be used in inverted OPVs [104, 107, 133, 134]. Though there are different methods such as chemical vapor deposition (CVD) and spray pyrolysis for depositing ZnO , spin-coating ZnO from ZnO sol-gel is the preferred method because of low cost, composition controllability and also because of the resultant homogenous films with good optical properties [102, 135].

Due to its numerous benefits when used as an electron selective layer for inverted OPV, ZnO is used in the experiments conducted for this thesis. Thermally evaporated MoO_3 is used as the hole transport layer. MoO_3 has emerged as the preferred choice for the hole transport layer. The conduction band of MoO_3 is high

enough from the LUMO of active layer to ensure excellent electron blocking capabilities [104]. Fig 2-13(a) shows the schematic of an inverted OPV using a ZnO as the electron selective layer and (b) shows the energy level diagram.

Figure 2-13: (a) Schematic of an inverted OPV device with ZnO electron selective layer and (b) the energy level diagram (adapted from [104]).

2.5 Nanostructures in OPV

In comparison with uniform featureless layers, nanostructured metal oxide can aid in enhancing the device performance in three ways: by increasing the interfacial area between metal oxide and active layer, by providing better charge collection and by scattering incident light as well as light trapping improving light absorption [100, 136]. Compared to planar ZnO layer, nanostructured ZnO layer offers more areas of contact between active layer and ZnO. This allows for faster extraction of electrons from the active layer to the electrode. These nanostructures, especially the nanopillars/nanorods, by virtue of their orientation offer excellent direct charge transport pathways to the electrodes, thereby improving the device performance [100]. The nanostructures also aid in increasing the light absorption in active layer. These structures scatter and reflect incident light, effectively increasing optical path length. Incident light trapping provided by the nanostructures is significant in view of the active layer thickness limitations. By employing such structures, the light

absorption can be enhanced while maintaining the satisfactory transport properties provided by a thinner active layer [2].

Metal oxide nanostructures have been demonstrated successfully in OPVs, with majority of the studies reported on TiO_2 and ZnO nanostructures [2, 79, 100, 133, 137-139]. Various nanostructures such as TiO_2 and ZnO nanowires and nanotubes are the most widely reported structures used in OPVs [77, 79, 100, 128, 140-142].

As zinc oxide is the metal oxide of choice for the electron selective layer in inverted OPVs fabricated for the investigations for this thesis, the rest of discussions on nanostructures are confined to those of ZnO origin. Nanostructures have been demonstrated and well documented using ZnO nanopillar and nanorod structures in OPVs [77, 79, 100, 133, 137, 143]. The research on nanostructured ZnO was started to improve the performance of the hybrid heterojunction OPV where the ZnO acts as the acceptor and the conjugated polymer acts as donor. Fig. 2-14 shows the schematic, SEM and J - V characteristics of an OPV hybrid device with ZnO nanopillars. Compared to the original bilayer hybrid OPVs, the use of nanostructures offer better control over the morphology [79, 137, 144]. The backfilling of conjugated polymer into the nanostructures provides larger interfacial area, which in turn improves the charge separation and the nanostructures act as antennas for better charge collection. They also carry out the role of scattering centers, thereby increasing optical path length and absorption [133].

Figure 2-14: (a) Schematic representation and (b) cross-sectional SEM image of P3HT/ZnO hybrid OPV (the scale bar is 200nm) and (C) J - V characteristics of the hybrid device with and without nanopillars [79, 137].

In spite of the promises, the overall efficiency of these hybrid OPVs was much less compared to P3HT:PCBM BHJ inverted OPVs. The inherently small exciton diffusion lengths of <10 nm requires the spacing between the nanopillars to be of around that dimension to ensure the complete dissociation of all excitons formed. However, this is hardly the case and, hence, the device performance improvement suffers.

Introducing ZnO nanostructures in inverted BHJ OPV devices solves this problem whereby the PCBM acts as the acceptor and the role of ZnO is more evident in efficient charge collection. Fig. 2-15(a) illustrates the schematic of an inverted BHJ OPV employing ZnO nanostructure as the electron selective layer. Fig.2-15(b) shows the SEM image of the ZnO nanostructure formed using contact printing and Fig. 2-14(c) is the cross-sectional image of the OPV device. The ZnO nanostructures are clearly visible in the SEM image.

Figure 2-15: (a) Device schematic, SEM of (b) nanostructured ZnO and (c) OPV device employing the ZnO nanostructured layer [139].

The ZnO nanopillars in BHJ OPV are efficient sites of electron collection and provide highly directed conducting pathway to the electrode [100]. This leads to better device performance with an efficiency of 1.22% (Fig. 2-16).

Figure 2-16: J - V characteristics of BHJ OPV with/without nanostructured ZnO electron selective layer [139].

Chapter 3: Porous zinc oxide in electron selective layer of inverted organic photovoltaics

3.1 Introduction

As discussed in the previous chapter, the use of nanostructured ZnO as intermediate layer of organic solar cells can result in improved performance as a consequence of increased interfacial area, better charge collection and light trapping effects [100, 126, 133, 139, 145-147]. ZnO nanopillar and nanorod structure fabrication is usually a high temperature, elaborate process [100, 133, 137]. Porous ZnO structure can also show similar improvements with the advantage of ease of fabrication. Active layer coated on nanopillars/nanorods will result in a rough and non-uniform layer and there are reports of such rough active layer increasing the recombination, thus lowering the fill factor of the OPV devices[133]. Porous devices will have the added benefit of providing artifact-free surface for uniform deposition of the subsequent active, intermediate and metal layers. If adequate penetration of active layer material in these porous ZnO structures can be ensured, then the efficiency improvement can be guaranteed.

Porous ZnO has found numerous applications including antireflective coatings, gas sensing and photocatalytic application and various methods have been reported for the synthesis of ZnO porous layers [148-153]. The use of porous zinc oxide structure for fabrication of hybrid OPV, with ZnO acceptor layer and P3HT (poly(3-hexylthiophene)) as the donor layer, has been demonstrated [76]. Polyethylene glycol (PEG) was used as porosity inducing agent. Fig. 3-1 illustrates the device structure, the SEM image of porous ZnO structure used and the energy level diagram and Table 3-1 gives a comparison of various device parameters for the reference and porous ZnO OPVs. It was observed that all device parameters displayed substantial improvement upon the incorporation of ZnO porous structure for both chloroform and chlorobenzene solvents.

Figure 3-1: Schematic of device structure, energy level diagram and the SEM image of the porous structure [76].

Table 3-1: Comparison of the device parameters for reference and porous ZnO OPVs [76]

	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF	η
Bilayer	320	0.31	0.42	0.04%
Porous ZnO/P3HT from chloroform	360	1.09	0.52	0.21%
Porous ZnO/P3HT from chlorobenzene	400	1.14	0.53	0.24%

The use of polyethylene glycol with ZnO nanocrystal layer in regular OPV (ITO/PEDOT:PSS/Active layer/ZnO, ZnO-PEG/Al) has also been reported [154]. However in this previous work, the role of PEG was not to induce porosity, but to hybridize the ZnO nanocrystal layer, which resulted in larger nanocrystal domains with fewer domain boundaries (Fig. 3-2). The ensuing reduction in series resistance and improved electrical contact to the Al layer were determined to be the factors

leading to an enhanced device performance with an 11% improvement in the current density reported.

Figure 3-2: AFM image of (a) ZnO, (b) ZnO-PEG(2.5%) and (c) ZnO-PEG (5%) [154].

Moreover, a rugged ZnO layer, induced by solvent extraction, has been studied for inverted OPV(ITO/ZnO/Active layer/ VO_x /Ag) [155]. This rugged ZnO layer was reported to improve the current density by 20% and resulted in an efficiency level of 3.69% by virtue of improved surface area and interfacial contact between the active layer and rugged ZnO layer. However, although overall efficiency enhancement was observed as a result of this rugged layer, this ZnO film did not exhibit a high degree of porosity (Fig. 3-3). Thus, the use of zinc oxide porous structure in BHJ active layer inverted OPV has not been demonstrated successfully fully utilizing its benefits to date.

Figure 3-3: (a) SEM image and (b) surface profiling image of the solvent-treated ZnO film [155].

In this chapter, the use of porous structure in the poly(3-hexylthiophene) and phenyl-C61-butyric acid methyl ester (P3HT:PCBM) bulk heterojunction inverted organic solar cell, made of porous ZnO utilizing polyethylene glycol (PEG) as porosity inducing organic template, is demonstrated to serve as a highly scattering electron selective layer. This work is published in A. Nirmal et al., Optics Express, 2014. 22(S6): p. A1412-A1421 [156], and this chapter is adapted from this journal publication (copyright granted by OSA Optics Express).

3.2 Experiments

3.2.1 ZnO sol-gel preparation

ZnO sol-gel was prepared by using zinc acetate dehydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] (99.95% Fluka) as the precursor, ethanol [$\text{CH}_3\text{CH}_2\text{OH}$] (>99% Sigma Aldrich) as the solvent and monoethanolamine [$\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$] (Sigma Aldrich) as the chelating agent [104]. The process flow is illustrated in Fig. 3-4. This precursor, dissolved in anhydrous ethanol, acts as a source of both zinc and oxide. Previous studies done on ZnO sol with precursor concentration varied from 0.75 to 0.10 M showed that 0.10 M solution exhibits the highest optical transmittance and short circuit current density

[104]. Hence, 0.10 M ZnO sol-gel was used for all the investigations here. This solution was refluxed for 2 h at 80°C to obtain a milky solution. Monoethanolamine (MEA) was then added as stabilizing agent and a transparent solution was obtained, which was magnetically stirred for 12-15 h at 60°C to form the resulting ZnO sol-gel.

Figure 3-4: Flowchart illustrating the sol-gel preparation method for our ZnO sol-gel.

Sol-gel for coating a ZnO porous structure was formed by the addition of suitable concentrations of polyethylene glycol (PEG) (Fig. 3-5) to the ZnO sol-gel solution. Upon addition of PEG to the ZnO sol-gel, an organic-inorganic network configuration was obtained by the polycondensation between PEG and the complex products in the sol [135]. The function of PEG was to serve as a structure directing agent and lead to the formation of porous structure. Subsequent to the addition of PEG, the ZnO sol-gel had to be warmed to ensure homogeneity before spin-coating the solution. Fig. 3-6 illustrates the flowchart for ZnO sol-gel preparation with addition of PEG. The resultant solution was spin-coated on the desired substrate, followed by annealing. It was during this process, after the sol-gel spin-coating, that

the ZnO porous structure was formed. The concentration of PEG in the ZnO sol-gel solution is an important factor that determines the pore size of the resultant film.

Figure 3-5: Structure of polyethylene glycol (PEG).

Figure 3-6: Flowchart illustrating the preparation method for porous ZnO sol-gel.

3.2.2 OPV device fabrication

In this section the process flow for the fabrication of OPVs in the experiments is described. Fig. 3-7 illustrates the general process flow followed for the fabrication of the inverted OPV device.

Indium doped tin oxide (ITO) on glass was used as substrate for the OPV device fabrication. The ITO on the glass substrate was first patterned to define the area in which the OPV devices would be fabricated. Four OPV devices, each with an area of 10.5 mm^2 , can be fabricated on this patterned ITO substrate. Upon patterning, the substrate was subjected to an ultrasonic clean in detergent, DI water, acetone and finally in isopropyl alcohol (IPA). After the cleaning, substrates were baked in oven at 80°C for a minimum of 5-6 h. Before using them for device fabrication, the substrates were exposed to oxygen plasma for 5 min. This treatment has been proven to improve the work function of ITO [157]. Using ZnO sol-gel, a ZnO layer was spin-coated on the patterned ITO substrate, at a spinning speed of 3000 rpm. The resultant thickness of ZnO was $\sim 40 \text{ nm}$. This layer was then annealed in ambient air at 150°C to obtain a crystalline ZnO layer. This process formed the ZnO electron selective layer for inverted OPV.

The rest of the processing was carried out in glovebox environment to avoid exposure to ambient air, which is detrimental to the OPV device. A 1:1 solution of poly(3-hexylthiophene) and phenyl-C61-butyric acid methyl ester (P3HT:PCBM) in chlorobenzene solvent at a concentration of 40 mg/mL was used to spin-coat active layer onto the ZnO layer at a spinning speed of 2000 rpm to obtain a thickness of $\sim 200 \text{ nm}$. This P3HT:PCBM ratio, spinning speed and solvent combination exhibited the best performance amongst different combinations investigated. The P3HT:PCBM layer was then annealed at 100°C to form the bulk heterojunction active layer for the OPV. In the as-deposited P3HT:PCBM active layer, P3HT crystallites needed for efficient mobility and charge transport within the active layer were not adequately formed because of the fine dispersion of PCBM [39]. The annealing of the active layer was indispensable for the favorable phase segregation

while also enabling P3HT crystallite formation. This leads to better charge transport and thus optimizes device performance [14, 30, 82].

