Design and fabrication of excitonic solar cells

Aung Ko Ko Kyaw

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DESIGN AND FABRICATION OF EXCITONIC SOLAR CELLS

AUNG KO KO KYAW

School of Electrical and Electronic Engineering

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To my beloved parents

“ကျေးဇူးရှင်မိဘနှစ်ပါးနှင့် သင်ဆရာ မြင်ဆရာ ကြားဆရာအားလုံးအား ဤကျမ်းဖြင့်ကန်တော့ပါ၏။”

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SUMMARY

The excitonic solar cells (XSCs), including organic solar cells (OSCs) and dye-sensitized solar cells (DSSCs), have attracted a great interest due to their huge potential of low cost technology compared to conventional silicon solar cells. Although the technologies of XSCs have advanced significantly, XSCs still need to be improved in various aspects to become tangible in energy market. The important criteria of a solar cell are efficiency, cost and life time. Hence, the research in this dissertation focuses on the design of XSCs with better choice of materials and device architecture for either enhancement in stability and efficiency or reduction of cost.

In spite of over 7% power conversion efficiency, the OSC based on bulk-heterojunction concept has limitation in device stability due to diffusion of oxygen into the organic layer through pinholes and grain boundaries in Al cathode and the degradation of transparent conductive oxide (TCO) electrode, which is etched by poly (3,4-ethylene dioxythiophene):(polystyrene sulfonic acid) (PEDOT:PSS) buffer layer. To overcome this problem, an inverted structure was implemented. The reverse polarity of charge collection in an inverted structure allows the usage of air-stable high-work-function metal as top electrode and gets rid of TCO/PEDOT:PSS interface. In our design, TCO is modified with sol-gel derived zinc oxide (ZnO) to exclusively collect electrons from active layer and block holes. A thermal-evaporated molybdenum oxide (MoO_3), which is inserted between active layer and top electrode, increases the fill factor of the device due to exciton/electron blocking property. It was observed that the efficiency of an inverted structure OSC can be further improved by manipulating the resistivity, energy level and optical property of ZnO

layer with appropriate amount of indium doping. We also verified that the stability of device in air is significantly improved by inverted structure.

DSSC, another type of XSC, is also a promising alternative to silicon photovoltaic technology. However, it is estimated that conducting glass is the most expensive part of DSSC and it incurs 60% of total cost. Therefore, we designed top-illuminated structure which can be fabricated on inexpensive opaque substrates such as metals or plastic foils with metal coating. Although the efficiency of the top-illuminated cell is about 20% lower than the traditional bottom-illuminated cell, it reduces the cost of DSSC tremendously by eliminating the usage of expensive TCO. Ti is more suitable to be used as electrode in top-illuminated DSSC than other metals because of minimum catalytic activity on redox reaction and high resistance to corrosion. Another approach to eliminate TCO is replacing with transparent carbon nanotube (CNT) electrode. However, the catalytic activity to redox reaction limits its application as working electrode in DSSC. Therefore, the implementation of DSSC with CNT electrode was realized by modifying CNT with titanium-sub-oxide (TiO_x) which inhibits the charge-transfer kinetic at CNT/redox solution interface and facilitates the unidirectional flow of electrons in the cell. To our best knowledge, this is the first demonstration of CNT as working electrode for liquid-type DSSC. Based on this finding, we also realized DSSC with all carbon electrodes.

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Common Abbreviations

Abbreviations	Full expressions
AFM	Atomic force microscopy
Ag	Silver
Al	Aluminum
AM 1.5G	Air Mass 1.5 Global
Au	Gold
BPhen	Bathophenanthroline
BHJ	Bulk heterojunction
C ₆₀	Fullerene
CNT	Carbon nanotube
Cs ₂ CO ₃	Cesium carbonate
CuPc	Copper phthalocyanine
D-A	Donor-acceptor
DSSC	Dye-sensitized solar cell
FE-SEM	Field emission scanning electron microscope
<i>FF</i>	Fill factor
F-PCBM	Fullerene derivative with a fluorocarbon chain
FTO	Fluorine doped tin oxide
GZO	Gallium doped zinc oxide
HOMO	Highest occupied molecular orbital
HWF	High work-function
<i>I_{sc}</i>	Short-circuit current

IPCE	Incident photon-to-electron conversion efficiency
ITO	Indium tin oxide
<i>I-V</i>	Current-Voltage
IZO	Indium-doped zinc oxide
J_{sc}	Short-circuit current density
LED	Light emitting diode
LiF	Lithium fluoride
LUMO	Lowest unoccupied molecular orbital
LWF	Low work-function
MDMO-PPV	Poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene)
MoO ₃	Molybdenum oxide
Nb ₂ O ₅	Niobium oxide
Ni	Nickel
NiO	Nickel(II) oxide
OECD	Organization for Economic Co-operation and Development
OLED	Organic light-emitting diodes
OSC	Organic solar cell
OTFT	Organic thin film transistors
P3HT	Poly(3-hexylthiophene)
PCBM	1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C ₆₁
PC ₇₀ BM	1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C ₇₁
PCDTBT	poly[N-900-hepta-decanyl-2,7-carbazole-alt-5,5-(40,70-di-2-thienyl-20,10,30-benzothiadiazole)

PCPDTBT	poly[2,6-(4,4-bis-(2-ethylhexyl)-4 <i>H</i> -cyclopenta[2,1-b;3,4-b']dithiophene)- <i>alt</i> -4,7-(2,1,3benzothiadiazole)]
PCE	Power conversion efficiency
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate)
PPV	Polyphenylenevinylene
Pt	Platinum
R_s	Series resistance
R_{sh}	Shunt resistance
SEM	Scanning electron microscope
SnO ₂	Tin oxide
TCO	Transparent conductive oxide
Ti	Titanium
TiO ₂	Titanium dioxide
TiO _x	Titanium (sub) oxide
V ₂ O ₅	Vanadium oxide
V_{oc}	Open-circuit voltage
WO ₃	Tungsten trioxide
XSC	Excitonic solar cell
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZnO	Zinc oxide

Chapter 1 Introduction

1.1 Motivations

1.1.1 Energy Demand and Environmental Issues

Global energy demands have been increasing with economic growth and rising standards of living since past few decades. Global energy consumption rate will be even higher in the next few decades due to the rapid growth in energy demand in emerging non-OECD (Organization for Economic Co-operation and Development) countries like China and India [1-2]. Total world consumption of marketed energy is projected to increase by 53% from 505 quadrillion* British thermal unit (Btu) in 2008 to 770 quadrillion Btu in 2035 [1]. Presently, the major energy resources supporting the global consumption are fossil fuels – oil, gas and coal with percentages of 35%, 21% and 25% respectively, as depicted in Fig. 1-1.

However, it is questionable that fossil fuels are able to keep this contribution level in 2050 and beyond simply because they are not abundant on the Earth. The fossil fuels consumed today were formed several hundred million years ago and they are no longer naturally formed. Hubbert peak theory and curves predict that the production rate of non-renewable resources approximates a bell curve and thus when the peak of production is over, it declines exponentially. Historically, oil production in the United States has followed the theoretical Hubbert curve. U.S. oil production reached its peak in 1970 and

* A quadrillion is equivalent to 10^{15} in short scale.

by the mid-2000s it had fallen to 1940s levels. Likewise, all of the world's major producing countries are expected to reach their peaks in next few years. In 2004, total world reserves were estimated to be 1.25 trillion barrels and daily consumption was about 85 million barrels. With this reserve-to-production ratio (R/P), the estimated oil depletion will be in next 40 to 50 years [3]. A better synopsis is for natural gases that can last for about 60 years and coal, being the most abundant, for 150 years [4].

Figure 1-1 World total energy supply (2005) by source. Note: Mtoe is million tons of oil equivalents [2]

In addition to energy security issue, the world is facing a series of major atmospheric environment issues as a consequence of the carbon dioxide emission from burning fossil fuels. There is now visible and unequivocal evidence of climate change impacts due to anthropogenic greenhouse gas (GHG) emission, principally CO₂ – its current level of 380 ppm is much higher than the pre-industry (18th century) level of 280

ppm [5]. Global mean surface temperature has increased by 0.3-0.6° C since the late 19th century and the global sea level has risen by 10-25 cm, most likely due to human activities [6]. The impact of this warming and sea-level rise has increased the frequency and severity of natural catastrophe. Hence, even though the energy security problem can be overcome by combustion of fossil fuels in short term; they will elevate the GHG level to a critically dangerous level. Despite all the seemingly negativities, we have renewable energy sources which neither run out nor harm to environment. Therefore, only approach to meet the increasing energy demand while maintaining a stable GHG level is to boost the contribution of clean energy in the future energy supply and invest more in renewable energy technologies.

1.1.2 Photovoltaic Technology and Solar Cells

A direct solar to electricity conversion through photovoltaic (PV) system is one of the renewable energy technologies we should exploit because the Sun is the greatest energy source among various renewable energy sources. It delivers power continuously to the earth, 1.2×10^5 terawatts (TW) that exceeds the rate at which human society uses energy, currently about 13 TW [7]. Moreover, the environmental impact of PV technology is even more subtle compared to other renewable energy sources and almost negligible. For instance, the burning of biomass still emits CO₂ in spite of net zero emission due to re-absorption of CO₂ from growing replenished plants. Even though hydroelectric energy does not release any atmospheric pollutants, damming rivers change water flow, amount

and quality of water in the downstream and cause negative impact on biodiversity [8]. However, solar energy technology neither pollutes nor impacts on biodiversity. PV system even does not have environmental impacts on noise level and wildlife (birds), which are not negligible in wind energy technology [9]. Moreover, solar panels have capability of installation at rooftop and building façade, which further reduces the visual effect, transmission infrastructure and grid lines.