Molybdenum oxide (MoO_3) was used as the electron blocking layer in inverted OPV structure for all the experiments. The MoO_3 was deposited from a MoO_3 source in the molecular chamber of the thermal evaporator. The pressure in the molecular chamber was kept under 10^{-4} Pa and 15 nm of MoO_3 was deposited. For inverted OPV, silver was deposited as the anode by thermal evaporation. 70 nm of silver electrode was deposited in the metal chamber kept under 10^{-4} Pa. The deposition of silver through a shadow mask defined the device area of 10.5 mm^2 . Once the device was completed, it was subjected to post-fabrication annealing at 150°C in nitrogen environment for morphology optimization [39].

Figure 3-7: Process flow of our inverted OPV device fabrication.

3.2.3 OPV device characterization

Current density-voltage (J - V) and incident photon-to-current conversion efficiency (IPCE) measurements under solar simulator were the main characterizations performed on the fabricated OPV devices. AM1.5 global reference spectrum, 25°C cell temperature and 100 mW/cm² irradiance are the standard operating conditions

used for OPV *J-V* measurements [20]. Hence, the solar simulator with AM1.5G filter was calibrated with optical powermeter to provide simulated light intensity of 100 mW/cm² and I-V characteristics of the fabricated OPVs were measured using a Keithley sourcemeter under ambient conditions. From the I-V characteristics obtained and the device area measurements, the open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF) and efficiency (η), which are the central OPV performance parameters, can be extracted.

IPCE spectra were measured using PV (photovoltaic) cell spectral response\EQE (external quantum efficiency) measurement system. IPCE is the ratio of number of output electrons to the incident photons measured for wavelengths ranging from 300 to 800 nm. The information is very useful as this metric gives efficiency at specific wavelengths. The integrated area of the spectra gives the measure of short circuit current density. The PV cell spectral response\EQE system has a xenon light source and triple grating monochromator for accurate measurements.

For surface studies of thin films, scanning electron microscopy (SEM) and contact angle studies were used. SEM images were obtained using SEM, JSM-5600LV, which can be used for obtaining precise topographical information. It is also equipped with energy-dispersive X-ray spectroscopy (EDS) for X-ray analysis useful for elemental and compositional analyses. For nanostructured layers such as porous structures, SEM images give an exact understanding of the density and size of these structures, this is imperative in analyzing the behavior of devices. Contact angle studies were carried out to evaluate the wettability and adhesion properties of the thin films. For OPV devices where the active layers are spin-coated on the underlying ZnO layer, determining these properties is crucial. Contact angle measurements were performed using a video contact analyzer, which provides accurate and straightforward contact angle measurements with the aid of computer imaging.

In cases where absorption/reflection spectra were required, PerkinElmer UV/Vis/NIR spectrophotometer system was used. The system provides wavelength range from 175 to 3300 nm and an integrating sphere for high precision reflectance and scattered transmittance measurements. The same characterization tool was also used for haze

factor studies. Haze factor indicates the light scattering capability of a layer and is measured as a ration between the diffuse and total transmission.

3.3 Results and Discussion

Experiments were performed to investigate the effect of porous ZnO structure on the OPV device parameters and performance. In the following subsections, the experimental results and influence of various processing parameters on the device performance are discussed and analyzed in detail.

3.3.1 Device structures

The porous ZnO OPV structure fabricated for these experiments was similar to the inverted structure discussed in the preceding section, with the exception of a porous ZnO layer between the intermediate ZnO layer and the active P3HT:PCBM layer (Fig. 3-8). The porous ZnO layer was spin-coated using the PEG mixed ZnO sol-gel prepared using the method described earlier. For reference, OPV structures without porous layer were also fabricated. The rest of the device structure was identical for the devices with both non-porous and porous ZnO electron selective layers.

Figure 3-8: Schematic representation of OPV devices with (a) non-porous ZnO layer and (b) porous ZnO layer, along with respective SEM images showing the porous and non-porous ZnO layer in the corresponding devices (scale bars - 20 μ m).

3.3.2 Effect of annealing temperature of porous ZnO layer

The ZnO layer spin-coated from PEG-added ZnO sol-gel has to be annealed to obtain the desired porous ZnO layer. The annealing temperature was varied to study the effect on the porous structure induced by PEG. For non-porous ZnO layer, the annealing temperature used was 150°C. In initial experiments, where an annealing temperature of 150°C was used for the PEG-added layer, the porosity was not completely manifested (refer to the SEM image in Fig. 3-9(a)). This may be due to residual traces of PEG left in the film as a result of using insufficient temperature for the anneal. Annealing temperature of upto 350°C is suggested for guaranteeing complete removal of PEG [76]. However, this temperature would drastically increase the chances of indium ions of ITO diffusing into the glass substrate, thus degrading the device performance [133]. On the other hand when the ZnO layer was annealed at a temperature of 250°C, the resultant layer quality was degraded and unusable as

can be seen from the SEM image of this layer in Fig. 3-9(c). At an intermediate annealing temperature of 200°C, evident porosity was obtained and pores were very well defined. Fig. 3-9(b) shows the SEM image of layer annealed at 200°C. Hence, for the porous layer used in these experiments, the ZnO:PEG layer was annealed at 200°C, while maintaining the integrity of ITO substrate.

(a)

(b)

(c)

Figure 3-9: SEM images of porous ZnO layer with layer annealed at (a) 150°C, (b) 200°C and (c) 250°C.

3.3.3 Impact of spinning speed of active layer

In the initial experiments, porous and non-porous devices were fabricated using the same process conditions that gave the best result for the reference sample. Three layers of ZnO were spin-coated and the active layer was coated from chlorobenzene solvent at a spinning speed of 2000 rpm. However, contrary to expectations, the porous devices showed degraded performance when compared to the reference samples. At least 24 devices of each type were studied. Fig. 3-10 shows the J - V curve of the best fabricated porous and non-porous devices and given below is also a table (Table 3-2) comparing the extracted device parameters of these devices.

Table 3-2: Device parameters of non-porous and porous ZnO OPV.

		V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
Non-porous ZnO OPV		0.627	8.937	0.60	3.15%
Porous ZnO OPV		0.610	6.688	0.61	2.49%

Figure 3-10: J - V characteristics of OPVs with porous and non-porous ZnO layer.

From the J - V characteristics in Fig. 3-10 and Table 3-2 it is clear that the open circuit voltage and the fill factor of the porous and non-porous devices are similar. The reason for the low efficiency of the porous devices lies in the lower short circuit current density of the porous structure. However, the porous structure promises to improve the short circuit current by better charge collection. One of the reasons for this contradictory behavior could be the unsatisfactory filling of the pores.

In using the porous ZnO structure, one of the main factors that can ensure the promised enhancement in device performance is the adequate filling of the pores with the active layer material. As it is evident that, in addition to the pore size, the spinning speed of the active layer material also has an impact on filling of pores. Thus, systematic experiments were carried out to study the effect of the spinning speed on the device performance. Slower speeds (800-1000 rpm) can lead to better filling of the porous structure. Slower spinning speeds will also lead to coating of thicker active films, which can in turn allow for better absorption; however, on the downside thicker films translates to higher series resistance and longer charge

transport distances, which can result in lesser charge collection and, hence, poorer device performance [133]. Due to this, active layer thickness is usually maintained at <200 nm for OPV structures. However, in the case of porous structure, the improved penetration, which comes with the slower spinning speed, may mitigate some of the ill effects of the thicker films.

To verify this claim, experiments were performed by varying the spinning speed for active layer coating. For the reference samples, the slower spin-coating (thicker active layer) leads to devices with degraded performance (Fig. 3-11(a)). However, for the porous devices, the reduction in spinning speed allows for a marked improvement in performance (Fig. 3-11(b)).

(a)

(b)

Figure 3-11: J - V characteristics of OPVs with (a) non-porous ZnO layer and (b) porous ZnO layer, with active layer coated at different spinning speeds (at 2000 rpm and 800-1000 rpm).

Table 3-3 lists the extracted device parameters of these devices. The enhanced performance of porous structured device with active layer coated at slower speed can be attributed to the improved penetration of active layer material, which leads to better charge collection, complementing the increased absorption in the thicker active layer.

Table 3-3: Device parameters of non-porous and porous ZnO OPV with active layer spin-coated at different spinning speeds (at 2000 rpm and 800-1000 rpm).

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
Non-porous ZnO OPV (2000 rpm)	0.627	8.937	0.60	3.15%
Non-porous ZnO OPV (800-1000 rpm)	0.590	9.275	0.38	2.07%
Porous ZnO OPV (2000 rpm)	0.610	6.688	0.61	2.49%
Porous ZnO OPV (800-1000 rpm)	0.617	9.693	0.59	3.50%

3.3.4 Effect of PEG concentration

To study the effect of PEG concentration on the porous structure and, hence, on the device performance, ZnO sol-gel solutions with varying PEG concentrations were used to spin-coat porous ZnO layer. The ZnO:PEG ratio was varied from 2:1 to 6:1 to investigate the effect on distribution of pores, pore size and performance of the resultant OPV devices. From the experiments, it was observed that the ZnO:PEG ratio above 5:1 was too minute to result in sufficient porosity in the ZnO layer and performance of such devices was comparable to the reference non-porous sample. ZnO:PEG ratio below 3:1 also was found to be unsuitable as they have an overconcentration of PEG (Fig. 3-12). In such cases the excess PEG, instead of aiding in porous structure formation, conglomerates to form PEG precipitates, which adversely affects the OPV device performance [135]. Hence, for these experiments, ZnO-to-PEG ratio of 3:1, 4:1 and 5:1 were utilized.

Figure 3-12: SEM image of porous ZnO layer using ZnO:PEG ratio 2:1.

To study the porous structure induced by the PEG, scanning electron microscopy (SEM) studies were carried out. ITO substrates were coated using ZnO sol-gel with ZnO:PEG ratios of 3:1, 4:1 and 5:1 and the SEM images were obtained for these samples. Fig. 3-13 shows the SEM images of porous ZnO layers with different ZnO:PEG ratios. From the images it can be seen that the concentration of PEG in the solution has marked influence on the resultant porous layer.

(a)

(b)

(c)

Figure 3-13: SEM images of porous ZnO layer using ZnO:PEG ratios of (a) 3:1, (b) 4:1 and (c) 5:1 (all scale bars are 20 μ m).

From Fig. 3-13, we can observe that the pore size and density of distribution of pores increases with decreasing ZnO:PEG ratios. The pore sizes were 4-18 μ m, 3-8 μ m and 2-4 μ m for ZnO:PEG ratios of 3:1, 4:1 and 5:1. The distribution of pores also increases with the decrease in ZnO:PEG ratio as can be seen from the SEM images. The sample with ZnO:PEG ratio of 4:1 seems to have the best defined pores. Samples with ZnO:PEG ratios of 3:1 have shallower pores, which are less well-defined and appear to have an PEG precipitation around the pores.

OPV devices with porous ZnO electron selective layer with ZnO:PEG ratios of 3:1, 4:1 and 5:1 were fabricated for studying the effect of porous structure on OPV device performance. Influence of active layer spin-coating speed for devices with all different ZnO:PEG ratios were examined. Current density-voltage characteristics of porous ZnO OPV devices with active layer spin-coated at 2000 rpm are presented in Fig. 3-14. From the resultant *J-V* characteristics, the performance parameters of OPV, namely V_{oc} , J_{sc} , FF and PCE, were extracted and listed in Table 3-4. From the results, it is evident that this active layer spinning speed is inadequate for satisfactory pore filling at all three ZnO:PEG ratios. Hence, the slow spinning speed of 800-1000 rpm is used for all further experiments.

Figure 3-14: Current density-voltage (J - V) characteristics of OPVs having porous ZnO layer with different ZnO:PEG ratios and active layer spin-coating speed of 2000 rpm.

Table 3-4: Device parameters of porous ZnO OPV with different ZnO:PEG ratios and active layer coated at spinning speed of 2000 rpm.

ZnO:PEG ratio	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
2:1	0.586	5.917	0.55	1.92%
3:1	0.610	6.688	0.61	2.49%
4:1	0.601	6.230	0.58	2.15%

Along with porous ZnO OPVs, devices with non-porous ZnO layer were also fabricated as a reference. Current density-voltage measurements were performed on these devices (Fig. 3-15). The extracted device parameters are listed in Table 3-5. An analysis of these values and characteristics indicate that the devices with the porous ZnO layer using ZnO:PEG concentrations of 4:1 and 5:1 provide higher current density and efficiency compared to the non-porous device. Among all these devices, device with the ZnO:PEG ratio of 4:1 provides the best results with a current density of 11.34 mA/cm^2 and an efficiency of 4.07%, which is a 35% increase in current density and 30% increase in efficiency. There is an increase in the efficiency when the ZnO:PEG ratio is decreased from 5:1 to 4:1, which can be attributed to the increased pore size due to increase in PEG concentration (as can be seen from the SEM images). However, further decrease in ZnO:PEG ratio to 3:1 leads to deteriorated performance. From SEM images it can be observed that, for the ZnO:PEG ratio of 3:1, though the pores appear larger, they are less well-defined and traces of excess PEG are visible, affecting the device performance adversely.

Figure 3-15: Current density-voltage (J - V) characteristics of OPVs having porous ZnO layer with different ZnO:PEG ratios of 3:1, 4:1 and 5:1, together with the non-porous reference device.

Table 3-5: Device parameters of the best porous ZnO OPV with different ZnO:PEG ratios and non-porous reference device fabricated.