At present, single crystal silicon based solar cells which reach power conversion efficiency (PCE) of 24.4% for the best laboratory cells [10], account for more than 90% of the market share. Silicon-based solar cell technology is still dominating in today's PV market due to the maturity of the silicon processing technology, sufficient material supply (the second most abundant element on the earth)* and high module efficiency (~ 20%). However, the cost of solar electricity generated from silicon solar cell is still an order of magnitude higher than electricity generated from fossil fuel (<US\$0.05/kWh) due to the high cost incurred from energy intensive process at high temperature (400-1400° C), high vacuum condition with lithography processes. Multi-junction solar cells yield higher PCE than silicon solar cell and up to 40% of PCE was demonstrated recently using a metamorphic GaInP/GaInAs/Ge multi-junction structure [11] yet the cost is so high that currently they became a privilege only to space applications. However, there is opportunity to use solar concentrators in conjunction with multi-junction solar cells so that the “effective area” of solar cells is substantially increased for window or building integrated scenarios. As an alternative, thin film solar cells based on polycrystalline

* In another more precise way, it is not silicon (Si) that is abundant in the earth's crust but rather silicon dioxide (SiO₂) from which the Si has to be extracted, purified and grown into large crystals using energy costly procedures.

silicon, amorphous silicon and inorganic semiconductors such as CdTe/CdS, Cu(In,G)Se₂ (CIGS), are currently being developed to reduce the cost. Nonetheless, to achieve costs that are truly competitive with fossil fuel energy sources, it is generally believed that new technologies, often termed third generation solar cells must be developed.

Figure 1-2 Efficiency –cost trade off for three generations of solar cell technology [12]

Fig. 1-2 shows the solar cell generation map made by Martin A. Green [12]. According to the third generation concept, we have two options: (1) to develop solar cells expected to be expensive but highly efficient, i.e., the efficiency must exceed Shockley-Queisser limit [13], or (2) to develop solar cells that are moderately efficient and inexpensive. However, the current efficiency of the crystal silicon based solar cell is approaching to the theoretical limit of 30% and it is difficult to further improve unless hot carriers generation, up-conversion and down-conversion technologies are exploited.

Hence, the excitonic solar cells using organic and nanostructure materials have attracted a great interest due to its huge potential of low cost technology. The inexpensive fabrication process such as solution-process techniques, the flexibility and light weight makes this technology attractive for application in new markets such as mobile electronics, home appliances, outdoor lifestyle and automotive application in addition to electricity generation. Presently, such technology has not been fully developed despite multiple companies are involved in this emerging field. Further improvement in the efficiency, stability and scalability are still required to be widely available in the market

1.2 Conventional Versus Excitonic Solar Cells

The existing solar cells can be classified into two categories: conventional solar cells and excitonic solar cells (XSCs). The former category, conventional solar cells, consists of silicon and other inorganic solar cells while most of the organic-based solar cells, including dye-sensitized solar cell (DSSC), fall into category of XSC. They are called “excitonic solar cell” because, as the name implies, tightly-coupled electron-hole pairs (excitons) are generated upon photon excitation in XSCs rather than nearly free electron-hole pairs in the case of conventional solar cells. In an inorganic semiconductor, the greater delocalization of the carrier wave functions and a narrower Coulomb potential well due to larger dielectric constant commonly result in the photogeneration of free electrons and holes at the room temperature. In contrast, the light absorption in an organic semiconductor does not produce free electrons and holes readily for two reasons: (1) the

non-covalent electronic interactions between the molecules are rather weak compared to the interatomic electronic interactions of covalently bonded inorganic semiconductors, allowing the electron's wave-function to be localized in the potential well of its conjugated hole (and vice versa), and (2) the dielectric constant of organic semiconductors is usually low compared to inorganic semiconductors, leading to the wider Coulomb potential well [14]. Owing to different natures of charge carriers generation and separation, the operation of XSC is fundamentally different from that of conventional solar cell.

Conventional photovoltaic cells are built on p-n junctions of silicon or other inorganic semiconductors. A p-type semiconductor consists of hole (mobile charge) and acceptor (ionized impurity atom) while an n-type semiconductor consists of electron and donor. When p and n-type semiconductor are joined together, a layer without mobile charge carrier called space charge region or depletion region is formed near the junction due to the diffusion of mobile charges and compensation with opposite charge carriers. This space charge sets up a built-in electric field which opposes the diffusion across junction. At equilibrium, the diffusion current due to concentration gradient is balanced by the drift current due to electric field and no net current flows in the semiconductor. Fig. 1-3 (a) depicts the charge distribution in the p-n junction and the energy band diagram at thermal equilibrium. Under illumination, the absorption of photons with energy higher than the band gap of the semiconductor results in generation of electron-hole pairs which can be thermally dissociated. Because of the electric field in the depletion region, electrons are drifted towards n-side while holes are drifted towards p-side as shown in Fig. 1-3(b). This separation of charges results in the current flows from n to p-side when the cell is short-circuited. However, the photo-generated minority electrons in p-region

coexist with majority holes before they are swept across the junction and vice versa in n-region. Since both electrons and holes coexist in the same type of material, conventional p-n junction cells are called minority carrier devices and their efficiencies are highly dependent on the ability of photogenerated minority carriers to be swept out of the junction before recombining with the majority carriers [15]. Therefore, conventional solar cells must be made from pure and defect-free materials with high degree of crystallinity, to prevent from significant recombination. The purification of materials requires energy intensive process at high temperature (up to 1400°C) and high vacuum condition, which makes the conventional solar cells high cost and long energy payback time.

Figure 1-3 (a) Schematic structures of p-n junction and its energy band diagram in equilibrium (b) illustration of charge carriers generation and separation under illumination

Figure 1-4 Schematic of electrical charge generation in excitonic solar cells

In contrast to conventional solar cells, the XSCs consist of an acceptor and a donor where usually light is absorbed and excitons are generated upon photo-excitation. (It is worth mentioning that the definitions of “donor” and “acceptor” used in the context of organic solar cells are different from those commonly used in semiconductor technology. Herein, “acceptor” refers to the material which can accept the electrons dissociated from excitons and generally it is an n-type material while “donor” refers to the material which can donate electrons dissociated from excitons and generally it is a p-type material.) No significant space charge region is formed in XSCs because the individual size of particles is too small compared to the Debye length of the material and the whole part of the particle falls into depletion region upon contact [16]. Therefore, the dissociation of excitons occurs only at acceptor/donor interface, driven by band offset at the interface, as shown in Fig. 1-4 [15]. After dissociation, electrons are injected into acceptor and holes

are injected into donor. Since electrons and holes do not coexist in the same chemical phase, they are unlikely to recombine^{*}. Because electrons are transported through electron-rich region and holes are transported through hole-rich region, the XSCs are also called majority carriers devices. Hence, the defect-free materials are not necessarily required for the XSCs and they can be fabricated with less expensive materials and process. More interestingly, they can be made on flexible substrates, allowing roll-to-roll manufacturing for further cost reduction. The unique working principle of XSC allows the use of inexpensive and non-energy-intensive manufacturing processes for economically viable energy production without significant CO₂ emission.

1.3 Research Goal and Major Contributions

During the past decade, scientists and engineers from various fields of expertise put a lot of effort in the research area of excitonic solar cells. Although the technologies of XSCs have advanced significantly, the efficiency and stability still need to be improved to fulfill the commercial requirements. In principle, the primary way to improve the device performance is to apply new materials with properties of broad absorption range, high charge carrier mobility, and long stability. On the other hand, the device performance can be also enhanced by optimizing device structures. Moreover, the cost of XSCs can be further reduced by replacing expensive electrode with the one made from cheap and abundant materials. The aim of the present work is to design XSCs with better choice of

^{*} The condition is more applicable to DSSC and bi-layer OSC. The carriers are more likely to recombine in bulk-heterojunction OSC due to the nanoscale network of acceptor and donor. Bi-layer and bulk-heterojunction OSCs will be discussed in next chapter.

materials and device architecture for either enhancement in stability and efficiency or reduction of cost. Fabrication and characterization of cells to prove the design-concept is also another aspect of this work. The major contributions of the thesis can be divided into two major parts. First part is design, fabrication and optimization of inverted-structure organic solar cells (OSCs) for the better stability of devices. Various metal oxides are introduced as buffer layers and their properties' influence on the performance of OSCs are studied. Second part is design and fabrication of DSSCs with alternative electrodes which can replace conventional fluorine-doped tin oxide (FTO) and indium tin oxide (ITO) for further cost reduction. The electron transport and collection mechanisms in the devices are also proposed for individual designs.

1.4 Overview of thesis

Chapter 2 presents the fundamentals of solar cells as a preface to the thesis for the better understanding of the explanations in the later parts. A brief review on OSC and DSSC is also included in this chapter to give the overview of current research and the operation principles of OSC and DSSC.

Chapter 3 describes the synthesis of ZnO sol-gel and its application as electron-selective buffer layer for realization of inverted-structure OSC. The influence of sol-gel method and surface treatment of ZnO film on the performance of OSC is also presented.

Chapter 4 presents a novel inverted-structure OSC in which the active bulk-heterojunction layer is sandwiched between ZnO electron-selective buffer layer and MoO₃ hole-selective

buffer layer. The advantage of incorporating hole-selective layer in inverted OSC, and the correlation between the concentration of ZnO sol-gel and the performance of device are also discussed.

Chapter 5 describes the synthesis and properties of indium-doped ZnO (IZO) which has potential to improve the performance of inverted OSC due to enhanced optical and electrical properties compared to ZnO. The effect of doping and relative humidity on the properties of the film is also elaborated in this chapter. Finally IZO was applied as electron-selective layer in OSC. The possible factors for the improvement of efficiency are also proposed.

Chapter 6 presents the top-illuminated DSSC fabricated on the various metal substrates at low temperature process. The advantages of top-illuminated structure over conventional structure and the reason for the higher fill factor in top-illuminated cells are discussed. The effect of metal on the performance of cell is also revealed.

In Chapter 7, DSSC with titanium-oxide-modified carbon nanotube transparent electrode is reported. The challenges for the application of carbon nanotube electrode are addressed and the method to overcome these issues is discussed.

Chapter 8 describes the realization of DSSCs with all carbon electrodes, which could make the leap to emergence of truly cost-effective and flexible DSSCs. The modification of carbon nanotube films with relevant materials at both working and counter electrodes for the improvement of efficiency was also discussed.

Finally, the conclusion of the whole dissertation and outlook for both OSC and DSSC are presented in Chapter 9.