ZnO:PEG ratio	V_{oc} (V)	J_{sc} (mA/cm²)	FF	η
3:1	0.613	8.095	0.55	2.74%
4:1	0.632	11.338	0.57	4.07%
5:1	0.627	9.310	0.57	3.34%
Ref.	0.627	8.397	0.60	3.15%

To analyze the repeatability of performance by employing porous structure in ZnO electron selective layer, the efficiency was extracted from 24 devices for each ZnO:PEG ratio (Fig. 3-16(a)). The values symbolized in the box plot are shown in Fig 3-16(b). The trend of efficiency is evident from the figure with the ZnO:PEG ratio of 4:1 proving to be unsurpassed for OPV efficiency enhancement. The mean values of V_{oc} , J_{sc} and FF for porous OPV devices with ZnO:PEG ratio of 4:1 were 0.621 V, 9.29 mA/cm² and 0.55 respectively.

(a)

(b)

Figure 3-16: (a) Efficiency trend for different ZnO:PEG ratios extracted from 24 devices. (b) Values symbolized in the box plot.

Nanostructured ZnO layers can also provide additional hybrid junction between ZnO:P3HT, in addition to the P3HT:PCBM junction, which can add to the total current density[79]. To investigate the contribution of the junction formed by ZnO-P3HT on the final current density of the porous ZnO OPV, devices were fabricated without the addition of PCBM to the active layer mix and compared with porous and non-porous BHJ devices. The current density results are summarized in Table 3-6.

Table 3-6: Current densities of porous ZnO PV, non-porous ZnO PV and porous ZnO PV with pure P3HT.

ZnO:PEG ratio in pure P3HT samples	Porous with pure P3HT (mA/cm²)	Non-porous with P3HT:PCBM (mA/cm²)	Sum of Non- porous with P3HT:PCBM and porous with pure P3HT (mA/cm²)	Porous with P3HT:PCBM (mA/cm²)
4:1	-0.250	8.397	-8.647	-11.338
5:1	-0.107	8.397	-8.504	-9.310

The data shows, that though the ZnO:P3HT junction may contribute to the overall current density, it is not the sole major contributor.

Incident photon-to-current conversion efficiency spectra of the devices with different ZnO:PEG ratios were measured as described in the previous section and the IPCE spectra are presented in Fig. 3-17. The IPCE data follows the trend of short circuit current density and thus provides an additional support to the correlation between the porous structure and the device performance as discussed.

Figure 3-17: IPCE spectra of OPVs having porous ZnO layer with different ZnO:PEG ratios with the active layer coated at slow spinning speed (800-1000 rpm).

To understand the effect of PEG concentration on the ZnO layer characteristics, contact angle and absorption measurements were subsequently carried out. Contact angle measurements provide information on the quality of the layer under study in terms of wettability and adhesion properties. Layers with good wettability and adhesion have smaller contact angles. Hydrophilic surfaces have contact angles smaller than 90° . Samples were coated with non-porous ZnO layer and porous ZnO layers with the ZnO:PEG ratios of 3:1, 4:1 and 5:1 and water contact angle measurements were performed using a video contact analyzer. Table 3-7 lists the results of the contact angle measurements for these samples. From the data, it is evident that the contact angle is the lowest for the ZnO:PEG ratio of 4:1. This indicates that the wettability is most favorable for the ZnO:PEG ratio of 4:1. Good wettability ensures better adhesion of the subsequent active layer. For the ZnO:PEG ratio of 3:1, the wettability is substantially compromised and this may be due to the excess PEG present. This in turn affects the spin-coating of the active layer and can lead to degraded performance for the device employing the ZnO:PEG ratio of 3:1.

Table 3-7: Contact angle measurements of ZnO layer with different ZnO:PEG ratios.

ZnO:PEG ratio	Contact angle
3:1	81.9
4:1	59.4
5:1	64.7
Ref.	67.2

Active layer was spin-coated on porous samples with different ZnO:PEG ratios and absorption measurements were carried out. Absorption curves obtained from the

measurements performed on these samples are depicted in Fig. 3-18. As can be seen from the figure, the porous ZnO structure with the ZnO:PEG ratio of 4:1 shows higher absorption at all the wavelengths. The absorption profile of the sample with the ZnO:PEG ratio of 3:1 is markedly lower from the rest of the characteristics. As can be seen from the contact angle measurements in Table 3-7, sample with the ZnO:PEG ratio of 3:1 has the lowest wettability. The increase in the PEG concentrations in the porous ZnO layer with the ZnO:PEG of 3:1, left traces on the sample (as can be seen in Fig. 3-13(a)) and affected the spin-coating of active layer and, hence, its absorption. From both measurements, the ZnO:PEG ratio of 4:1 is found to be the most ideal for the porous ZnO layer. The contact angle and absorption results of the samples can thus be correlated to the device performance.

Figure 3-18: Absorption spectra of OPVs having porous ZnO layer with different ZnO:PEG ratios with the active layer coated at slow spinning speed (800-1000 rpm).

3.3.5 Haze factor studies on porous ZnO layer

As aforementioned, employing porous ZnO layer in OPV leads to notable improvement in performance and this may be mainly due to light trapping, increasing

absorption and enhanced surface area, interfacial contact and charge collection by sufficient pore-filling. The pores induced by PEG in the porous ZnO structure can act as incident light scattering centers. Fig. 3-19 shows the schematic of how the micropore in porous ZnO layer can act as scattering centre. This scattering can lead to improved absorption which would further enhance the device performance. This can be verified using haze factor measurements performed on porous and non-porous ZnO coated ITO samples.

Figure 3-19: Schematic of micropore acting as scattering centre in porous ZnO OPV.

Total and diffused transmissions were measured using a PerkinElmer UV/Vis/NIR spectrophotometer system. To measure the diffused transmittance, the configuration of the integrating sphere has to be changed [158]. In routine transmission measurements, the reflection port is fitted with the white reflectance standard to collect all transmitted light to obtain the total transmission measurement. For accurate measurements, the total transmission need to be first calibrated to the baseline with no sample present in the sample holder. The configurations used for total transmission measurements are illustrated in Fig. 3-20. Figs. 3-20(a) and 3-20(b) are the set-ups used for obtaining the baseline for calibration needed for total transmission studies.

Figure 3-20: Configuration for (a) the calibration for total transmission studies and (b) the total transmission measurements [158].

In the case of diffuse transmittance, the direct transmitted light is not included in the calculations. To achieve this, the white reflectance standard is removed from the reflection port of the integrating sphere setup so that the direct transmitted light is not accounted for by the integrating sphere in the calculations. As with total transmission studies, for accurate measurement of diffused transmission calibration needs to be performed with no sample present in the sample holder. The configurations used for diffused transmission measurements are illustrated in Fig. 3-21. As can be observed, for the diffused transmission calibration and the actual measurement, the white reflectance standard is removed to disregard direct transmission.

Figure 3-21: Configuration for (a) the calibration for diffused transmission studies and (b) the diffused transmission measurements [158].

From the transmission values obtained, the haze factor can be calculated as follows [158] for the wavelength range of interest:

$$\text{Haze} = [(T_4/T_2) - (T_3/T_1)] \quad (1)$$

where T_1 is the total transmittance data with no sample, T_2 is total data with the sample, T_3 is the diffused transmission data with no sample and T_4 is the diffuse with the sample.

To study the light scattering effects with the aid of haze factor of the porous samples, transmission measurements were carried out on ZnO-coated ITO samples following the set-up described above. Apart from the set-up, the rest of the measurement procedure is the same for obtaining the total and diffused transmission curves. Results of total transmission studies on the samples are shown in Fig. 3-22(a) and results of diffuse transmission studies in Fig. 3-22(b). The total transmission and diffused transmission are the highest for the porous ZnO layer with the ZnO:PEG ratio of 4:1 compared to devices with other porous and non-porous ZnO layers.

(a)

(b)

Figure 3-22: (a) Total transmission and (b) diffused transmission of OPVs with porous ZnO layer with different ZnO:PEG ratios and non-porous ZnO (reference device).

From the total transmission and diffused transmission results, the haze factor can be extracted for different samples. Fig. 3-23 shows the calculated haze factor results. The haze factor was the highest for the sample with the ZnO:PEG ratio of 4:1 and corroborates with the rest of the results. The increased scattering in the sample with the ZnO:PEG ratio of 4:1 leads to improved light trapping and absorption and, hence, aids in enhancing the efficiency compared to the reference non-porous OPV device.

Figure 3-23: Haze factor of OPVs with porous ZnO layer using different ZnO:PEG ratios and non-porous ZnO (reference device).

3.4 Summary

With the introduction of porosity in the ZnO electron selective layer of the inverted OPV, a marked improvement in the device performance compared to the non-porous reference device was observed; a current density of 11.34 mA/cm^2 and an efficiency of 4.07% have been obtained. The superior performance of this device can be attributed to the porous layer created and controlled using polyethylene glycol template with optimized ZnO:PEG ratio and active layer spin-coating speed. The porous ZnO layer acts as a scattering enhancer, thus providing increased light trapping. This role of porous layer has been substantiated by the device measurements and the layer characterizations performed. This efficient light trapping leads to increased absorption and, hence, to enhanced current density and eventually higher power conversion efficiency.

Chapter 4: Doped porous zinc oxide in electron selective layer of inverted organic photovoltaics

4.1 Introduction

In order to improve the electrical conductivity of the zinc oxide sol-gel layer, employed as the electron selective layer of OPV, without compromising the internal resistance, various doping methods for ZnO have been demonstrated [107, 108, 159-167]. The electrons from oxygen vacancies and the zinc interstitial sites are the source of ZnO conductivity. Upon doping, the dopant ions substitution at these interstitial sites leads to generation of free carriers, thus improving the electrical conductivity of the film. Doped ZnO films have found applications as photoconductors, and sensor elements [159]. ZnO interlayers doped with aluminum [108], cesium [161] and indium [165] have been also demonstrated to result in enhanced device performance in OPVs. The increased conductivity manifests as reduced internal resistance in OPV devices employing doped ZnO [161].

Compared with undoped ZnO, aluminum-doped ZnO, deposited from sol-gel, boasts 3 orders of magnitude increase in conductivity [108]. The conductivity reported for aluminum-doped ZnO and undoped ZnO are $2.35 \times 10^{-3} \text{ Scm}^{-1}$ and $2.22 \times 10^{-6} \text{ Scm}^{-1}$ respectively. This allows for the use of thicker electron selective layers, which are robust, ensures complete coverage along with low density of pinholes, and are thus attuned with large-scale printing of OPV. Undoped ZnO layers, with their inherent low conductivity, are usually incompatible for such large-scale deployment due to the thickness limitation imposed to keep the series resistance under check. Unlike undoped ZnO, the thickness of doped-ZnO layers can be increased without compromising the fill factor and, hence, the OPV device performance.

Cesium-doped ZnO OPV also exhibited three orders of higher conductivity compared to undoped ZnO while utilizing a water-based sol-gel approach and at a

lower annealing temperature facilitating the use of flexible substrates [161]. The conductivity reported for cesium-doped ZnO is $2.77 \times 10^{-3} \text{ Scm}^{-1}$. Indium-doped ZnO also demonstrated lower resistivity (35 Ω/square) and improved transmittance in comparison with undoped ZnO (42.3 Ω/square). Indium-doped ZnO prepared by using the sol-gel route has been demonstrated in inverted OPV [165].

From previous discussions, the benefits of nanostructured metal oxides mainly increase the interfacial area between the metal oxide and active layers, providing better charge collection and light trapping improving optical absorption, which have been well proven [100, 136]. Therefore, by combining doping and nanostructure formation on the interlayer, significant increase in OPV device performance should be achieved.

The use of cesium-doped (Cs-doped) TiO_2 nanostructure has been previously demonstrated in both OPV and OLED. The fabricated OPV showed improved open circuit voltage, short circuit current density and fill factor, resulting in enhanced device efficiency. The superior performance is attributed to better polymer/metal contact, electron extraction efficiency and hole blocking capabilities provided by the nanocrystalline Cs-doped TiO_2 interlayer [162]. The decreased conduction band level of Cs-doped TiO_2 presents a fine Ohmic contact and, hence, better electron efficiency while the deep valence band facilitates efficient hole blocking.

(a)

(b)

(c)

Figure 4-1: SEM image of (a) undoped TiO_2 layer and (b) Cs-doped TiO_2 layer. (c) J - V characteristics of OPV devices with and without Cs-doped TiO_2 .

The motivation behind the use of porous structure to replace the popular nanorod/nanopillar structures in metal oxides has already been discussed in chapters 2 and 3. Compared to such structures, porous layers can provide all the benefits of using nanostructures without the hassle of uneven surface topography; for uniform deposition of the subsequent active, intermediate and metal layers. In the previous chapter, the use of porous zinc oxide structure was demonstrated to be highly beneficial when applied to the electron selective layer of OPV. This prompted the interest in studying the combined effects of doping and application of porous microstructures in ZnO interfacial layer in inverted OPV devices.