Chapter 2 Background on excitonic solar cells

2.1 Fundamentals of solar cells

2.1.1 Equivalent circuit diagram (ECD)

ECDs are frequently used to model the electronic behavior of complex semiconductor devices with a network of ideal electrical components such as diodes, current or voltage sources, resistors and capacitors. In a typical solar cell (either conventional or excitonic solar cell), the photocurrent (I_{ph}) resulting from the generation of charge carriers after absorption of photon, can be modeled as a current source while a junction formed between p and n -type materials (acceptor and donor) is represented by a diode. Under applied bias, the diode generates a current which flows in the opposite direction of the photocurrent. Therefore, ECD of an ideal solar cell can be modeled by an ideal current source in parallel with a diode as shown in Fig. 2-1(a) [17]. From the ECD, the relationship between the current and applied voltage can be expressed as Eq. 2.1.

$$I = I_{ph} - I_s \left(e^{\frac{V}{nV_T}} - 1 \right) \quad (2.1)$$

The second term in the right side of equation refers to the diode current, which is governed by its saturation current (I_s) and ideality factor (n). V_T is often referred to as the thermal voltage that equals to kT/q , where k , T and q are Boltzmann constant, temperature in Kelvin and charge of electron respectively.

Figure 2-1 Equivalent circuit diagram of a typical solar cell (a) ideal solar cell and (b) non-ideal solar cell with external load

In practice, there is no ideal solar cell hence a shunt resistance (R_{sh}) and a series resistance (R_s) are added to the model as shown in Fig. 2-1(b). R_{sh} represents the loss of carriers via leakage paths; these may include the recombination and trapping of the carriers during their transit through the cell. R_s is attributed to the finite conductivity of the semiconducting materials, the contact resistance between the semiconductors and the adjacent electrodes, and the resistance associated with electrodes and interconnections. R_s also increases with a longer traveling distance of charge, e.g. thicker transport layers. Incorporating R_{sh} and R_s into the ECD, the I - V relationship can be expressed as

$$I = I_{ph} - I_s \left(e^{\frac{V + IR_s}{nV_T}} - 1 \right) - \frac{V + IR_s}{R_{sh}} \quad (2.2)$$

In principle, R_s needs to be minimized (ideally zero) so that most of the electrical potential is applied to the load. R_{sh} needs to be maximized (ideally infinity) so that all the

current is passing through the load. An external load resistor, R_L , represents that a solar cell is connected to an external load. Alternatively, a source meter can be connected to the cell when current-voltage (I - V) characteristic of the cell is measured.

2.1.2 Current-voltage (I - V) characteristic and electrical parameters

I - V characterization is an important measurement for a solar cell because many electrical parameters including power conversion efficiency can be extracted from I - V response. In the dark, the applied forward bias on the device generates a current that flows in the direction opposite to that of photocurrent. It will increase substantially when the forward bias is larger than the built-in potential of the device. This current is usually called the dark current which relates to applied voltage with Eq. (2.3)

$$I_{dark} = I_s (e^{\frac{V}{nV_T}} - 1) \quad (2.3)$$

In fact, this dark current refers to the current passing through the diode in ECD which is the second term in Eq. (2.1). Under illumination, the I - V characteristic follows Eq. (2.2). A typical I - V curve for a cell in the dark and under illumination is shown in Fig. 2-2. The shape of the curve under illumination is similar to that in the dark, but crosses the first, third and fourth quadrant due to the added photocurrent.

Figure 2-2 Current-Voltage characteristics of a typical solar cell

The short-circuit current (I_{sc}) is measured at the condition when the applied voltage equals zero. From Eq. (2.1), I_{sc} is equal to I_{ph} and hence increases linearly with the incident light intensity [18]. The open-circuit voltage (V_{oc}) is measured under the condition when there is no external load connected, i.e. open circuit. In this condition, there is no current flow between the two terminals of the device, i.e. $I = 0$ and $V = V_{oc}$. From Eq. (2.1)

$$I_{ph} - I_s (e^{\frac{V_{oc}}{nV_T}} - 1) = 0$$

$$V_{oc} = nV_T \ln\left(\frac{I_{ph}}{I_s} + 1\right) \cong nV_T \ln\left(\frac{I_{ph}}{I_s}\right) \quad (2.4)$$

Hence, V_{oc} increases logarithmically with the photocurrent and light intensity. R_{sh} can be derived by taking the inverse slope of I - V curve around 0V:

$$R_{sh} = \frac{dV}{dI} \Big|_{V=0} \quad (2.5)$$

This is because at very small voltage the diode is not conducting and the current driven by the external voltage (positive or negative) is only determined by $R_{sh} + R_s$ with typically R_{sh} being much larger. R_s can be estimated from the inverse slope at a positive voltage greater than V_{oc} where the I - V curve becomes linear.

$$R_s = \frac{dV}{dI} \Big|_{V \geq V_{oc}} \quad (2.6)$$

This is because at high positive external voltage the diode becomes much more conducting than R_{sh} so that R_s can dominate the shape of the I - V curve.

At particular current and voltage amongst the data points in the fourth quadrant, the product of current and voltage gives the maximum power (P_{max}). This point is called the maximum power point while the current and voltage at this point is denoted as the current and voltage at maximum power point (I_{MPP} and V_{MPP}) respectively. The larger the area of rectangle ($I_{MPP} \times V_{MPP}$) the more the I - V curve resembles a rectangle with area $V_{oc} \times I_{sc}$. The ratio of these two areas is called the fill factor (FF) which relates P_{max} with V_{oc} and I_{sc} . FF also represents the quality of the shape of I - V curve. Mathematically, FF can be written as:

$$FF = \frac{V_{MPP} I_{MPP}}{V_{oc} I_{sc}} \quad (2.7)$$

The higher FF the more the I - V curve resembles a constant current source with maximum voltage and the higher is the electric power that can be extracted.

The most important parameter that determines the performance of a solar cell is the power conversion efficiency (PCE or η) which is defined as the ratio of the maximum output power to input power (P_{in}).

$$\eta = \frac{P_{\max}}{P_{in}} = \frac{V_{MPP} I_{MPP}}{P_{in}} = \frac{FF \times V_{oc} \times I_{sc}}{P_{in}} \quad (2.8)$$

P_{in} is an important experimental parameter to compare the results of PCE and hence standard test condition should be used. This condition is set as AM1.5 spectrum illumination with an incident power density of 100mW/cm^2 at 25°C . The details of standard test condition will be elaborated in section (2.1.4).

2.1.3 Quantum Efficiency

Since the sensitivity of a solar cell varies with the wavelength of the incoming light, another important parameter which determines the performance of a solar cell is the quantum efficiency (QE) which shows the spectral response of the device at individual wavelength over the solar irradiation. QE basically measures the ratio of electron count over the photon count. External quantum efficiency (EQE or η_{ext}) is defined as the ratio of photo-generated electrons (holes) collected at the cathode (anode) to the number of incident photons at certain wavelength. Mathematically, it can be expressed as:

$$\eta_{\text{ext}}(\lambda) = \frac{N_{\text{electrons}}(\lambda)}{N_{\text{photons}}(\lambda)} = \frac{I(\lambda)/q}{P_{in}(\lambda)/hc/\lambda} = \frac{I(\lambda)hc}{\lambda P_{in}(\lambda)q} = \frac{1240 \cdot I(\lambda)}{\lambda(\text{nm}) P_{in}(\lambda)} \quad (2.9)$$

where q is the charge of electron, c is speed of light, h is Plank's constant, $I(\lambda)$ is the current generated by the cell at wavelength λ and $P_{in}(\lambda)$ is the incoming power at wavelength λ . EQE is also known as the incident photon to current conversion efficiency (IPCE). Given the spectrum of the incident light $S(\lambda)$, the photocurrent can be calculated using:

$$I_{ph} = \int \frac{q\lambda}{hc} \eta_{ext}(\lambda) S(\lambda) d\lambda \quad (2.10)$$

In some cases, it may be preferable to express an efficiency of a solar cell without considering its absorption efficiency. Internal quantum efficiency (IQE or η_{int}) is more appropriate way to represent the efficiency in such case. IQE is the ratio of the number of collected charges at the electrode to the number of absorbed photons. Thus, IQE is also known as absorbed photon to current conversion efficiency (APCE). It is related with EQE by absorption efficiency, η_A .

$$\eta_{ext} = \eta_A \eta_{int} \quad (2.11)$$

2.1.4 Standard reporting conditions for solar cells

In actual operation or test, the value of measured PCE depends on the irradiance,^{*} spectrum of the irradiance and measurement temperature. Irradiance intensity on a cell affects the charge carrier density, level of saturation, temperature etc. The spectrum dependence of PCE can be easily seen from equation (2.10). Temperature affects the

^{*} The irradiance is defined as the power of electromagnetic radiation per unit area incident on a surface

material properties, such as thermal voltage and mobility, of the semiconductors used in the cells.

Figure 2-3 (a) Illustration of air mass concept (b) The radiation spectrum of AM0, AM1.5G and AM1.5D, source from National Renewable Energy Laboratory

On passing through the atmosphere, the solar spectrum is partially attenuated by the absorption of oxygen, ozone in the ultraviolet region and water vapor, carbon dioxide, methane in the infrared. This attenuation is described by the *Air Mass* (AM) factor since the absorption increases with the mass of air through which the radiation pass. For a thickness of l_0 of the atmosphere, the path length l through the atmosphere for radiation at an incident angle α relative to the normal to the earth's surface is given by

$$l = l_0 \cos \alpha \quad (2.12)$$

The ratio I/I_0 is called AM factor. This definition is illustrated in Fig. 2-3(a). The spectrum outside the atmosphere is denoted as AM0 and that on the surface of the earth for perpendicular incidence as AM1. The standard spectrum for moderate weather is AM1.5 which corresponds to a solar incident angle of 48° relative to the surface normal. The AM1.5 spectra are further divided into global and direct terrestrial reference spectra, notated as AM1.5D and AM1.5G, respectively. AM1.5G includes both direct and diffuse radiation whereas AM1.5D includes direct radiation only. Approximately, the power densities of AM1.5G and AM1.5D spectra are 93.06 mW/cm^2 and 84.6 mW/cm^2 respectively [19]. The actual irradiation, however, varies with season, climate, day time and position of the sun.

Due to the variation of these factors in actual test conditions, the reported PCE are usually not comparable. It is critical to accurately determine the PCE values from different research groups to enable a fair comparison of results. Significant efforts have been made in the past and reference test conditions for various solar applications have been established by the American Society for Testing and Materials (ASTM). The reference conditions are accepted by the PV community worldwide as the standard reporting condition (SRC). It is defined by measurement temperature (25°C), spectral irradiance (AM1.5G), and total irradiance (100mW/cm^2) [17]. The PV community has arbitrarily taken the term ‘One Sun’ to mean a total irradiance of 100mW/cm^2 although neither AM1.5G nor AM1.5D spectrum actually gives this value. Therefore, the total irradiance of SRC is the irradiance of AM1.5G spectrum normalized to 100mW/cm^2 . The fact that the SRC only approximates the “Real-World” spectrum and total irradiance is unimportant so long as the difference between the photocurrents measured for various PV

technologies are the same and methods for the correlation between results from the SRC spectrum and from the “real world” spectra is established.

2.2 Organic Solar Cells

Organic solar cells (OSCs) are photovoltaic devices employing molecular optoelectronic materials, including conjugated polymers and small molecules. The former refers to organic molecules with long carbon chains, and small molecules refer to those with molecular weight less than 1000. As an advantage over the traditional inorganic semiconductors, conjugated polymers allow processing from solution at room temperature by application of spin coating or even conventional printing technique. These features pave the way for low-cost large-scale production of all kinds of different organic optoelectronic devices – even integrated on a single substrate. It, moreover, has the possibility to achieve ultra thin, light weight and flexible cells, driving today’s economic interest [20].

2.2.1 Evolution of organic solar cells

There has been a tremendous effort to develop OSC within a few decades. The field started by the application of small organic molecules [21-22]. The first generation of OSC was a metal-insulator-metal (MIM) tunnel diode with single organic layer sandwiched between two metal electrodes of asymmetrical work function. The cell was

based on the Schottky-barrier effect and had a rather poor PCE of range from 10^{-3} to $10^{-2}\%$, but reached a remarkable 0.7% for merocyanine dyes in the early days [21-23]. The main reason for the low efficiency is that most of the excitation states formed during photon absorption in the film cannot be efficiently dissociated into free electrons and holes so that they can contribute to the power generation. A breakthrough was achieved by introducing the bi-layer heterojunction concept where two organic layers are deposited one after the other and sandwiched between the two electrodes. The two layers in the heterojunction were of specific electron and hole transporting properties, one of electron donor (D) type and another of electron acceptor (A) type respectively. Tang reported in 1986 about 1% conversion efficiency with this concept [24]. Later, Hiramoto and co-workers pioneered the work of introducing the concept of an organic tandem cell structure by stacking two heterojunction devices [25]. They also developed a three layer p-i-n like structure with a co-deposited interlayer between the donor and acceptor layers [26]. In early days, the small molecules were usually deposited by thermal evaporation but solution-processed small molecules were developed later on [27-28]. Recently, Sun et al. reported solution-processed small-molecule solar cells with efficiency 6.7%, which is an important demonstration of small molecule solar cell [29]. Up-to-date, the world record efficiency of 9.8% was announced by Heliatek using low-temperature-deposited small molecules in tandem structure.*

In the meantime, conjugated polymers were incorporated into OSC as well. Initially, single layer devices with conjugated polymers were showing only efficiencies of

* The announcement by Heliatek is available at <http://www.heliatek.com/>

less than 0.1%. The observation of a photoinduced electron transfer from optically excited conjugated polymers to the C60 molecule [30-31] and the observation of greatly increased photo-conductivities upon C60 addition to the conjugated polymers [32-34] led to the development of polymer-fullerene bilayer heterojunction. The next important concept is the bulk heterojunction (BHJ) concept, where the blend of the two organic materials is sandwiched between the two electrodes of the device. The structure is still the basic structure for polymer based OSC today. A few years ago, Sung et al. reported 6.1% efficiency with quantum efficiency approaching 100% using polymer-fullerene with BHJ structure [35]. Recently, Liang et al. reported 7.4% efficiency using BHJ composed of a new polymer from the benzodithiophene polymer family (PTB7) and a fullerene derivative (PC₇₁BM) [36]. In November 2010, Konarka announced that their single junction organic based solar cell has obtained the efficiency of 8.3%, which is the highest efficiency for single polymer solar cell.* Nonetheless, it is still required to move further to reach the target efficiency of 15% for commercialization and more effort and research need to be carried out.

2.2.2 Organic semiconductor materials

Based on the type of bonding interactions between the constituent atoms and molecules, solids are traditionally classified as covalent, ionic, metallic, or molecular. Although some organic solids exhibit metallic or ionic characteristics, the majority of

* The announcement by Konarka is available at <http://www.konarka.com>

organic solids belong to the category of molecular solids. Each molecule has a stable structure due to the strong covalent bonding between atoms. But the intermolecular interaction forces that hold the molecules together is primarily of the van der Waals type, which is considerably weaker than that of covalent or ionic bonds. Hence, organic materials differ significantly in their optical, mechanical, and electronic properties from the conventional semiconductors.

Figure 2-4 Classification of organic materials with increasing structural complexity [20]

Figure 2-5 Chemical structures of some typical molecular semiconductors used in OPVs

Organic materials can be further divided into three types. With increasing structural complexity and molecular weight, there are small molecular weight compounds, polymers, and biological molecules, as shown in Fig. 2-4. Small molecular weight compounds are often referred as “small molecules”, but in fact they can be quite large, consisting of up to a few hundred atoms, and having molecular weights $MW < 1000$. Polymers are long-chain macro-molecules consisting of an undefined number of repeating units, therefore their MW can be anywhere from a few thousand to more than a million. The molecules having the highest structural complexity are of biological origin, such as DNA. The term organic electronic materials or organic semiconductors usually refer to small molecules and polymers. Both have been used as the active materials in electronic and optoelectronic devices. The chemical structure of some commonly used molecular semiconductors in OSC are shown in Fig. 2-5.

The intrinsic charge carrier concentrations of organic semiconductor at room temperature in the dark are nearly negligible; they can be nearly regarded as insulator. However, the charge carrier concentration can be increased by “doping” yet the techniques for doping are different from inorganic materials. Unlike inorganic counterparts in which doping is accomplished by substitution of atoms in a lattice by atoms with more or less valence electrons, in organic semiconductors doping is usually achieved by the introduction of foreign molecules. It is worth mentioning that in organic semiconductors, the ‘dopants’ are not substitutional but are additional molecules that diffuse into the semiconductor and undergo redox reactions with semiconductor to remove or add an electron.

Donor or p-type materials can be doped by exposing to oxygen or other strong oxidizing agents such as iodine. The doping effect is achieved by transferring an electron from the ground state of an organic semiconductor to the oxidizing agent, resulting in an increased charge carrier concentration in the hole conductor. Whereas, exposing to reducing agent or introducing alkali metals, phenothiazine and also semiconductors with low ionization potential are used to dope n-type materials. This technique is generally known as chemical doping.

We note that compared to doped inorganic semiconductors, organic semiconductors can have very few mobile charges available, particularly in the dark. For example, the hole concentration of P3HT is in the range of 1×10^{15} to $1 \times 10^{17} \text{ cm}^{-3}$, which is one to three orders of magnitude lower than carrier concentration of typical inorganic semiconductor [37-38]. However, extra mobile charges due to illumination can make a large difference. Hence, they can sometimes be described as photo-conducting insulators. For instance, a mixture of CuPc:C60 system, commonly used in OSC, does not show an improved behavior in charge transport properties when it is in the dark yet it leads to an enhancement in photoconductivity under illumination [32-34]. This is a result of the photo-induced charge transfer [30] and hence this process is known as photodoping [39].

2.2.3 Exciton in organic semiconductor

An exciton is the photoexcited state of an electron-hole pair bound together by the Coulomb attraction. Excitons are broadly classified in three classes depending on the

strength of the Coulomb attraction. They are: (a) the Frenkel exciton, (b) the charge-transfer exciton (CT) and (c) the Mott-Wannier exciton as shown in Fig. 2-6. A Frenkel exciton corresponds to a molecular excited state where electron and hole reside on the same molecule. The radius of the exciton, R , is less than or close to the lattice constant, a . With increasing intermolecular interactions, the excitonic state may delocalize over two or more adjacent molecules, forming a charge-transfer (CT) exciton. While Frenkel and CT excitons are present in organic semiconductors, highly delocalized, hydrogen-like Mott-Wannier excitons with $R \gg a$ are commonly found in inorganic semiconductors. Due to the Coulombic interaction between the constituent electron and hole, the Frenkel or CT excitons are tightly bound, with a binding energy ranging from 0.1 eV to 1.4 eV, while that for Mott-Wannier excitons in inorganic semiconductors is only a few meV.

Figure 2-6 Schematic representation of three types of excitons in solid: (a) Frenkel excitation (b) charge transfer excitation and (c) Mott-Wannier excitons [40]

Strictly speaking, CT excitons are considered as an important intermediate state in creating of free carriers from Frenkel excitons. A neutral exciton consists of an electron

and hole located in the same spatial region and possesses no dipole moment. The situation is different when there is a material interface such as the acceptor/donor interface in OSC. The Coulombically bound electron and hole can be located in spatially separate region across the interface, resulting in CT exciton possessing a dipole momentum. When the electron donor and/or acceptor are organic semiconductors, the low dielectric constants ensure that charge separation at the interface does not give free charge carriers but rather a bound electron-hole pair across the interface (localized at different molecules), i.e., a CT exciton.

The motion of excitons in organic semiconductors can be diffusion among molecules and later charge transfer or energy transfer between different species of molecules. Similar to the transport of single carriers, exciton diffusion in organic semiconductors can occur through band transport or via the hopping process. The weak intermolecular interactions also lead to limited exciton mobility in organic semiconductors.