To this end, in this chapter, the use of porous structure in indium-doped ZnO (IZO) and aluminum-doped ZnO (AZO) electron selective layers for poly(3-hexylthiophene) and phenyl-C61-butyric acid methyl ester (P3HT:PCBM) bulk heterojunction inverted organic solar cell was investigated. OPVs employing these layers show enhanced device performance compared to devices with both undoped ZnO layers and doped ZnO layers devoid of porous structures. As with the porous ZnO electron selective layer, the porous IZO and porous AZO electron selective layers act as efficient scattering layers within the respective OPV devices. This work

is published in A. Nirmal et al., Journal of Sol-Gel Science and Technology, 2016: p. 1-8. (DOI 10.1007/s10971-016-3999-y) [168], and this chapter is adapted from this journal publication (copyright granted by Springer).

4.2 Porous indium-doped ZnO (IZO) electron selective layer for OPV

4.2.1 IZO sol-gel preparation

ZnO sol-gel for ZnO electron selective layer in OPV was prepared by following method described elsewhere [104] and this has been used to form ZnO electron selective layer for all the previous devices. When preparing doped ZnO sol-gel, a dopant source was used along with the precursor during sol-gel formation, with the dopant concentration determining the doping level in the sol. For doping ZnO with indium, indium chloride was used as the dopant source, zinc acetate dihydrate was used as the precursor and anhydrous ethanol was used as the solvent. This solution was magnetically stirred at 80°C for 2 h before monoethanolamine was added as stabilizing agent followed by further stirring at 60°C for 12-15 h. The sol-gel thus prepared was used for spin-coating IZO layer.

The indium doping level can be controlled by modifying the dopant source concentration. There is always a maximum doping level that manifests as optimal device performance, after which any further increase in dopant concentration will lead to performance degradation. Initial increase in doping with successful substitution increases free carriers and, hence, conductivity while doping beyond the optimal threshold with no scope, for substitution leads to assimilation of impurities from dopant source, electron scattering and grain boundary barrier effects [159].

Previous studies reported on indium doped ZnO, also using indium chloride as the dopant source, investigated different doping levels (0 - 3 at.% indium doping) and

determined that indium doping at 1 at.% is the optimal doping level for applications such as electron selective layer in OPVs [165]. XPS spectra studies were done to study stoichiometry of the IZO film and it was found that the actual indium content was ~0.91%. IZO layer with this indium doping demonstrated the highest conductivity and the lowest work function, facilitating electron extraction, thus resulting in the highest short circuit current density among OPVs with IZO layer having different indium doping levels. Based on these results, the indium doping of 1at % was used for IZO of all the OPV devices under investigation.

The IZO sol-gel thus prepared was used to spin-coat electron selective layer for non-porous IZO reference OPV device. For inducing porosity, polyethylene glycol (PEG) was added to the as-prepared IZO sol-gel and magnetically stirred for a few hours to form a homogenous solution. As with the porous ZnO, the role of the PEG is to form an organic template to support IZO and assist in the formation of a porous structure by inducing a phase separation between the solvent and zinc oxide adsorbed on PEG [135]. The PEG-added IZO sol-gel was spin-coated as electron selective layer and upon annealing, porous structure was developed in the IZO layer. Varying the IZO:PEG ratio affects the pore size and distribution of pores. Such films were used to form the electron selective layer for the porous IZO OPV devices. The flowchart for non-porous and porous IZO sol-gel preparation is illustrated in Figs. 4-2(a) and 4-2(b).

Figure 4-2: Flowchart illustrating the sol-gel preparation method for (a) non-porous IZO and (b) porous IZO.

4.2.2 IZO OPV device fabrication

The OPV device structures fabricated for these studies (ITO/IZO/P3HT:PCBM/MoO₃/Ag) are sketched in Fig. 4-3. The device under study has a porous IZO layer as shown in the SEM image in Fig. 4-3(a) and the reference device with non-porous IZO layer is depicted in Fig. 4-3(b).

Indium doped tin-oxide on glass was used as the substrate for these experiments, too. IZO spin-coated from IZO sol-gel was used as the electron selective layer. For reference structure, the IZO sol-gel was spin-coated as it is and for the porous structure the PEG-added IZO sol-gel was spin-coated on ITO substrate. Upon subsequent annealing, porous ZnO layer was obtained for the sample coated with PEG-added IZO sol-gel. The rest of the processing was identical for both porous and non-porous structures. A 1:1 ratio of P3HT:PCBM (40mg/mL) in chlorobenzene solvent was used as the active layer and was spin-coated on the electron selective layer, followed by annealing at 100°C for 10 min. The samples were then transferred to the evaporator for the deposition of MoO₃ hole selective layer and silver electrode to complete the device fabrication. The fabricated devices were then subjected to post annealing in N₂ ambient at 160°C for 10 min.

Figure 4-3: Schematic representation of OPV devices fabricated along with SEM image of (a) porous IZO layer and (b) non-porous porous IZO layer.

4.2.3 Results and Discussion

J-V measurements, IPCE spectra, absorption/reflection spectra, haze factor measurements and contact angle measurements for fabricated devices were carried out as described in section 3.2.3.

OPVs with indium doped zinc oxide electron selective layers spin-coated at various speeds and annealed at a range of temperatures were studied and the device parameters extracted are listed in Table 4-1 and Table 4-2 respectively.

Table 4-1: Device parameters of OPV devices with different spin-coating speeds for IZO electron selective layer.

IZO layer spinning speed	V_{oc} (V)	J_{sc} (mA/cm²)	FF	η
2000 rpm	0.581	7.714	0.43	1.95%
2500 rpm	0.595	8.295	0.55	2.72%
3000 rpm	0.606	7.267	0.53	2.32%

Table 4-2: Device parameters of OPV devices with different annealing temperature for IZO electron selective layer.

IZO layer annealing temperature	V_{oc} (V)	J_{sc} (mA/cm²)	FF	η
150	0.595	8.295	0.55	2.72%
200	0.605	7.657	0.53	2.47%
250	0.606	7.267	0.49	2.14%

From these optimization studies, IZO layer processed at a spin-coating speed of 2500 rpm and an annealing temperature of 150°C was found to exhibit the best performance. Hence, these processing conditions were maintained for fabricating all IZO electron selective layers.

As with the devices employing ZnO interlayer, spinning speeds of the active layer also had to be optimized to ensure efficient pore-filling. Inadequate pore-filling can hinder optimal device performance by exaggerating the ill-effects of thicker active layer produced by slower spinning speed of the active layer. Investigations proved that slower active layer coating speeds (800-1000 rpm, spin-coating at 800 rpm for 18secs followed by 1000 rpm for 30secs) resulted in the better performance of porous IZO devices.

Table 4-3: Device parameters of OPVs with different spin-coating speeds for active layer.

Active layer spinning speed for porous IZO	V_{oc} (V)	J_{sc} (mA/cm²)	FF	η
800-1000 rpm	0.602	9.038	0.55	3.08%
2000 rpm	0.600	6.383	0.56	2.16%

Next the effects of PEG concentrations on the IZO layer were studied. The IZO:PEG ratios were varied from 2:1 to 6:1 to control the pore size by varying the PEG concentrations added to the as-prepared IZO sol-gel. Interestingly, similar to undoped ZnO layer, for ratios below 3:1, the pronounced PEG concentration causes undesirable precipitation on the IZO layer, which reduces the wettability of the layer. The subsequent spin-coating of active layer was thus affected. IZO:PEG ratios above 5:1 barely induces porosity and characterization results are similar to OPV devices with non-porous IZO layer. So, studies were confined to devices with IZO layer having IZO:PEG ratios of 3:1, 4:1 and 5:1. J - V characteristics of these porous devices are shown in Fig. 4-4. The extracted device parameters of these devices, V_{oc} , J_{sc} , FF and η are listed in Table 4-4. From the values it is clear that, as with porous ZnO devices, the IZO:PEG ratio of 4:1 exhibits the most favorable performance. Analysis given on the detailed characterization of porous ZnO devices with various

ZnO:PEG ratios discussed in the previous chapter should suffice to explain the results obtained for porous IZO devices using various IZO:PEG ratios as well.

Figure 4-4: Current density-voltage (J - V) characteristics of OPVs using IZO:PEG ratios of 3:1, 4:1 and 5:1 for IZO electron selective layer.

Table 4-4: Device parameters of OPV devices using IZO:PEG ratios of 3:1, 4:1 and 5:1 for IZO electron selective layer.

IZO:PEG ratio	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
3:1	0.585	7.581	0.54	2.48%
4:1	0.600	9.436	0.54	3.07%
5:1	0.601	8.295	0.55	2.72%

For the rest of the investigations, the IZO:PEG ratio of 4:1 was used to form the porous IZO devices. Together with OPV devices using non-porous and porous IZO electron selective layer, OPV device with a ZnO electron selective layer was also fabricated for comparison. The results of the best performing devices from all three categories were used for all further comparisons.

The J - V curves of ZnO, porous and non-porous IZO devices are presented in Fig. 4-5. The extracted device parameters (V_{oc} , J_{sc} , FF and PCE) are listed in Table 4-5. From the data of 24 samples, the mean values of V_{oc} , J_{sc} , FF and η for IZO porous OPV devices calculated were 0.59 V, 8.81 mA/cm², 0.53 and 3.01% respectively.

The doped-ZnO device gives higher short circuit current density and subsequently, a higher η compared to the OPV device having undoped ZnO interlayer. This can be attributed to the improved conductivity and, hence, better charge extraction provided by the indium-doping of ZnO.

The decrease in the work function of the IZO-doped layer, though beneficial, has adverse effect on the V_{oc} and FF of the device [165]. This results in higher leakage current, which affects the fill factor of the device and is seen as the low shunt resistance. The low electron injection barrier leads to high charge concentration of charges at the barrier which lowers V_{oc} . This can be observed in the device parameters listed in Table 4-5. However, the marked increase in the short circuit current density compensates for the slight decrease in the FF and V_{oc} and leads to overall improved performance of the doped-ZnO device.

Figure 4-5: Current density-voltage (J - V) characteristics of OPVs with porous IZO, non-porous IZO and non-porous ZnO electron selective layer.

Table 4-5: Device parameters of OPVs with porous IZO, non-porous IZO and non-porous ZnO electron selective layer.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
IZO Porous	0.600	9.436	0.54	3.07%
IZO Non-porous	0.595	8.295	0.55	2.72%
ZnO Non-porous	0.613	7.267	0.59	2.64%

Among all the three devices, the OPV device with porous IZO interlayer exhibits the best performance. Here, the influence of the porous structure comes into play. Porous structure, with its enhanced charge collection and incident light scattering effects, compliments the influence of the doped-ZnO layer such as improving the electrical conductivity and reducing the electrical resistivity of electron selective ZnO layer, further improving the short circuit current density.

The efficiency of OPV devices are heavily influenced by the type and quality of the interlayers used. These interlayers not only affect the energy level alignment but also the active layer morphology, recombination, charge collection efficiency and device stability [28, 118, 119]. Though there is an increase in performance of OPV device with porous IZO layer when compared to OPV device with non-porous IZO and OPV device with ZnO layer, this percentage of increase is less compared to the results of OPV device with porous ZnO layer with optimal ZnO:PEG ratio of 4:1 (Table 3-5) . However, it needs to be noted that the processing conditions used for present and previous studies were optimized for the IZO layer and ZnO layer respectively and hence are different and doesn't allow for a direct comparison. The lower spin speeds used for the IZO layers results in a thicker layer which may lead to higher series resistance consequently adversely affecting the J_{sc} and FF [119]. Contact angle studies were performed using video contact analyzer to determine the wettability and adhesion properties of the porous IZO thin films. Smaller contact angles are indicative of better wettability and adhesion [22, 104]. Porous IZO had a contact angle of 68.8° . Porous ZnO with optimal ZnO:PEG ratio of 4:1 has a contact angle of 59.4° (Table 3-7). The lower wettability of porous IZO indicates that the consequent spin coating of active layer will be affected. The wettability of the interlayer affects the active layer film morphology and this in turn has an impact on the absorption, charge dissociation and transport and thus on the efficiency of the fabricated devices [28].

Scanning electron microscopy studies carried out on the IZO layer using IZO:PEG ratios of 3:1, 4:1 and 5:1 are shown in Fig. 4-6. Upon addition of PEG to the IZO sol-gel, porosity is induced in the resultant spin-coated IZO layer. The pore size is influenced by the IZO:PEG ratio. From the SEM images the density difference in the

distribution of pores for the different IZO:PEG ratios is clearly visible. The pore sizes were 3-7 μm , 5-6 μm and 3-4 μm for ZnO:PEG ratios of 3:1, 4:1 and 5:1. The porosity is clearly visible and the pores are well defined for the IZO:PEG ratio of 4:1.

Figure 4-6: SEM images of the porous IZO layers using IZO:PEG ratio of (a) 3:1, (b) 4:1 and (c) 5:1.

Normalized IPCE spectra of the devices with porous and non-porous IZO electron selective layers are presented in Fig. 4-7. Measurements were performed on the completed OPV devices. The IPCE is higher for the porous IZO device compared to that of the non-porous IZO device; this is in agreement with short circuit current trend of these devices.

Figure 4-7: Normalized IPCE spectra of OPVs with porous IZO and non-porous IZO (IZO ref.) layer.