Energy transfer between a molecule (initial exciton site) and another molecule (final exciton site) may occur through Förster energy transfer. Fig. 2-7 (a) shows that an exciton that carries its excitation energy can be transferred from the material with the higher bandgap to the other if both the hole and electron can decrease their energy thereby. This process of excitation energy transfer which is accompanied with some energy loss is also known as Förster energy transfer and can be used to shift the emission band of the exciton towards lower energies in LEDs. Förster energy transfer can also be utilized in

OSC since it carries excitons from the shorter wavelength absorber to the longer wavelength absorber [41].

Figure 2-7 Illustration of the interface between two different organic semiconductors that facilitate (a) energy transfer and (b) charge transfer

Besides energy transfer to another molecule, charge transfer may occur and excitons may also dissociate into a free electron and hole when it is subjected to an electric field or at hetero-interfaces. Since the binding energy of excitons in inorganic semiconductor is very small (1 - 40 meV), a built-in electric field at p-n junction or even thermal energy at room temperature is able to dissociate the excitation. However, binding energy of exciton in organic material is so large that an intense electric field of $\sim 10^6$ V/cm is needed to cause Frenkel excitons to dissociate [42]. One of the most effective means to dissociate an exciton is to use a donor/acceptor (D/A) hetero-interface with large enough offset between LUMOs of D and A as shown in Fig. 2-7 (b) [24]. The band offset between HOMOs of D and A molecules and/or that between their LUMOs provides excess energy for the interfacial dissociation of an exciton. Typically about 0.4 eV offset is required to overcome the exciton binding energy of 0.4 eV. Otherwise charge transfer

may occur but the excitons do not split into their constituent charges and recombine eventually at the D/A interface. Hence a D/A hetero-interface must be effectively optimized to improve the efficiency of OSC.

2.2.4 Photovoltaic Energy conversion process in OSC

Figure 2-8 The conversion steps and the corresponding loss mechanisms for the conversion of photons to free carriers in OSC

The excitonic energy conversion process of incident photons into electricity in OSC is accomplished by five consecutive steps: (1) generation of exciton by light absorption, (2) diffusion of exciton to D-A interface, (3) exciton dissociation by the

charge transfer at the D-A interface into free electron and hole, (4) charge transport to electrodes, and (5) charge collection by electrodes. These are shown schematically in Fig. 2-8. The different steps of the conversion process together with the prevalent loss mechanisms in OSC are described below.

2.2.4.1 Light absorption and exciton generation

The first step of photovoltaic conversion process in OSC is the absorption of photons with appropriate energy by organic materials leading to the generation of excitons. Every single photon incident on the OSC, however, does not generate exciton because of the losses. The exciton generation is generally limited by the absorption efficiency (η_A) which can be defined as

$$\eta_A = \frac{\text{the number of photon generated excitons}}{\text{the number of incident photons}}$$

Due to weak intermolecular interactions, when the organic molecules interact with the incident light, the oscillator strength is normally higher compared to inorganic materials. As a result, their absorption coefficients are up to $\alpha \sim 10^5 \text{ cm}^{-1}$ in their most strongly absorptive regions [42], at least one order of magnitude higher than most inorganic semiconductors ($\alpha \sim 10^4 \text{ cm}^{-1}$). Thus, according to equation

$$\eta_A = (1 - e^{-\alpha d}) \quad (2.13)$$

, where d is the thickness of the film, an absorption of $> 85\%$ can be obtained in a 50nm to 100nm thick organic film in a cell with a reflective electrode. However, due to the mismatch factor in the refractive indices of glass/ semiconducting polymers and air,

appreciable amount of the light is lost due to reflection. Moreover, 100% transmission is never achieved when incident light passes through the transparent electrode. The reflection loss at the interface of two materials and transmission loss at transparent electrode become significant in a multilayered thin film OSC because it reduces the light absorption in the active layer.

From a material point of view, the incident photon energy, $E = h\nu$, has to be larger than or equal to the energy difference between the HOMO and the LOMO, or simply called band gap, of the semiconducting polymers. Due to the large bandgap in most semiconducting polymers, only a small fraction of incident solar light is absorbed. In the case of inorganic semiconductor, e.g., Si which has bandgap of 1.1eV is able to absorb 77% of the solar irradiation whereas most of the commercially available semiconducting polymers have bandgaps larger than 2.0 eV limiting the possible absorption to only 30% of solar spectrum. Recently, low bandgap polymers, such as PCPDTBT and PTB1, are introduced yet their bandgaps are still higher than those of inorganic counterparts [43-44].

2.2.4.2 Exciton diffusion to the donor-acceptor interface

Once an exciton is photogenerated, it typically diffuses to a remote site. At the same time, the exciton can decay either radiatively or nonradiatively to its ground state with typical lifetimes from picoseconds to nanoseconds. Alternatively, in condensed phases, some excitons may be trapped in defect or impurity sites. As efficient exciton dissociation in the next step only occurs at the D-A interface, excitons generated far from the interface must diffuse to the interface within its life time. Hence, the performance of OSC is also limited by the exciton diffusion efficiency (η_{ED}) which can be defined as

η_{ED} = the number of diffusing excitons to D-A interface/ the number of photogenerated excitons

The exciton diffusion efficiency is governed by equation (2.14), where d is the absorbing organic layer thickness [45].

$$\eta_{ED} = e^{-d/L_D} \quad (2.14)$$

The diffusivity D_{ex} , or equivalently, the exciton diffusion length L_D , in an organic material is limited due to weak intermolecular interactions. Typically, $L_D \sim 100\text{-}200 \text{ \AA}$, is considerably shorter than the optical absorption length [46]. Therefore, although in an organic D-A heterojunction that is thick enough to absorb a significant portion of the incident light, only a small fraction of photogenerated excitons can reach the D-A interface, leading to $\eta_{ED} \ll 100\%$. This efficiency can be greatly enhanced in a spatially distributed D-A interface that intermingles the donor and acceptor molecules where the D-A phase separation length is the same order of magnitude as the exciton diffusion length.

2.2.4.3 Exciton Dissociation

As the electron and hole in the exciton are not free charge carriers, a driving force must exist to dissociate it to free electrons and holes. A strong electric field is able to overcome the binding energy of the exciton and assist the exciton dissociation. However, with a typical built-in electric field in OSC, a field-induced exciton dissociation efficiency of $\eta_{FIED} < 10\%$ is estimated. Therefore, other driving forces need to be employed for efficient exciton dissociation.

Figure 2-9 Energy level diagram for an excitonic solar cell with a band offset

It has been observed that without an electric field, efficient exciton dissociation can also occur at certain organic semiconductor heterojunction with appropriate energy level offset. In such heterojunctions, exciton induces electron transfer to the larger electron affinity (χ) material and holes transfer to the smaller ionization potential (IP) materials. In other words, larger electron affinity material and smaller ionization potential material serve as ‘electron acceptor’ and ‘electron donor’ respectively, and the interface is commonly referred as organic donor-acceptor (D-A) interface. The dissociation of the strongly bound exciton is energetically favorable when the HOMO and LUMO level offsets between the donor and acceptor materials are sufficiently large to overcome the exciton binding energy. Through the charge-transfer process, a hole in the HOMO of the donor and an electron in the LUMO of the acceptor molecule are created by the dissociation of an exciton, as illustrated in Fig. 2-9. As the driving force only exists

where the two materials are in close contact, only excitons within the exciton diffusion length can be effectively dissociated.

It is reported that fullerene and its derivatives are strong electron acceptors [30]. They are able to break photoexcited excitons apart into charge carriers efficiently. Ultrafast photoluminescence decay studies showed that the photo-induced charge transfer in such blends happens within a time scale of 45 fs. This is much faster than other relaxation process (usually occurs at around 1 ns) [47]. The reverse electron transfer from fullerenes back to the polymer is extremely slow. Thus, the quantum efficiency of this dissociation process is close to 100% at the polymer-fullerene interface.

2.2.4.4 Charge transport towards electrodes

Once the excitons are successfully dissociated, the charge carriers need to transport towards the electrodes. These charge carriers are unable to travel independently unless a driving force is applied. The driving force may include the electrical field created by a chemical potential gradient and the work function difference between the two electrodes. A chemical potential gradient in electrons and holes is built up at the D-A interface. This gradient is generally defined by the difference between the HOMO of donor and LUMO of acceptor. This internal electric field determines the maximum V_{oc} and contributes to a field-induced drift of the charge carriers. Even without built-in potential, i.e, two electrodes are the same material; the chemical potential driving force can also induce the asymmetric photovoltage. However, in order to enhance the charge transport, asymmetrical contacts are used, e.g., a cathode with a low work function for electron collection and an anode with a high work-function for hole collection, to generate

an external field in short circuit conditions according to a metal-insulator-metal configuration.

The charge carriers may recombine with a rate related to the device structure and the morphology of the active layer. The donor and acceptor have to generate a percolation pathway for photogenerated charge carriers to travel before they are successfully collected by the electrodes. In a planar D-A heterojunction, the photogenerated holes and electrons are spatially separated, so that the recombination between them is unlikely. Hence, the charge transfer efficiency η_{CT} , which is defined as

$$\eta_{CT} = \frac{\text{the number of dissociated excitons transported to electrodes}}{\text{the number of dissociated excitons at D-A interface}}$$

is near unity. For bulk heterojunction, since the photogenerated electrons and holes have a significant spatial overlap, the recombination of charges in the mixed layer can be very significant and hence η_{CT} is smaller than unity.

2.2.4.5 Charge collection at the electrodes

In this last step of the photocurrent generation, the free electron and holes reaching the electrodes will be collected by the electrodes and flow to the external loading circuit. When the acceptor LUMO level matches the Fermi Level of cathode, and the donor HOMO matches the Fermi level of anode, an ideal ohmic contact would be established for efficient carrier collection at the electrodes.

ITO is commonly used as an electrode for both OLEDs and OSC. It is a highly degenerate n-type semiconductor with low resistance, high work-function and high transmittance in the visible. However, variations of ITO parameters, such as work-function, surface morphology, sheet resistance, etc. are common not only for ITO from different manufacturers but also for different batches from the same manufacture. The variation in the properties of the ITO will influence charge collection. Evaporated metals such as silver (Ag) or aluminum (Al) are used as cathode. The interfacial layer such as LiF is used to lower down the work function of the cathode and make ohmic contact. However, in practical, a perfect ohmic contact is difficult due to the availability and limitations of materials and electrodes involved. The interfacial band bending, energy offset and chemical effect at the metal-organic interface also affects the carrier collection. Due to these losses mechanism, the charge collection efficiency, η_{CC} , which is defined as

$$\eta_{CC} = \frac{\text{the number of free charge carriers collected at electrode}}{\text{the number of free charge carriers transported to the electrodes}}$$

is also always less than 1. Taking into account individual loss in each process, EQE and IQE of an OSC can be written as:

$$\eta_{EQE} = \eta_A \times \eta_{IQE} = \eta_A \times \eta_{ED} \times \eta_{CT} \times \eta_{CC} \quad (2.15)$$

$$\eta_{IQE} = \eta_{ED} \times \eta_{CT} \times \eta_{CC}$$

From the equation 2.15, it is observed that individual components of η_A , η_{ED} , η_{CT} are η_{CC} are important to achieve high EQE. Nevertheless, η_A and η_{CT} will be bottleneck for further improvement of power conversion efficiency in future because of the nature of organic

semiconductors in narrow absorption spectrum and low carrier mobility as well as the tradeoff between two parameters.

2.2.5 Photovoltage in organic solar cell

The photovoltage of inorganic photovoltaic is determined by a built-in potential (Φ_{bi}) equal to the difference in the Fermi energy levels of the n-doped and p-doped layers. The photovoltage of OSC is governed by a different mechanism which is not well known. Theoretically, the potential energy stored within one pair of separated positive and negative charges is equivalent to the difference in their respective quasi-Fermi levels, or often denoted as the difference in the electrochemical potentials. The larger the quasi-Fermi level splitting remains during charge transport through the interfaces at the contacts, the larger will be the photovoltage [48]. When the quasi-Fermi level splitting persists during charge transport through the interfaces at the contacts, the V_{oc} will approach this Fermi level splitting.

The built-in electrical potential in organic semiconductor devices arises from the work function difference of the anode and the cathode, according to metal-insulator-metal (MIM) model. However, Brabec et al. experimentally showed that the influence of Φ_{bi} on V_{oc} is not significant [49] while others reported that the variation of V_{oc} can be more than 0.5V due to the changes in work-function of the cathode [50]. There were a number of studies focusing on the V_{oc} dependence on LUMO-HOMO level changes, electrode Fermi levels and chemical potential gradients of the OSC. But quantitative relationships are not

well understood. Though for ideal (ohmic) contacts no loss is expected, energy level offsets or band bending at non-ideal contact can lead to a decrease in the photovoltage.

2.3 Dye-sensitized solar cells

The dye-sensitized solar cell (DSSC) is a promising alternative to conventional silicon photovoltaic technology due to high photon-to-electricity conversion efficiency, low-cost and easy fabrication. The capability of large-scale manufacturing from abundant, environmentally friendly and non-toxic materials without expensive and elaborate apparatus makes this technology particularly attractive. The cell concept is also believed to reduce the energy payback time^{*} significantly compared to traditional silicon cells because it does not require energy intensive process at high temperature. In addition, DSSC can be engineered into flexible and mechanically robust cell through roll-to-roll production. Contrary to silicon solar cell, it completely departs from the classical solid-state p-n junction device. In fact, it is a photo-electrochemical system in which electrolyte in the form of liquid, gel or solid is filled between a photo-sensitized semiconductor electrode and metallic counter electrode. A sensitizer which chemically adsorbs on the surface of a wide band gap semiconductor is responsible for light absorption. Charge separation takes place at the interface of sensitizer and semiconductor via photo-induced electron injection from the excited state of sensitizer into the conduction band of

^{*} The energy payback time is defined as the ratio of the energy input during life cycle of a PV module (which includes the energy requirement for manufacturing, installation, energy used during operation, and energy needed for decommissioning) to the annual energy saving due to electricity generated by the PV module.

semiconductor. The regeneration of sensitizer is possible by electron donation from the redox system of electrolyte to oxidized state of the sensitizer. Up to now, DSSC based on nanocrystalline TiO_2 electrode, Ru-polypyridyl-complex dye, liquid electrolyte with iodide/triiodide redox couple and Pt counter electrode offers the best efficiency. The highest reported efficiency of DSSC ($\sim 11\%$) is even higher than amorphous silicon solar cell (9.5%), appealing to manufacturing of inexpensive and highly efficient solar cell. However, further improvement in the efficiency, stability and scalability are still required to realize into commercialization.

2.3.1 History of Dye-sensitized Solar Cell

The discovery of dye-sensitized semiconductor is considered to be forerunner in the emergence of DSSC. The first case of dye-sensitized semiconductor was revealed as early as in 1873 by Vogel via the dye sensitization of silver halide emulsion which was applied in photography [51]. In 1887, Moser applied this concept in the photoelectric effect by using the dye erythrosine on silver halide electrodes [52]. Various cyanine and related dyes are adsorbed onto silver halide microcrystal to extend the spectral response in the visible region for photography application. Some semiconductors studied on spectral sensitization are ZnO , CdS etc. Putzeiko and Trenin first reported sensitization of pressed ZnO powder by adsorbed rhodamine B, eosin, erythrosine and cyanine dyes in 1949 [53-54]. Nevertheless, the mechanism of electron injection from photo-excited dye molecule into wide band gap semiconductor was not clear until late 1960s: whether it was through

energy transfer from the dye to defect centers in the underlying crystal or through direct electron transfer from the excited states of the dyes [55]. The injection of electrons from organic dye to semiconductor was discovered only in 1964 by Namba and Hishiki [56] and in 1968 by Tributsch and Gerischer et al. [57-58] with their work on ZnO. This early electrochemical work demonstrated that excited dyes on the surface of the ZnO were oxidized to produce photocurrents that could be sustained through the addition of reducing agents to the solution that would reduce the photo-oxidized dye. In 1971, conversion of photon to electric current by mean of electrochemical reactions of excited molecules was firstly demonstrated by Tributsch et al. employing chlorophyll molecules adsorbed on single crystal ZnO electrode, in contact with an electrolyte containing suitable electron donors [59-60]. This kind of reaction is analogous to the primary steps of photosynthesis and chlorophyll-sensitized reactions in photosynthetic membranes, which can be applied to elucidate the concept of electrochemical kinetics. Later, fundamental researches were done on ZnO and TiO₂ single crystal electrode but the efficiency of the devices was still poor [61-62]. The main problem was that dye anchorage on a flat surface is poor and only 1 to 2% of incident light could be absorbed by dye. Thicker dye layers increased the resistance of the cell without contributing to the additional current generation [58]. In the following years, the chemisorption of the dye on the surface of the semiconductor was developed to enhance the linkage and dye loading [63-64]. While the investigation on photoelectrode materials and semiconductor-electrolyte interface were being carried out [65-68], new dyes were also developed. Ruthenium (II) polypyridine complex was started to use to sensitize SnO₂ electrode in 1975 by Gleria and Memming and TiO₂ electrode in 1977 by Clark and Sutin [69-70]. Introductions of dispersed

particles with a high roughness factor, instead of planar semiconductor, not only provides large surface area but also generates multiple reflection at the rough surface, allowing to capture more incident light by a monolayer of dye with a high molar extinction coefficient [71-72]. With these improvements in light harvesting and photoelectrode materials, a conversion efficiency of 7.1-7.9% under simulated solar light and 12% in diffuse daylight was achieved in 1991 [4]. This achievement is really exciting and further motivates more research activities in photo-electrochemical cell. Through continuous improvement, today the state-of-art technology has driven the efficiency of cell to more than 11% [73]. Another evolution to this classic system was implementation of solid-state dye-sensitized cell by replacing the liquid electrolyte with (quasi) solid-state electrolytes such as hole transport materials [55, 59], polymeric matrix electrolyte [60-61], quasi-solid molten salt (ionic liquid) [52], and nanocomposite gel electrolyte [51, 62, 64] to prevent leakage and evaporation of volatile liquid electrolyte. However, the efficiency of this solid-state DSSC is lower than traditional DSSC mainly due to difficulties in filling of pores and low conductivity.

2.3.2 Basic principle of dye-sensitized solar cell

As DSSC is developed based on photo-electrochemical system, its working principle is much different from conventional p - n junction solar cell. In a p - n junction of silicon or inorganic semiconductor, the electronic contact between p and n components form a depletion layer or space charge region near the metallurgical junction where

photogenerated electron-hole pairs were separated by internal electric field. Both majority and minority carriers coexist in the same volume of semiconductor. Because the separated charge carriers can recombine in the bulk via defects, high purity material is crucial in p - n junction solar cell to minimize the recombination.