Absorption measurements performed on the porous and the non-porous IZO layers are presented in Fig. 4-8. Samples with the porous IZO and the non-porous layers were prepared and P3HT:PCBM BHJ active layer was spin-coated on these samples for absorption measurements. As can be seen from Fig. 4-8, the porous IZO structure using ZnO:PEG ratio of 4:1 shows higher absorption compared to the sample with non-porous IZO layer. As with the porous ZnO layer, we hypothesize that the increased absorption exhibited by the porous IZO layer can be due to improved scattering provided by the porous structure. To verify this hypothesis, haze factor studies were carried out on the porous and the non-porous samples.

Figure 4-8: Absorption spectra of OPVs with porous IZO and non-porous IZO (IZO ref.) layer.

Textured conductive oxide layer can scatter light efficiently and the haze factor studies have been shown to quantify this scattering [169]. The total and diffused transmittance from the microstructured surface was measured using the setup elaborated in Chapter 3 and the haze factor was extracted as a ratio of these transmittance levels. These measurements were carried out on the porous and the non-porous IZO-coated ITO samples. From the results of the total transmission measurements and the results of the diffuse transmission ones, the haze factor results were extracted and are presented in Fig. 4-9. The haze factor was found to be higher for the sample using IZO:PEG ratio of 4:1 and corroborates with the rest of the results.

Figure 4-9: Haze factor of OPVs with porous IZO layer and non-porous IZO (IZO ref.) layer.

Therefore, the hypothesis that the pores in the porous structure serves as efficient centers for light scattering is verified. It is this efficient light scattering, which leads to increased absorption as seen in Fig. 4-8. Thus, the increased scattering in OPV device with porous IZO electron selective layer, results in improved light trapping by virtue of its porous structure and consequently enhanced efficiency compared to the reference OPV devices with non-porous IZO electron selective layer.

4.3 Porous aluminum-doped ZnO (AZO) electron selective layer for OPV

Aluminum is inexpensive, non-toxic and abundant and aluminum-doped ZnO shows three orders of magnitude higher conductivity compared to undoped ZnO [108, 170]. Aluminum-doped zinc oxide has been demonstrated in a-Si, CIGS and also in organic solar cells. AZO has also been successfully used in inverted OPVs [107, 170, 171]. Here, encouraged by the promising results of employing porous structure on indium-doped ZnO electron selective layer of inverted OPV, investigations were carried out to see if the porous structure could be used on differently doped-ZnO

electron selective layer to obtain similar results. With this aim, studies were carried out on the aluminum-doped ZnO porous and non-porous inverted OPV structures.

4.3.1 AZO sol-gel preparation

For doping ZnO with aluminum, aluminum hydroxide acetate was used as the dopant source, zinc acetate dihydrate was used as the precursor and anhydrous ethanol was used as the solvent [107]. The solution was then magnetically stirred for 2 h at 80°C before adding monoethanolamine as the stabilizing agent. The resultant sol was magnetically stirred at 60°C overnight before use. 1 at% of Al-dopant has been reported to give the best performance among OPV devices with AZO doped in the range between 0.5 and 2 at% [107]. The dopant concentration variation from 0.5 to 2 at% gave efficiencies ranging from 1.77 to 2.59% with the best efficiency at Al doping of 1 at%. Hence, the same was used for our experiments.

The AZO sol-gel thus prepared was used to spin-coat the electron selective layer for the non-porous AZO reference OPV device. For inducing porosity, polyethylene glycol (PEG) was added to the AZO sol-gel and magnetically stirred before spin-coating. Upon annealing, porous structure was induced in the sample spin-coated with PEG-added AZO sol-gel. Similar to OPV devices with the porous IZO layer, studies carried out using AZO:PEG ratios of 3:1, 4:1 and 5:1 and efficiencies of 2.59%, 3.51% and 2.84% was obtained. As can be seen from Table 4-6, AZO:PEG ratio of 4:1 provides the best device performance. Therefore, the AZO:PEG ratio of 4:1 was used for preparation of the porous AZO layer for further investigations.

Table 4-6: Device parameters of OPV devices using AZO:PEG ratios of 3:1, 4:1 and 5:1 for AZO electron selective layer.

AZO:PEG ratio	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
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3:1	0.608	7.411	0.58	2.59%
4:1	0.612	9.660	0.59	3.51%
5:1	0.605	7.798	0.60	2.84%

The flowchart for the non-porous and porous AZO sol-gel preparation is presented in Figs. 4-10 (a) and (b).

(a)

Figure 4-10: Flowchart illustrating the sol-gel preparation method for (a) the non-porous AZO and (b) the porous AZO.

4.3.2 AZO OPV Device fabrication

The OPV device structures fabricated for these studies (ITO/AZO/P3HT:PCBM/MoO₃/Ag) are sketched in Fig. 4-11. The reference structure has a non-porous AZO layer as shown in the SEM image in Fig. 4-11(b) and the device with the porous AZO layer is depicted in Fig. 4-11(a). Apart from the electron selective layer, the rest of the OPV structure and processing conditions were identical with that used for the IZO electron selective layer experiments; namely, the ITO on glass substrate, P3HT:PCBM in chlorobenzene solvent as the active layer, MoO₃ as the hole selective layer and silver as the top electrode respectively.

For the electron selective layer, AZO spin-coated from AZO sol-gel was used. For the reference structure, the AZO sol-gel was spin-coated as it was before annealing

and for the porous structure, the PEG-added AZO sol-gel, using AZO:PEG ratio of 4:1, was spin-coated on the substrate followed by annealing to induce porosity. The rest of the processing was identical for both the porous and non-porous structures. The P3HT:PCBM active layer was spin-coated, followed by annealing at 100°C for 10 min. The samples were then transferred to the evaporator for the deposition of MoO₃ hole selective layer and silver electrode, which were then subjected to post-annealing in N₂ ambient at 160°C for 10 min.

Figure 4-11: Schematic representation of OPV devices with (a) the porous AZO layer and (b) the non-porous porous AZO layer, along with respective SEM images showing the porous and non-porous AZO layer in the corresponding devices.

4.3.3 Results and Discussion

J-V measurements, IPCE, EQE, absorption, contact angle, transmission and the haze factor measurements were performed using the same methods as for the porous and non-porous IZO electron selective layer OPV devices.

To compare the performance of the aluminum-doped ZnO with the undoped ZnO electron selective layer, the OPV device with an undoped ZnO electron selective layer was also fabricated under similar processing conditions. Current density-voltage measurements were then performed on these OPV devices fabricated with porous and non-porous AZO devices and non-porous undoped ZnO layers. Fig. 4-12 shows the resultant current density-voltage (J - V) curves of the ZnO, the porous and the non-porous IZO devices. From these measurements, the OPV device performance parameters such as V_{oc} , J_{sc} , FF and PCE were then extracted (Table 4-7). From the data of 24 samples, the mean values of V_{oc} , J_{sc} , FF and η for IZO porous OPV devices calculated were 0.61 V, 8.78 mA/cm², 0.58 and 3.48% respectively.

As anticipated, compared to the OPV device with the undoped ZnO interlayer, the aluminum-doped ZnO OPV device gives higher short circuit current density and subsequent higher efficiency. The three orders of magnitude higher conductivity provided by aluminum doping was responsible for this outcome. Even with aluminum-doped ZnO, addition of the porous structure affects the OPV device performance favorably. The ability of the porous structure to serve as a light scattering layer, with its enhanced charge collection, thus seems to be independent of the doping agent used.

Figure 4-12: Current density-voltage (J - V) characteristics of OPVs with the porous AZO, non-porous AZO and non-porous ZnO electron selective layer in OPV.

Table 4-7: Device parameters of the porous AZO, non-porous AZO and non-porous ZnO electron selective layer in OPV.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
AZO porous	0.612	9.660	0.59	3.51%
AZO non-porous	0.612	8.200	0.57	2.87%
ZnO non-porous	0.610	7.267	0.59	2.64%

As seen in section 4.2.3, similar to porous IZO, the device performance of OPV with porous AZO layer is lower compared to porous ZnO layer and the discussions presented there is valid for porous AZO OPV device also.

To verify the existence of porosity in the AZO layer, SEM studies were carried out on the samples spin-coated with the AZO sol-gel using the AZO:PEG ratio of 4:1. The SEM images of the porous AZO layers are shown in Fig. 4-13. From these images, it can be seen that the AZO:PEG ratio of 4:1 has induced sufficient porosity with well-defined pores.

Figure 4-13: SEM images of porous AZO layer using AZO:PEG ratio of 4:1.

IPCE spectra measurements were then performed on the completed OPV devices with the porous and non-porous AZO electron selective layer. The normalized IPCE curves of these devices are presented in Fig. 4-14. As projected, in corroboration with the device performance results, the IPCE is enhanced for the porous AZO device compared to that of the non-porous IZO device. Thus, the OPV device with the porous AZO layer has higher short circuit current density and higher IPCE among the OPV devices fabricated.

Figure 4-14: Normalized IPCE spectra of OPVs with the porous AZO and non-porous AZO (AZO ref.) layer.

For absorption measurements, samples with the porous and the non-porous AZO layers were prepared and a P3HT:PCBM BHJ active layer was spin-coated under the same conditions used for the completed devices. Absorption curves of these samples are presented in Fig. 4-15. As with IZO samples, the porous AZO structure using the AZO:PEG ratio of 4:1 shows higher absorption compared to the sample with the non-porous AZO layer and if the haze factor measurements concur, then the enhanced absorption in the porous AZO sample can also be attributed to the improved scattering provided by the porous structure.

Figure 4-15: Absorption spectra of OPVs with the porous AZO and non-porous AZO (AZO ref.) layer.

For computing the haze factor, the total and diffused transmittance from the porous and the non-porous AZO-coated ITO samples were measured. From the results of total transmission studies and the results of diffused transmission characterizations, the haze factor results were extracted as their ratio. The resultant haze factor curves are presented in Fig. 4-16. Samples with the porous AZO layer exhibited a higher haze factor and this result provides justification for the claim of higher scattering provided by the porous structure, which affords higher absorption in the OPV active layer and results in improved short circuit current density and hence, a higher PCE.

Figure 4-16: Haze factor of OPVs with the porous AZO and non-porous AZO (AZO ref.) layer.

4.4 Comparison between IZO and AZO porous ZnO electron selective layer for inverted OPV devices

As observed in the previous sections, the porous doped-ZnO electron selective layer with indium and aluminum doping agents are both efficient light scattering layers and have aided in improving the overall performance on the inverted OPV device. In this section, the device performance and characterization results of these differently doped-ZnO OPV devices are compared to try to understand the influence of the doping agents. This comparison is valid as the thickness of both AZO and IZO layers are both ~50nm.

The J - V curves and the extracted device parameters for the OPV devices with IZO and AZO porous electron selective layers are shown in Fig. 4-17 and Table 4-8, respectively. From these results, it is clear that the current density and efficiency are

higher for the AZO device. The V_{oc} and FF are also less diminished for the AZO OPV device devcompared to the IZO OPV device.

Figure 4-17: Current density-voltage (J - V) characteristics of OPVs with the porous IZO and porous AZO electron selective layer.

Table 4-8: Device parameters of the porous IZO and porous AZO electron selective layer in OPV.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
IZO porous	0.600	9.436	0.54	3.07%
AZO porous	0.612	9.660	0.59	3.51%

The sol-gel and PEG ratio was maintained at 4:1 for both the indium- and the aluminum-doped ZnO layers. However, the density of distribution of pores induced appears to be slightly more for the AZO layer compared to that induced in the IZO layer. The typical SEM images of the porous IZO and the porous AZO layers are shown in Fig. 4-18.

Figure 4-18: SEM images of (a) the porous IZO layer and (b) the porous AZO layer, both using a doped-ZnO:PEG ratio of 4:1.

The haze factor results are also slightly different for the porous IZO and AZO devices, as can be seen from Fig. 4-19. The porous structure of the samples is what affects the haze factor studies. The slightly increased density of distribution of pores in the AZO sample has resulted in a better haze factor and hence, higher light scattering.

Figure 4-19: Haze factor of OPVs with the porous IZO and the porous AZO layer

The difference in the OPV device performance between the porous IZO and AZO is also reflected in the absorption curves. Absorption curves of these two types of devices are presented in Fig. 4-20. The absorption of the AZO porous layer is higher than that of the IZO porous layer. This is in agreement with the higher light scattering as predicted by the haze factor comparisons.

Figure 4-20: Absorption spectra of OPVs with the porous IZO and AZO layers.

The difference in absorption curves can thus be partly due to the difference in porous structure between the two layers (Fig. 4-17). The wettability of the doped-ZnO layer also has a role to play, as it affects the spin-coating and adhesion of the active layer and hence, affects the device performance. Contact angle measurements provide information on the quality of the layer under study in terms of wettability and adhesion properties. Layers with good wettability and adhesion have smaller contact angles. Table 4-8 lists the results of the contact angle measurements for the porous IZO and AZO layers using doped-ZnO:PEG ratio of 4:1. From Table 4-9, it can be seen that the wettability is most favorable for the porous AZO. For the porous IZO,

the wettability is lower and this can affect the subsequent active layer spin-coating and can in turn affect the absorption.

Table 4-9: Contact angle measurements of IZO and AZO layer using doped-ZnO:PEG ratio of 4:1.

	Contact angle (°)
Porous IZO	68.8
Porous AZO	61.4

The marginally better porous structure, layer wettability and resultant film quality are the advantages of the AZO porous layer compared to the porous IZO layer. This is manifested as improved absorption, better haze factor and better current density. Hence, between the indium-doped and aluminum-doped porous ZnO electron selective layers, the OPV device with the latter interlayer gives slightly better device performance.

4.5 Summary

As described in the previous chapter and this chapter, the method of inducing porosity by the addition of PEG to a metal oxide sol-gel has proved to be an excellent route to enhanced light scattering and absorption. Earlier studies have been reported wherein OPV devices employing ZnO nanopillars and nanorods lead to increased light absorption by the scattering provided by the nanostructures. The enhanced performance of such OPV devices was also partly credited to better charge collection provided by the ZnO nanopillar and nanorods. These nanostructures served as current pathways for the collection of dissociated electrons and enables direct transport to the electrode. However, the creation of such structures was highly process intensive. Unlike ZnO nanopillar/nanorod structures, the increased absorption exhibited by porous layers can be attributed to the improved light scattering provided by the porous structure. In addition, PEG-induced porosity has the advantage of ease of fabrication. In this chapter PEG-induced porosity is shown to be a transferable technique for power conversion efficiency enhancement in OPV. Here, the porous structure was successfully demonstrated on two differently doped-ZnO electron selective layers, namely indium-doped ZnO layer and aluminum-doped ZnO layer, with very similar results. Though the performance improvement factor varies with the doping by virtue of the quality of the resultant porous film, the enhancement of PCE performance of porous OPV device in comparison with non-porous OPV device is indisputable in both indium-doped ZnO layer and aluminum-doped ZnO cases. This technique can be used for other metal oxides for both inverted and regular structure of OPV and can also prove to be compatible with different active layer materials. Porous metal oxide layers thus provide efficient scattering centers, increase absorption in the active layer to provide improvement in the resulting OPV performance while at the same time being an inexpensive and highly portable class of materials compatible with large-scale manufacturing process for OPV.

Chapter 5: Zinc oxide photonic crystal in electron selective layer of inverted organic photovoltaics

5.1 Introduction

Numerous approaches have been demonstrated in the attempt to improve the light absorption in active layers of organic photovoltaics. The direct route of increasing the active layer thickness to improve the incident light absorption is not an option for OPVs due to the low mobility of charge carriers within the active layer [19, 83, 89, 172]. Thicker active layers lead to increased series resistance, which adversely affects the device performance. Hence, other avenues need to be explored. Some studies have involved modifying the topography of the substrate or the interlayers of the OPV. These include V-shaped and microprism substrates, substrates on textured films, modified electrodes and buried nanoelectrodes among many others [53, 54, 98, 136, 173-179]. A few attempts have also been made in creating structures within the active layer itself as in the case of active layer embossing [53, 180]. All these structures revolve around the basic idea of inducing light trapping, thereby increasing the optical path length of the incident light and, thus, resulting in better light absorption.

The use of photonic crystal (PC) structure can also achieve this aim of improving the absorption in the active layer of OPVs. PC structures have a periodic pattern on a layer, with the pattern filled in with a material of a differing refractive index. This ordered structure together with the alternating high and low refractive index structure allows manipulation and localization of incident light, resulting in efficient light trapping over a wide wavelength range [138]. PC structures provide enhanced light trapping by virtue of light diffraction and optical bandgap properties [181]. These structures can also raise the absorption in the active layer by increasing the optical path length of incident light by way of light scattering and optical interference [182]. Photonic crystals have already been applied successfully in inorganic solar cells

[183-187]. With its highly ordered periodic nanostructures, PCs have provided drastic improvement in incident light absorption in these solar cells, which translates to high power conversion efficiencies for the devices.

The transfer of photonic crystal technology to organic solar cells is beneficial since in addition to the efficient light trapping effect, the use of PCs can increase the light absorption at the band edge of polymers (around the red/NIR region of spectra) [175]. A theoretical study was carried out on P3HT (poly(3-hexylthiophene)) photonic crystal-like structure embedded in PCBM (phenyl-C61-butyric acid methyl) in an OPV device [188]. This structure was shown to enable coupling of slow Bloch modes into the active layer (Fig. 5-1(a)). The result was a 35.6% improvement in the optical absorption in the 600-700 nm wavelength range (Fig. 5-1(b)).

Figure 5-1: (a) Active layer structure and (b) absorption and mode density of P3HT/PCBM blend vs. P3HT PC in PCBM [188].

Application of photonic crystal structure in OPV is sparse [138, 182, 186]. There has been a report of photonic crystal structure formed on BHJ active layer of a regular OPV device [186]. Fig. 5-2 shows the device structure, the photograph and the SEM image of the OPV device fabricated. This structure used PEDOT:PSS as the hole transport layer and a blend of P3HT and TDPTD (Poly(3-(2-methyl-2-hexylcarboxylate)) as the active layer. Nanocrystalline ZnO forms the electron selective layer. The BHJ with photonic crystal structure is evident in the SEM image.

A 30% increase in current density was observed for this device compared with featureless BHJ layer. This was attributed to the optical interference provided by the resonant structures of the PC geometry.

(a)

Figure 5-2: (a) Device structure, photograph and (b) SEM and cross-sectional images of OPV devices with planar and photonic crystal embossed BHJ [186].

Formation of PC structure on active layer has its drawbacks. Such imprinting can raise contamination issues, since the OPV performance is very sensitive to active layer contamination. Additionally, the alternating thick and thin layers of the resultant active film can adversely affect the charge transport and collection [175].

This also encourages recombination of carriers. An alternative, to utilize the benefits offered by PC structure in inverted OPV, is to apply such structure either on the substrate or on the electron selective layer.

A ITO/TiO_x/P3HT:PCBM/WO₃/Ag inverted OPV device with photonic TiO₂ crystal structure layer has also been demonstrated [182]. Fig. 5- 3 shows the SEM images of the TiO₂ PC layer and of the OPV device employing this layer. Compared to featureless TiO₂ layer, the PC device showed enhanced device performance on account of the enhanced absorption offered by the TiO₂ PC structure.

Figure 5-3: Cross-sectional SEM images of (a) TiO₂ PC on ITO and (b) SEM inverted OPV device with TiO₂ PC electron selective layer [182].

In this chapter, the use of PC structure in the poly(3-hexylthiophene) and phenyl-C61-butyric acid methyl ester (P3HT:PCBM) bulk heterojunction inverted organic solar cell, by employing such a structure in electron selective ZnO layer, was investigated. The low refractive index ZnO PC structure when conformally coated with P3HT:PCBM active layer, provides the index contrast necessary for the optical

interference in the PC and, thus, aids in increasing the optical path length of incident light and subsequently enhances absorption in the active layer.

5.2 Experiments

5.2.1 Photonic crystal structure formation

The PC structure used in the experiments was obtained by a method similar to that discussed in literature [182]. This method of PC layer formation has been demonstrated on active layers of both regular and inverted OPVs and has been proven to be compatible with large-scale fabrication and also with a range of materials [182]. The process is illustrated in Fig. 5-4.

The first step in the process is to prepare the plastic mold, which is used to create the ZnO PC layer. A master template is created with the desired PC pattern. Elastomer like PFPE (perfluoropolyether) is generally used to form the plastic mold [189]. The molding elastomer is poured on the master template and allowed to form the plastic mold. The plastic mold thus has the inverted photonic crystal pattern. Once satisfactorily produced, this plastic mold can then be used to form PC structure on any compatible material by contact printing.

For forming ZnO PC structure in electron selective layer of inverted OPV, ultrasonically cleaned ITO on glass was used as a substrate. ZnO precursor solution was dropped on this substrate, while ensuring that the surface was completely covered. The plastic mould with desired structure was placed on the precursor coated substrate and firmly held in place to transfer the photonic crystal structure to the precursor layer. The sample with the plastic mold was then placed on a hot plate for annealing. This was required for the successful transfer of the PC design from the mold to the ZnO layer (period = 600 nm, height = 200 nm and radius = 200 nm). The plastic mold was then carefully peeled back to reveal the periodic ZnO structures on the ITO substrate.

Figure 5-4: Flowchart of the method used for preparation of the photonic crystal structure on ZnO.

Fig. 5-5 shows the photographs of the ZnO photonic crystals formed on ITO coated glass using the method discussed above. The iridescence, which is a characteristic of photonic crystal structure, is clearly visible in the photograph.

Figure 5-5: Photographs of the ZnO photonic crystal structure formed on ITO coated glass.

The SEM image of the ZnO photonic crystal fabricated is shown in Fig. 5-6.

Figure 5-6: SEM image of the ZnO photonic crystal structure fabricated (scale bar is 1 μ m).

5.2.2 OPV device fabrication

The inverted OPV device structures used for these studies (ITO/ZnO:PC/P3HT:PCBM/MoO₃/Ag) are illustrated in Fig. 5-7. Two types of devices were fabricated on ultrasonically cleaned ITO coated glass substrate. The first type of devices used a planar ZnO electron selective layer and this group was used as reference devices. The ZnO layer for these devices was spin-coated from a ZnO sol-gel prepared as mentioned in detail in the previous chapters by using zinc acetate dihydrate as the precursor, anhydrous ethanol as the solvent and monoethanolamine as the stabilizing agent. The second type of devices had a ZnO PC structure in their electron selective layer. A 1:1 ratio of P3HT:PCBM (40 mg/mL) in chlorobenzene solvent was used as the active layers for both type of devices. The active layers were spin-coated on the electron selective layer. Subsequent annealing was performed at 100°C for 10 min to optimize the active layer morphology. The samples were then transferred to the evaporator for the deposition of MoO₃ hole selective layer. Silver electrode was deposited through shadow mask to define device areas. The completed OPV devices were then subjected to post annealing in nitrogen ambient at 160°C for 10 min.

Figure 5-7: (a) Schematic representation of the fabricated OPV devices. Illustration of (b) ZnO photonic crystal layer and (c) planar ZnO layer (reference device) used in the devices.

5.3 Results and Discussion

J-V measurements, IPCE spectra, absorption/reflection spectra, haze factor measurements and contact angle measurements for fabricated devices were carried out as described in section 3.2.3. In the following subsections the experimental results and effect of various parameters on the device performance of OPV devices with planar and photonic crystal ZnO layers are discussed and analyzed.

5.3.1 Effect of annealing on ZnO photonic crystal formation

In the initial photonic crystal experiments, the ZnO photonic crystal layer was directly imprinted on the ITO coated substrate before the rest of the device processing. *J-V* characteristics for these devices are shown in Fig. 5-8. Table 5-1,

shows the extracted device parameters for this ZnO PC device and reference OPV device with planar ZnO layer and is evident that the results are far from satisfactory.

Figure 5-8: *J-V* characteristics of OPV with the ZnO photonic crystal layer.

Table 5-1: Device parameters of OPV with the ZnO photonic crystal layer and reference OPV with planar ZnO layer.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
OPV with the ZnO photonic crystal layer	0.328	4.286	0.48	0.67%
Reference OPV with planar ZnO layer	0.613	7.267	0.59	2.64%

The OPV device with the ZnO PC did not show the promised enhancement in current density and also had extremely degraded open circuit voltage and low fill factor. The overall PCE was below 1%. This indicated an inherent flaw in the device fabricated. To understand the source of the performance degradation, a better understanding of the fabricated ZnO photonic crystal layer was necessary. Scanning electron microscopy studies were carried out to inspect the topography of the ZnO PC layer. SEM image of the ZnO PC layer on ITO is shown in Fig. 5-9.

Figure 5-9: SEM image of the initial ZnO photonic crystal layer on ITO substrate.

From the SEM image, it is clear that the ZnO PC layer is not well formed and barely recognizable, which explains the poor device performance. The incomplete formation of the photonic crystal layer led to an extremely rugged surface. This affects the subsequent spin-coating of active layer. Also, previous studies have reported that an exceptionally rugged interlayer such as this has an adverse effect on the OPV device, increasing the recombination, thus lowering the fill factor of the devices [133].

To obtain the desired ZnO PC layer, the PC layer formation process flow was reexamined and various parameters varied to investigate their influence on the final PC layer. From the investigations, the need for an additional baking step after the removal of the plastic mold was identified. The baking temperature was optimized to

200°C and the annealing time to 15-20 min. With the addition of this post-annealing step, a ZnO PC layer of satisfactory topography was obtained.

SEM image of the ZnO PC layer on ITO obtained after the annealing at 200°C for 15-20 min is shown in Fig. 5-10. The PC structure was well defined as can be seen from the image.

Figure 5-10: SEM image of the annealed ZnO photonic crystal layer on ITO substrate (scale bar is 1 μ m).

J-V measurements were performed on the OPV devices formed with the annealed ZnO PC layer. Compared to the previous un-annealed ZnO PC OPV device, the performance was greatly improved. *J-V* characteristics and the extracted device parameters of OPV devices with the post-annealed and the un-annealed ZnO PC layers are shown in Fig. 5-11 and Table 5-2, respectively.

Figure 5-11: J - V characteristics of OPVs with the un-annealed and annealed ZnO photonic crystal layer.

Table 5-2: Device parameters of OPVs with un-annealed and annealed ZnO photonic crystal layer.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
OPV with un-annealed ZnO photonic crystal layer	0.328	4.286	0.48	0.67%
OPV with annealed ZnO photonic crystal layer	0.507	6.599	0.44	1.46%

Therefore, the ZnO photonic crystal layer optimization markedly improved the short circuit current density. The manifestation of the PC layer properties is responsible for

this enhancement. The V_{oc} and the fill factor were also recovered for the annealed ZnO PC OPV device.