Figure 2-10 The main components of a dye-sensitized solar cell and schematic illustration of the working principle of the DSC

On the contrary, in a DSSC, an electron-conducting phase (n -type semiconductor) and a hole conducting phase (redox species or hole conductors) build a junction in bulk-heterojunction form. The main components of a typical DSSC are conducting glass (usually glass coated with FTO), semiconductor network, dye molecules attached to the semiconductor, iodide/triiodide (I^-/I_3^-) redox electrolyte and platinized conducting glass, from left to right in the schematic shown in Fig. 2-10. A porous network of interconnected

nanometer-sized crystallites of a wide band gap semiconductor is used as electron conducting phase. Anatase (TiO_2) crystallites have been a material of choice for electron conducting phase although alternative wide band gap oxides such as ZnO [70], SnO_2 [74], and Nb_2O_5 [75] have also been scrutinized. A monolayer of dye chemically adsorbed on the anatase is used as sensitizer. The whole network of anatase together with dye is immersed in electrolyte. Because the individual size of particles is too small compared to the Debye length of the material, the whole part of the particle is depleted upon contact with electrolyte and no significant space charge region is formed [16]. Upon illumination, dye is sensitized to the excited state (D^*) by light absorption and rapidly injects an electron into the conduction band (CB) of semiconductor while the holes, at least initially, remain on the ground state of dye (D). In contrast to p-n junction solar cell, the significant role of electric field in charge separation is not observed although an electric field exists at the electrolyte/semiconductor interface, which is due to a surface field established spontaneously by a charged dipole layer. (The dyes usually used are acidic due to carboxylic or phosphate groups and release proton upon binding with semiconductor film. In addition, when the film is immersed in a protic solvent such as electrolyte, the solvent also acts as proton donor. In a protic media, Li^+ or Mg^{2+} ions are potential determining ions for TiO_2 and charge the surface positively. Thus, the protons together with other cations in the electrolyte adsorb on the surface of TiO_2 and a dipole is formed across the Helmholtz layer between the negatively charged (iodide and dye) species and the cations. This dipole layer establishes a surface electric field pointing away from the TiO_2 surface.) Moreover, in a DSSC, injection of only one type of carrier (electrons, in the case of most of common DSSC) from the excited dye into the semiconductor is energetically possible

[16]. The ground state of dye (D) is subsequently restored by electron donation from iodide (I⁻) to the oxidized state of dye (D⁺). The iodide is regenerated in turn by the reduction of triiodide (I₃⁻) at the counter electrode with the aid of Pt catalyst. Concurrently, the recuperation of redox system is realized by transporting holes to the counter electrode either in a diffusion or hopping mechanism depending on the transporting mediator. The circuit is finally completed by electron migration via an external load [76].

2.3.3 Charge Transfer and Recombination Kinetics

In addition to the charge transfer process briefly discussed in above section, there are series of undesirable back reactions (recombination) opposing the forward reactions. Because the photogenerated current is the result of the dynamic competition between charge transfer and recombination process [77-78], the kinetics of these processes are important in DSSC. In a simple model, the electron extraction efficiency (η_{ext}) at the short-circuit condition can be defined as

$$\eta_{ext} = \frac{k_{trans}}{k_{trans} + k_{rec}} \quad (2.16)\eta$$

where k_{trans} and k_{rec} are the first-order kinetic constant for the electron transfer and recombination process respectively, indicating that an efficient cell should facilitate the forward reactions and suppress the back reactions.

Figure 2-11 The kinetics of the charge transfer and recombination process in a typical DSSC containing ruthenium complex-sensitized TiO_2 nanocrystalline film and I^-/I_3^- redox electrolyte. The forward reactions (charge transfer) and back reactions (recombination) are indicated in solid and dash arrow respectively.

The schematic of kinetics in the charge transfer and recombination process is illustrated in Fig. 2-11. The discussion in this section is based on a DSSC with the nanocrystalline TiO_2 film, ruthenium polypyridyl complexes dye and I^-/I_3^- electrolyte, which yields the highest energy conversion efficiency to date. The photo-excitation of dye (F1) occurs within a few femtoseconds upon illumination. The time scale of injection of electron from excited dye into the conduction band of TiO_2 (F2) is tens of femtoseconds to hundred of picoseconds, depending on the electronic coupling and energetic overlap between donor (D^*) and acceptor (semiconductor) states [53-54, 69]. The injected electrons in TiO_2 are rapidly thermalized by lattice collisions and phonon emissions within less than 10 fs. Since the excited state of dye (D^*) eventually returns back to its

ground state (D) radiatively or non-radiatively after some time, the injection process (F1) has to compete with the relaxation of dye (B1). This intramolecular relaxation of dye excited states also might complicate the injection process and change the timescale. However, the relaxation of dye from excited state to the ground state happens in nanosecond range which is three orders of magnitude slower compared to the injection [77, 79], as a result, the injection efficiency is close to unity. The reduction of oxidized dye, therefore, is facilitated by the electron donation from I⁻ in electrolyte (F3) which has to compete with recombination of injected electrons in TiO₂ with oxidized dye (B2). The half-time* for regeneration of most ruthenium complex dyes, in the presence of about 0.5M iodide is in the range of 100 ns to 10 μ s, depending on the precise composition of the electrolyte [79-85], whereas the recombination of electrons in TiO₂ with dye happens in milliseconds range [76], ensuring that the forward reaction is orders of magnitude faster than back reaction for regeneration of dye. The reaction between oxidized dye and I⁻ leads to the formation of diiodide radicals (I₂^{•-}) [84, 86-87]. This radical was observed in DSSC using nanosecond-laser spectroscopy [84, 86-87] and pseudo-steady-state photoinduced absorption spectroscopy [88].

Another important process is electron percolation along the nanocrystalline film towards electrode after being injected (F4). The injected electrons from the excited dye experience 10⁶ times the number of trapping and detrapping at the grain boundary of TiO₂ nanoparticles due to a large density of surface electron traps [89-91]. The electron diffusion coefficient in TiO₂ nanocrystalline film, therefore, is considerably low (5×10^{-5}

* The half-time is defined as the 50% of the time scale of the regeneration process; from capturing of electrons from iodide to returning back to ground state of dye.

cm²/s) and it takes about 10 ms to reach the conducting electrode [92-93]. Meantime, the electrons percolating along the nanocrystalline film can be recaptured by oxidized species (I₃⁻) in electrolyte (B3), within millisecond time range [76, 79]. The recombination of electrons in TiO₂ with I₃⁻ in electrolyte has been mostly studied using steady-state [94-95] or dynamic [96-98] measurements of the open-circuit potential. Since the kinetics of this back reaction (B3) is comparable to that of forward reaction (F4), the recombination of injected electrons with I₃⁻ in electrolyte is more serious than the other two back reactions (B1 and B2). Hence, it must be suppressed as much as possible to improve the charge conversion in DSSC. This recombination can happen at the interface between electrolyte and TiO₂ as well as part of conducting electrode which is exposed to the electrolyte. Nevertheless, the latter route is usually less important in the case of I⁻/I₃⁻ and can be further reduced by employing a compact blocking layer of metal oxide between the conducting electrode and mesoporous film [95]. The reactions for electron transfer process and competing back reactions are summarized below.

2.3.4 Photovoltage in dye-sensitized solar cell

Generally, photovoltage or open-circuit voltage (V_{oc}) is a function of the quasi-Fermi level splitting of p and n -type material. It also depends logarithmically on the light-generated and diode saturation current as mentioned in Eq. 2.4 in section (2.1.2). Sinton et al. suggested that in a p - n junction silicon solar cell V_{oc} can also be determined from the excess carrier concentration due to illumination [99].

$$V_{oc} = \frac{kT}{q} \ln \left[\frac{(N_A + \Delta n)\Delta n}{n_i^2} \right] \quad (2.17)$$

where N_A is the doping concentration, Δn is the excess carrier concentration and n_i is the intrinsic carrier concentration. This means that the more excess carriers are injected into the semiconductor the larger the photovoltage is attained. The concepts mentioned above are also generally applicable in DSSC.

Now, let's take a look at energetics of DSSC (Fig. 2-12) to better understand the concept of V_{oc} in DSSC. The energetics are referred to a DSSC with FTO electrode, TiO_2 nanocrystalline film, ruthenium polypyridyl complexes dye, I/I_3^- electrolyte and Pt counter electrode. Fig. 2-12(a) reveals the energy levels of individual layers in DSSC before contact. After TiO_2 is made contact with liquid electrolyte in the dark, the Fermi level of semiconductor (E_{FS}) is aligned to redox potential of electrolyte (E_{redox}) as well as the Fermi level of the two electrodes (E_F) under equilibrium condition (Fig. 2-12(b)). Strictly speaking, a band shift in conduction band of TiO_2 (E_C) is also observed upon contact with electrolyte after dye adsorption because of the solvation effects [100] and

Helmholtz layer dipole arises from the cation adsorption on the semiconductor surface due to the carboxylate or phosphate groups of the dye [91]. This band shift and band bending at the interface are neglected in this figure for simplicity. Under strong illumination at open circuit, equilibrium condition is disturbed and E_{FS} moves up to electron-quasi Fermi level (E_{Fn}^*) which is close to conduction band minimum of TiO_2 due to the accumulation of photogenerated electrons in the E_C of TiO_2 (Fig. 2-12(c)). Electron injection will also minimize any electric potential difference across the TiO_2 /FTO interface. The electrochemical potential of electrons in FTO and TiO_2 will be the same under the open circuit condition, resulting in an upward shift of conduction band of FTO to that of TiO_2 . Likewise, E_{redox} is shifted to hole-quasi Fermi level (E_{Fp}^*) owing to virtual hole injection into electrolyte. The difference between two quasi Fermi levels ($E_{Fn}^* - E_{Fp}^*$) determines the maximum attainable photovoltage of DSSC. As E_{Fn}^* cannot rise significantly above E_C of semiconductor under normal injection conditions and E_{Fp}^* is close to E_{redox} , the maximum photovoltage in DSC is generally expressed as $V_{oc(max)} = E_C - E_{redox}$.

However, as the experimental value of V_{oc} is smaller than expected value ($E_C - E_{redox}$) for all DSSC, there must be other limiting factor for attainable V_{oc} . Turrion et al proposed that the maximum attainable photovoltage is conditioned by the quasi-Fermi level of FTO ($E_F^*(FTO)$) rather than conduction band of TiO_2 [101]. The injection of photogenerated electrons shifts upward the equilibrium Fermi level of TiO_2 and FTO to the quasi (non-equilibrium) Fermi level. When V_{oc} value is reached, any additional increase of photon flux will raise Fermi level at TiO_2 but not at FTO. Thus the $V_{oc} = [E_F^*(FTO) - E_{redox}]/e$ does not further increase. In fact, a potential barrier occurs at FTO/

TiO₂ interface for applied bias close to or larger than V_{oc} . This barrier hinders the transport of electron from TiO₂ to FTO, making the $V_{oc(max)}$ smaller than expected value of

$$E_C - E_{redox}.$$

Figure 2-12 The energetics of individual layers in a typical DSSC (a) before contact each other (b) after contact under the equilibrium condition (in the dark) and (c) after contact in non-equilibrium condition (under illumination). The vertical axis on the left is the potentials referred to the vacuum level (VAC) and on the right is the potentials referred to the normal hydrogen electrode (NHE).