Based on the encouraging outcome obtained, the post-annealing step was added for the formation of ZnO PC layer for all the rest of the investigations. Reference OPV device with a planar ZnO electron selective was also fabricated for comparison with the ZnO PC device. Fig. 5-12 shows the J - V characteristics and Table 5-3, the extracted device parameters for these devices. Upon examining the results, we found that the V_{oc} and FF were still low compared to the planar ZnO layer and there was scope for improvement in the current density for ZnO PC device.

Figure 5-12: J - V characteristics of the OPV using the annealed ZnO photonic crystal layer and the reference OPV device with planar ZnO layer.

Table 5-3: Device parameters of the OPV using the annealed ZnO photonic crystal layer and the reference OPV device with planar ZnO layer.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
OPV with annealed ZnO photonic crystal layer	0.507	6.599	0.44	1.46%
Reference OPV with planar ZnO layer	0.613	7.267	0.59	2.64%

5.3.2 Effect of the underlying ZnO layer thickness

The photonic crystal structure was created on the sample coated with the ZnO precursor solution by applying manual pressure to the plastic mold. Hence, there was no means of ensuring a uniform thin ZnO layer below the photonic crystal. This layer is essential to ensure that the active layer does not come into direct contact with the ITO. To circumvent this issue, it was necessary that a robust, albeit thin film, of ZnO was already present on the ITO substrate before the sample was subjected to photonic crystal formation. With this objective, one layer of ZnO layer was spin-coated on the sample using the ZnO sol-gel used for the reference device. ZnO sol-gel was spin-coated on the ITO substrate at a spinning speed of 3000 rpm and was then subjected to annealing at 150°C for 20 min to obtain a crystalline layer of ZnO. ZnO photonic crystal layer was then formed on this sample in the method described previously.

Current density-voltage measurements were performed on the OPV devices with the ZnO photonic crystal structure and a thin ZnO underlying layer and also on the

reference device with planar ZnO layer. The resultant J - V characteristics are shown in Fig. 5-13.

Figure 5-13: J - V characteristics of the ZnO photonic crystal OPV with an underlying ZnO layer and the reference OPV with planar ZnO layer.

From J - V measurements, the device parameters were extracted (Table 5-4).

Table 5-4: Device parameters of the ZnO photonic crystal OPV with an underlying ZnO layer and the reference OPV with planar ZnO layer.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
ZnO PC OPV with underlying ZnO layer	0.554	7.421	0.45	1.87%
Reference OPV with planar ZnO layer	0.613	7.267	0.59	2.64%

From the J - V characteristics and Table 5-4, it can be seen that there is a slight improvement in the short circuit density. However, there is still room for improvement in the open circuit voltage of photonic crystal OPV device.

A uniform, homogenous and crystalline layer is imperative for the optimum performance of the device. A poor ZnO interlayer affects V_{oc} and FF and this in turn results in degraded efficiency of photonic crystal devices. In the case of the experiments performed here, the uniformity and coverage of thin ZnO layer may have been compromised during the photonic crystal structure formation.

As ZnO layer has a tremendous influence on the open circuit voltage of OPV devices a single layer of crystalline ZnO underlying layer may be insufficient to ensure a conformal and robust coverage of ZnO layer necessary for good device performance. To study this, underlying ZnO layers of different thicknesses were spin-coated on the ITO substrate. The J - V results are shown in Fig. 5-14 and the extracted device parameters are listed in Table 5-5.

Figure 5-14: J - V characteristics of photonic crystal OPVs with one and two underlying ZnO layers, together with the planar ZnO reference OPV.

Table 5-5: Device parameters of ZnO photonic crystal OPVs with one and two underlying ZnO layers, together with the planar ZnO reference OPV.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
ZnO PC OPV with 1 underlying ZnO layer	0.554	7.421	0.45	1.87%
ZnO PC OPV with 2 underlying ZnO layers	0.608	8.203	0.44	2.20%
Reference OPV with planar ZnO layer	0.613	7.267	0.59	2.64%

From the current density-voltage characteristics (Fig. 5-14) and the device parameters table (Table 5-5), it can be said that a thicker ZnO layer was robust enough to withstand the photonic crystal formation and also ensured a good coverage. This translated to a better open circuit voltage for the devices. The better ZnO layer also led to improved current density in the fabricated OPV device with ZnO PC.

5.3.3 Effect of spinning speed of the active layer

The OPV device with the ZnO photonic crystal was still found to lag behind the reference planar ZnO OPV in terms of device efficiency. One possible reason for the non-optimum device performance, especially the low fill factor could be the non-conformal active layer material filling of the photonic crystal structure [175]. The topography of the ZnO photonic crystal results in non-uniform thickness of active layer across the structure. Such deposition, especially overfill in the troughs,

translates to thick active layer in those areas resulting in increased series resistance, poor charge transport and efficiency degradation. Fig. 5-15 illustrates the deposition of active layer in such structures.

Figure 5-15: Schematic illustrating the deposition of active layer material on photonic crystal ZnO (adapted from [175]).

Conformal deposition of the active layer on the photonic crystal structure is necessary for ensuring optimum performance extraction from the active layer.

One of the parameters affecting the active layer deposition is the spinning speed used for coating the layer onto the ZnO PC structure. As seen in the preceeding chapters, for the porous ZnO-layer OPV devices, spin-coating the active layer at a slow spinning speed of 800-1000 rpm compared to a reference spinning speed of 2000 rpm proved to be extremely beneficial. This slow spinning speed aided in the satisfactory filling of the pores in the porous structure and aided in the marked improvement in the device performance. The benefits of using a porous structure could thus be completely exploited by employing a slower spinning speed for the active layer.

Hence, the influence of spinning speed of active layer on the performance of devices with ZnO photonic crystal layer was investigated. ZnO photonic crystal OPV with two layers of ZnO underlying layer and an active layer spin-coating speed of 2000 rpm was taken as the reference. Another set of ZnO PC OPV with the same process conditions except for a slower spinning speed of the active layer coating (800-1000 rpm) was also fabricated. Reference OPV device with a planar ZnO interlayer was also used for comparison.

J-V measurements were then performed on these devices and the resultant *J-V* characteristics are shown in Fig. 5-16. Device parameters extracted from the characteristics are listed in Table 5-6.

Table 5-6: Device parameters of ZnO photonic crystal OPVs with active layer spin-coated at 2000 rpm and 800-1000 rpm, together with the planar ZnO reference OPV.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
ZnO PC OPV (800-1000 rpm)	0.572	7.693	0.42	1.86%
ZnO PC OPV (2000 rpm)	0.608	8.203	0.44	2.20%
Planar ZnO reference OPV (2000 rpm)	0.613	7.267	0.59	2.64%

Figure 5-16: *J-V* characteristics of ZnO photonic crystal OPVs with active layer spin-coated at 2000 rpm and 800-1000 rpm, together with the planar ZnO reference OPV.

From the *J-V* characteristics (Fig. 5-16) and the device parameter list (Table 5-6), it can be clearly observed that the best performing photonic crystal OPV device in terms of PCE is still the ZnO PC device with the active layer spin-coated at the reference spinning speed of 2000 rpm. Contrary to expectations, different from the ZnO porous structure, the slow spinning speed of active layer was not advantageous for the ZnO photonic crystal layer. The device with the active layer coating at lower spinning speed exhibits the lowest V_{oc} and fill factor among all three types of devices with only a slight improvement in the current density compared to the reference OPV device with planar layer.

A possible explanation for the undesirable performance at low spinning speed may be as follows. In the case of the photonic crystal, due to the larger spacing between structures, the filling of the space between the microstructures is relatively uncomplicated compared to the filling of pores in the porous structure. Even at the reference spinning speed for active layer, there is adequate infiltration of active layer

material into the photonic crystal structure. The slower spinning speed does not offer much in terms of improving this infiltration.

For OPV device with the ZnO PC, the effect of slow spinning speed is seen mainly as the increased active layer thickness. For OPV application, thick P3HT:PCBM BHJ active layer is not generally preferred. Though thicker active layer results in higher absorption, increased series resistance manifests as a side effect of thicker layers. This affects the charge transport, leading to lower charge collection efficiency and ultimately reduced device performance [133]. With no increased infiltration to mitigate these downsides of thicker films, the device performance of the ZnO PC device employing lower active layer spinning speed suffers, though the photonic crystal structure provides a slight increase in the current density by virtue of its inherent properties.

To continue with the investigations on the effect of active layer spinning speed, ZnO PC devices with the active layer spin-coated at spinning speed higher than the reference spinning speed were fabricated. Spinning speeds ranging from 2000 to 3500 rpm were employed on ZnO PC devices for these studies.

Results of these experiments showed that the active layers coated at spinning speeds higher than 2500 rpm were unsuitable for these OPV devices. At these high spinning speeds, the device performance was lower than that of the ZnO PC device with active layer spin-coated at the reference spinning speed. The higher spinning speed may result in poor coverage and very thin active layer. A non-uniform active layer affects both the absorbance of incident light and also the charge transport through the layer.

Active layer spin-coated at a speed of 2500 rpm was found to exhibit the best performance among these devices. This spinning speed should have ensured the optimal deposition of active layer with sufficient coverage, while keeping the overfilling of throughs at the minimum. This results in the lowest series resistance and optimum conditions for charge transport. The devices employing 2500 rpm spinning speed for the active layer spin-coating were compared with both the reference OPV devices with planar ZnO layer and also the ZnO PC OPV device with the active layer spin-coated at a reference spinning speed of 2000 rpm (Table 5-7).

Fig. 5-17 compares the J - V characteristics of OPV devices having the ZnO PC layer with active layer spin-coated at 2000 and 2500 rpm, together with OPV device with the planar ZnO layer.

Table 5-7: Device parameters of ZnO photonic crystal OPVs with active layer spin-coated at 2000 and 2500 rpm, together with the planar ZnO reference OPV.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
ZnO PC OPV	0.609	8.939	0.52	2.79%
(2500 rpm)				
ZnO PC OPV	0.608	8.203	0.44	2.20%
(2000 rpm)				
Planar ZnO	0.613	7.267	0.59	2.64%
reference OPV				
(2000 rpm)

Figure 5-17: *J-V* characteristics of ZnO photonic crystal OPVs with active layer spin-coated at 2000 and 2500 rpm, together with the planar ZnO reference OPV.

The ZnO PC with the active layer spin-coated at a faster spinning speed of 2500 rpm showed the best efficiency among all the devices. The figure of merits of V_{oc} , J_{sc} , fill factor and the efficiency were all the highest for this device compared to the other ZnO PC OPV devices. From the data of 24 samples, the mean values of V_{oc} , J_{sc} , FF and η for ZnO PC OPV devices calculated were 0.608 V, 8.513 mA/cm², 0.51 and 2.71% respectively. The highest open circuit voltage and the fill factor for this device proves that the recombination losses, which plagued the other ZnO PC devices on account of the non-conformal active layer deposition, has been mitigated by optimizing the active layer spinning speed. The annealed ZnO PC layer with two underlying ZnO layers and an active layer spin-coated at 2500 rpm was thus proven to be the most suitable structure for application of our ZnO PC in inverted OPVs.

Upon comparing with the reference planar ZnO device, it can be seen that the efficiency is higher for the ZnO PC device. This increase is due to the enhanced current density offered by the ZnO photonic crystal structure compared to the planar

ZnO layer. The ZnO PC device provides ~23% increase in the current density. The ZnO PC layer provides better charge collection efficiency in addition to the light trapping benefits provided by the periodic PC structure. However, the V_{oc} and fill factor still remain lower than the reference sample and this curbs the overall PCE increase to 6%.

IPCE studies were performed on the reference device and on the optimized ZnO PC OPV device. The normalized IPCE spectra thus obtained is presented in Fig. 5-18. The IPCE data follows the trend of the short circuit current density and shows an improvement with the use of photonic crystal layer. The photonic crystal structure enables better light trapping, induces an increased optical path length, thus increasing the amount of photogenerated charge carriers. This is reflected in both the IPCE and the current density of the ZnO photonic crystal OPV device.

Figure 5-18: Normalized IPCE spectra of the planar ZnO reference OPV and the OPV with ZnO photonic crystal layer.

To verify higher absorption provided by the ZnO photonic crystal layer, absorption measurements were performed on the P3HT:PCBM BHJ active layer coated samples of both the ZnO PC structure and the planar ZnO layer on ITO substrate. The resultant absorption curves are presented in Fig. 5-19. As can be seen from the curves, the sample with ZnO PC structure shows higher absorption in the entire wavelength range. This enhanced absorbance of the ZnO PC structure is due to the incident light trapping induced by the PC topography and the properties resulting in higher absorption in the active layer. Thus, the absorption results of the samples correlate to the device performance.

Figure 5-19: Absorption spectra of the planar ZnO reference OPV and the OPV with ZnO photonic crystal layer.

5.4 Numerical simulation studies

Full electromagnetic solution can be a powerful tool to aid in the investigation and comprehensive understanding of the device behavior under the influence of various

parameters. For this purpose, we used Lumerical which is finite-difference time-domain (FDTD) simulation software and has been commonly employed for simulation studies in optical micro- and nano-resonators. We used the Lumerical software to develop a fully electromagnetic FDTD simulation of our ZnO photonic crystal to understand its effect on the incident light absorption in the active layer of inverted OPV.

The 3D device simulation was designed with different layer thicknesses and their respective refractive indices. Due to the square symmetry of the photonic crystal and incident broadband plane wave source, a single unit cell was considered to run the simulation. In these FDTD simulations, the ZnO photonic crystal structure with four-fold symmetry (period = 600 nm, height = 200 nm and radius = 200 nm) was used on top of the ZnO layer. The periodic boundary conditions were applied perpendicular to the organic solar cell layers, while physically matched layers were used as the boundary condition on the top and bottom of the solar cell design. Two 2D power monitors were used, first one located at the boundary between the P3HT:PCBM and the MoO₃ interface and other located at boundary between the P3HT:PCBM and the ZnO PC. These two power monitors helped in evaluating the light absorbed in the P3HT:PCBM active layer due to the presence of the ZnO photonic crystal on top of the ZnO underlying layer. Another 2D electric field monitor was used to visualize the electric field distribution in different organic layers (in a plane perpendicular to constituent layers of OPV device).

The refractive index of different organic layers at the central wavelength of 510 nm of the simulation plane wave bandwidth (400 to 700 nm) is shown in Fig. 5-20. The colour bar on the right gives the measure of refractive indices.

Figure 5-20: Refractive index of different organic layers in the simulated OPV device at 510 nm.

To study the effect of the layer thickness, ZnO PC OPV devices with one underlying ZnO layer and two underlying ZnO layers were simulated. Reference OPV device with a planar ZnO layer was also simulated for comparison.

The simulated light absorption in the active layer with respect to the incident plane wave wavelength for all the three types of devices mentioned above is shown in Fig. 5-21. It can be seen from these plots that the photonic crystal increases the absorption within the active layer by increasing the scattering path length in comparison to the reference planar ZnO OPV device. The ordered in-plane refractive index variation created within the P3HT:PCBM active layer due to the presence of ZnO PC is helpful in trapping and hence increases the absorption of light. The improvement is, however, not large because of the structure adapted using the available mold.

Figure 5-21: Simulated absorption in P3HT:PCBM active layer for the photonic crystal OPVs with one and two underlying ZnO layers, together with the planar ZnO reference OPV.

The electric field distribution inside the abovementioned three types of simulated OPV devices at the source wavelength of 510 nm is shown in Fig. 5-22. In Fig. 5-22 (a), for the reference OPV device with planar ZnO layer, it can be seen that the incident electric field is decayed within the active layer. For simulated devices with the ZnO PC, the field is trapped by virtue of the PC structure, as can be seen in Fig. 5-22 (b) OPV with single underlying ZnO layer. For simulated OPV with two underlying ZnO layers also (Fig. 5-22 (c)), the increase in the electric field intensity can be observed due to the presence of ZnO PC.

(a)

(b)

(c)

Figure 5-22: Simulated electric field distribution for (a) the reference OPV with planar ZnO layer, (b) the ZnO PC OPV with 1 underlying ZnO layer and (c) the ZnO PC OPV with 2 underlying ZnO layers.

The spinning speed of the active layer coating also affects the OPV device performance. Simulations studies were also performed to study the influence of the active layer thickness on the OPV device with ZnO PC. Reference OPV device with a planar ZnO layer was also simulated for comparison.

The electric field distribution inside the simulated OPV devices mentioned above at the source wavelength of 510 nm is shown in Fig. 5-23. In Fig. 5-23 (a), for the reference OPV device with a planar ZnO layer, it can be seen that the incident electric field is lower within the active layer when compared to devices with the ZnO PC. Fig. 5-23 (b) shows the electric field distribution in the OPV with an active layer spin-coated at the reference spinning speed of 2000 rpm. Fig. 5-23 (c) shows the electric field distribution in the OPV with an active layer spin-coated at the spinning speed of 2500 rpm, which gave the best experimental results. From figures, it is clear

that the electric field intensity is higher for the active layer spin-coated at a faster speed. This is in agreement with the conclusions drawn from the experiments conducted and discussed in the previous section.

(a)

(b)

(c)

Figure 5-23: Simulated electric field distribution for (a) the reference OPV with planar ZnO layer, (b) the ZnO PC OPV with active layer spin-coated at 2000 rpm and (c) the ZnO PC OPV with active layer spin-coated at 2500 rpm. ZnO layer thickness is 80nm.

5.5 Summary

Photonic crystals lead to enhancement of current density by virtue of its periodic structure and efficient charge collection. The quality of the ZnO photonic layer used, the underlying ZnO layer thickness and the speed on spin-coating speed of the P3HT:PCBM BHJ active layer on the ZnO PC layer all are shown to have a remarkable influence on the device performance. By careful optimization of these varied parameters, successful application of ZnO photonic crystal structure on the ZnO electron selective layer of inverted OPV device has been demonstrated. Simulation studies have also been carried out to further investigate the influence of ZnO PC structure on the electron selective layer of OPV devices. The efficient light trapping induced by these PC structures has led to a 23% increase in the current density in OPV devices employing the ZnO PC layer compared to OPV device with artifact free ZnO layer.

Chapter 6: Conclusion and future direction

6.1 Concluding remarks

With a looming energy and environmental crisis and a vital need for renewable, low cost energy source at its forefront, there is a greater focus on successful commercial application of organic photovoltaics. Amongst the various methods of achieving this which are under scrutiny, the application of microstructures in OPV is a promising avenue. Studies on such metal oxide microstructures can be readily applied to all compatible new generation active layers being explored, providing an instant efficiency enhancement route. This is the motivation for this thesis study on the use of metal oxide microstructures in organic photovoltaics.

In this thesis, the investigation on porous zinc oxide structure in OPV has shown promising results with 35% increase in current density and 30% increase in efficiency compared to OPVs with non-porous ZnO layer. This porous structure is formed by addition of polyethylene glycol to the ZnO sol-gel and, therefore, comes with an ease of fabrication compatible with industrial scale OPV fabrication. Previously, process-intensive ZnO nanopillar and nanorod structures have been studied as electron selective layers to enhance organic photovoltaics device performance by providing increased interfacial contact and charge collection [76, 155]. However, the studies conducted during the course of investigations of this thesis have shown that, in addition to the aforementioned advantages, the major contribution of the porous layer comes from its ability to act as scattering centres for incident light. Haze factor studies have shown that, compared to non-porous ZnO thin films, porous ones exhibit a marked improvement in light scattering. The optical path length of the incident light can thus be increased resulting in a concomitant enhancement of absorption in the active layer. This results in enhanced current density and device efficiency.

Porous structure has also been successfully demonstrated in doped electron selective ZnO layers of OPVs in this thesis. PEG was used to induce porous layer in indium-doped ZnO electron selective of OPV and an efficiency enhancement of ~17% was obtained in comparison with OPV device with non-porous indium-doped ZnO electron selective layer. When the porous architecture was applied to aluminum-doped ZnO electron selective layer, an efficiency enhancement of ~20% was obtained in comparison with OPV device with non-porous aluminum-doped ZnO electron selective layer. This was achieved as a result of increase in short circuit current density. As in the case of the porous ZnO layer, doped ZnO porous layers also retained the ability to serve as efficient scattering centers. Through these demonstrations, the portability of the porous structure architecture was established. This method of inducing porosity by the addition of PEG to a metal oxide sol-gel has thus been proven to be a universal technique for light scattering enhancement in OPV.

Earlier studies had reported the use of photonic crystals in active layer of OPV [182]. However, they resulted in an uneven topography, which can adversely affect the device performance by inducing recombination losses. Photonic crystal structure was also used on TiO₂ electron selective layer of OPV [182]. In this thesis, the application of photonic crystals to the more common ZnO electron selective layer in inverted OPV was investigated. These highly ordered structures provide the necessary refractive index contrast for optical absorption enhancement and lead to improvement in the device efficiency when compared to planar ZnO layers. Though ZnO photonic crystal structure investigations are still in their infancy, there is a tremendous opportunity for performance improvement by architecture optimization especially with the additional aid of numerical simulations.

6.2 Future work

6.2.1 Porous structures in OPV

A more in-depth examination of the device processing can help to further improve the performance of the OPV device with porous doped ZnO electron selective layer. Higher temperature processing can help in improving interlayer performance as a result of lower resistance, better charge transport and consequent lower fill factor [124, 133]. However, as discussed earlier, this temperature would drastically increase the chances of indium ions of ITO diffusing into the glass substrate, thus possibly degrading slightly the device performance [133]. Fluorine-doped tin-oxide or FTO has lower resistance (15 ohm/cm^2) than ITO [104] and by replacing ITO-on-glass substrate with FTO on glass substrate, higher temperature annealing may be a possibility to improve quality of porous doped interlayer without layer degradation.

By exploring other process modifications such as the use of melt infiltration [76, 137], whereby the infiltration of the active material into the microstructures can be further enhanced by annealing the active layer at high temperature and slow cooling, the device performance may be further improved. Another potential route is to improve the wettability of the doped porous film via self-assembled monolayer (SAMs) of appropriate dipole moments [118, 119]. The wettability of porous doped ZnO films affects the active layer film morphology and this in turn has an impact on the absorption, charge dissociation and transport and, thus, on the efficiency of the fabricated devices [28].

The role of PEG is to form the organic network to help in the formation of porous structure. It is the PEG that ultimately determines the pore size and distribution of pores. It has been suggested that if PEG is replaced with a ligand like n-butylamine with longer chains, the pore size can be increased [76]. The preliminary focus, however, could be on varying the hydrocarbon chain length of glycols. Further studies can also be carried out on various other doped zinc oxide materials to have a comprehensive comparison of doping agent's behaviour in porous structures.

Although the experiments conducted for this thesis were all on inverted OPVs, porous structure shows promise of being extended to p-type metal oxides as well. Preliminary studies were carried out on using PEG to induce porosity in MoO_3 hole selective layer in a regular structure OPV. MoO_3 was prepared using a sol-gel derived method in a solvent compatible with PEG using a method described elsewhere [121]. The device structure was of the form ITO/ MoO_3 /P3HT:PCBM/Ca/Ag. Initial results look promising. Upon successful application in MoO_3 layer, porous structure can be applied to other sol-gel derived p-type metal oxides such as NiO and V_2O_5 .

All solution-processed OPVs are gaining popularity as they offer compatibility with large-scale ink jet printing and flexible substrates and also roll-to-roll manufacturing. This also eliminates the need to employ more expensive high vacuum processing needed for thermal evaporation on certain metal oxides and the metal top electrode. Hence, the feasibility of employing porous structure in an all solution-processed OPV would also be a suitable and useful extension of this thesis.

6.2.2 Photonic crystals in OPV

The periodic structures are the backbone of efficiency enhancement provided by photonic crystals. However, improved light absorption provided by such structures are often accompanied by unfavorable electrical field distribution, which dampens the charge carrier transport and collection and, hence, affects the device performance in an adverse way [40, 190, 191] [186]. The dimension, spacing and shape of these structures have to be carefully optimized to maximize the advantages provided by the photonic crystal and these optimizations can be specific to the device architecture and also materials used in the device.

Numerical full electromagnetic solution is an important route to understand the light trapping mechanisms in photonic crystal structures. Such numerical simulations can be used to investigate the effects of the photonic crystal dimensions, shape and periodicity on the optical path length and light absorption, which can then be used in

the device implementation, to study experimentally the electrical effects. This avenue should be further explored to investigate ZnO photonic crystals of various dimensions and architecture to realize the full potential of the application of ZnO photonic crystal structure in inverted OPV.

In addition, the positioning of the photonic crystals in the device also affects the incident light manipulation. Several order increase in optical path length and, hence, optical absorption was demonstrated in silicon solar cells by using a textured photonic crystal as a backside reflector [183]. Thus, novel structures with photonic crystal structure below the ITO substrate and also on the top metal oxide layers can be investigated.

As with the porous structures, studies on photonic crystal structure can also be extended to other metal oxides including p-type oxides for regular OPVs and even to all solution-processed OPVs.

With more metal oxides and their microstructures carefully studied and successfully applied to regular and inverted OPVs, the OPV efficiency of >10% benchmark for the widespread commercial acceptance of OPVs may be readily achievable.

List of publications

1. A. Nirmal, A. K. K. Kyaw, X. W. Sun and H. V. Demir, “Microstructured porous ZnO thin film for increased light scattering and improved efficiency in inverted organic photovoltaics”, *Optics Express*, 2014. 22(S6): p. A1412-A1421.
2. A. Nirmal, A. K. K. Kyaw, X. W. Sun and H. V. Demir, “Demonstration of the portability of porous microstructure architecture to indium-doped ZnO electron selective layer for enhanced light scattering in inverted organic photovoltaics”, *Journal of Sol-Gel Science and Technology*, 2016: p. 1-8. (DOI 10.1007/s10971-016-3999-y)
3. A. Nirmal, A. K. K. Kyaw, K. Dev, J. Wang, X. W. Sun and H. V. Demir, “Light trapping in organic photovoltaics with nano-imprinted ZnO photonic crystals”, in process of submission.

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