Because V_{oc} depends on the photogenerated current and recombination current as discussed above, it can also be expressed mathematically using these parameters [94]. As

the resultant photocurrent is the competition between forward and back reaction, the observed photocurrent density J_{ph} is given by

$$J_{ph} = J_{inj} - J_r \quad (2.18)$$

where J_{inj} is the electron injection current resulting from dye sensitization and J_r is the recombination current arising from back reactions. J_{inj} is related to the incident photon flux I_0 ($\text{cm}^{-2}\text{s}^{-1}$) by the expression

$$J_{inj} = qAI_0 \quad (2.19)$$

where q is the charge of electron and A is the ratio of absorbed photon flux to I_0 . We consider two main back reactions for recombination current: (1) the back reaction between injected electrons in TiO_2 and oxidized dye molecule and (2) the back reaction between injected electrons and oxidized species in electrolyte. The recombination current depends on the kinetic constant of back reactions, the concentration of I_3^- in redox couple $[\text{I}_3^-]$ and oxidized dye $[\text{D}^+]$, and the difference between the electron concentration in the semiconductor in the dark n_0 and under illumination n . Thus, the recombination current density can be expressed as

$$J_r = qk_1[\text{I}_3^-](n - n_0) + qk_2[\text{D}^+](n - n_0) \quad (2.20)$$

where k_1 and k_2 are kinetic constant of back reaction with I_3^- in redox couple and oxidized dye respectively. The electron concentration n is exponentially related to the photovoltage V by the equation

$$n = n_0 \exp\left(\frac{qV}{kT}\right) \quad (2.21)$$

where qV is the difference between the Fermi level of TiO_2 under illumination and in the dark. At open circuit voltage ($V = V_{oc}$), J_{ph} become zero and from equation 2.19 and 2.20 we obtain

$$qAI_0 = qk_1[I_3^-](n - n_0) + qk_2[D^+](n - n_0) \quad (2.22)$$

Combining equation 2.21 and 2.22 yields the expression of V_{oc} with light intensity, the concentration of oxidized dye molecule and triiodide in electrolyte, and kinetic constant of back reactions as in following equation.

$$V_{oc} = \frac{kT}{q} \ln\left(\frac{AI_0}{k_1[I_3^-]n_0 + k_2[D^+]n_0} + 1\right) \quad (2.23)$$

Usually, $AI_0 \gg k_1[I_3^-]n_0 + k_2[D^+]n_0$ and V_{oc} can be simply expressed as

$$V_{oc} = \frac{kT}{q} \ln\left(\frac{AI_0}{k_1[I_3^-]n_0 + k_2[D^+]n_0}\right) \quad (2.24)$$

The order of rate of reaction and electron transfer coefficient are considered in some expressions but they are taken as unity herein, assuming that the recombination reaction between the injected electron and the oxidized dye molecule follows simple first-order kinetics. In Eq. 2.20, both localized electrons in the surface states and free electrons in the conduction band contribute to the recombination current. Moreover, in contrast to conventional solid-state devices, n_0 is not the same as the doping density of the

semiconductor. Because TiO_2 nanocrystalline film is in contact with the electrolyte, n_0 depends on the difference between the conduction band of TiO_2 (E_c) and redox potential of electrolyte (E_{redox}) and can be expressed as $n_0 = N_c \exp[(E_c - E_{redox})/kT]$ where N_c is the effective density of states in conduction band. Thus, a band shift in the dark due to solvation effects upon contact with electrolyte and Helmholtz layer dipole arises from dye adsorption will alter n_0 and affect V_{oc} .

Chapter 3 Efficient charge collection with sol-gel derived colloidal ZnO thin film in organic solar cells

3.1 Introduction

Zinc oxide (ZnO) is a highly attractive material to be used in optoelectronic devices due to its low-cost, being environmentally benign, large-band gap (3.37 eV), high electronic mobility and transparency in visible range [102-105]. ZnO films with various morphologies such as nanorod [105-106], nanoflower [103], nanowire [107], nanotube [108], nanoring [109] and nanosheet [110] were reported with their properties. Among various ZnO morphologies, nanorod structure was widely reported in both DSSC and hybrid photovoltaic devices due to its fast electron transport and large surface area. ZnO nanorod grown on ZnO dense film was previously demonstrated as an electron-collecting layer from P3HT:PCBM bulk-heterojunction with PCE 2.03 % [111] and 2.7 % [112]. However, report on applying colloidal ZnO thin film as an effective electron collector for polymer-fullerene blended bulk-heterojunction device is rare [113].

ZnO thin film can be produced by many techniques such as chemical vapour deposition, sputtering, molecular beam epitaxy, spray-pyrolysis and sol-gel process [114-118]. The colloidal ZnO thin film derived from sol-gel process has distinct advantages over other techniques due to its simplicity, cost-effectiveness, lower crystallization temperature, ability to tune colloid size from sol-gel chemistry and larger surface area coating capability [119-120]. Preceding studies on sol-gel derived ZnO film revealed that

the optoelectronic property of the sol-gel ZnO film is highly influenced by the concentration of sol-gel solution, number of coatings and annealing temperature [121-122]. In addition, controllable, stable and uniform dispersion of ZnO particles are highly dependent on the process of sol-gel.

In this experiment, instead of studying the optoelectronic property of a standalone ZnO film, we integrated the ZnO film into OSC as an electron collecting layer as shown in Fig. 3-1 and investigated the influence of sol-gel process on the performance and reliability of the OSC. We also studied the effect of surface treatment of ZnO film on the performance of the devices. With ammonia treated and thickness-tuned ZnO film, the PCE of the cell was significantly increased from 0.84% to 2.01% under one sun of simulated AM1.5 illumination.

Figure 3-1 (a) Device structure of bulk-heterojunction solar cell using ZnO as an electron collecting layer (b) Corresponding energy band diagram and thickness of individual layer. The electron transfer to the electrode through conduction band of ZnO is indicated by arrows.

Figure 3-2 Process flow chart showing the procedures for preparing ZnO sol-gel and thin film

3.2 Experimental

3.2.1 Sol-gel preparation

The preparation of sol used for ZnO thin film was similar to the literature [120]. Two different methods were applied to prepare the sol. In method A, zinc acetate dihydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ (99.95% Fluka) with 0.75 M, 0.5 M and 0.3 M concentration and ethanolamine $[\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}]$ (99+% Sigma-Aldrich) with the same concentration were dissolved in 2-methoxyethanol $(\text{CH}_3\text{OCH}_2\text{-CH}_2\text{OH})$ (99.8% Sigma-

Aldrich) and stirred for 12 h at room temperature. In Method B, zinc acetate dihydrate with 0.75 *M*, 0.5 *M* and 0.3 *M* concentration was first dissolved in anhydrous ethanol [CH₃CH₂OH] (99.5+% Aldrich) and rigorously stirred for 2-3 h at 80 °C. Subsequently, ethanolamine was added to the solution as sol stabilizer followed by thorough mixing process with magnetic stirrer for 12-15 h at 60 °C. The process flow chart for preparing sol-gel with different methods and coating thin film is shown in Fig. 3-2.

3.2.2 Device fabrication

In a typical device fabrication process, FTO (15 Ω/□) coated glass substrates (2 cm × 1.5 cm) were first cleaned by ultrasonic agitation in detergent, deionized water, acetone and isopropanol sequentially, followed by oxygen plasma treatment for 5 min. FTO was chosen as transparent electrode, instead of ITO, because of lower work function and better thermal stability. The prepared sols were spin-coated on the FTO-coated glass substrate with 3000 rpm. The process of coating was repeated a few times to acquire the desired thickness. After each coating, the synthesized films were heated at 150°C for 15 min to dry. After coating the last layer, the films were sintered at 350 °C for 1 h in the air to obtain crystallized ZnO. The ZnO thin film prepared by this method has been reported to have *c*-axis of the crystals normal to the substrate [120]. Some prepared ZnO thin films were immersed in 0.3 *M* ammonia in distilled water for 15 min for comparison purpose. After rinsing thoroughly with distilled water for several times, the films were dried in the laboratory oven at 80 °C to remove moisture completely.

After the thin-film process by sol-gel method, ZnO coated FTO glasses were transferred into a glove box for polymer spin coating. P3HT:PCBM (1:1 by weight) was spin-coated on ZnO film from a 40 mg/ml chloroform:chlorobenzene (1:1 by volume) solution at 900-1000 rpm. The thickness of the blend layer was about 150 nm. The polymer layer was dried at 80 °C under N₂ ambient for 10 min. Finally 10 nm Au and 70 nm Ag were deposited sequentially under 3×10^{-4} Pa by thermal evaporation through a shadow mask to form active area of 10.5 mm². The deposition rates for Au and Ag are 4 Å/min and 20 Å/min respectively. Au functioned as anode and Ag was used to protect the underlying layer. The fabricated devices were post-annealed at 150 °C under N₂ ambient for 10 min to obtain a penetrating network of blend layer. The complete device is similar to the sketch in Fig. 3-3.

Figure 3-3 The sketch of the complete device. The dimensions are not drawn in scale.

3.2.3 Characterization

Photovoltaic measurements were conducted by illuminating the devices under a solar simulator (Model 16S-002, Solar Light Company Inc.) with AM1.5G filter. The current-voltage (*J-V*) characteristics were performed using a Keithley 2400 Sourcemeeter.

All devices were tested in ambient conditions and simulated light intensity was adjusted to 100 mW/cm^2 calibrated with a Thorlabs optical power meter. The scanning electron microscopy (SEM) images were recorded using a JEOL Field Emission Scanning Electron Microscopy (FESEM) and thickness of layer was measured by a surface profiler (KLA Tencor P-15). XPS measurements were performed with a Kratos ESCA (model AXIS Ultra) using a monochromated Al $K\alpha$ ($h\nu = 1486.7 \text{ eV}$) X-ray source operated at 15 kV and 10 mA under 8.6×10^{-9} Torr.

3.3 Result and Discussion

3.3.1 Device Structure

Prior to fabrication of device, we verified the feasibility of our device structure based on energy band of individual material and previous work. In our device structure, it is appropriate to use ZnO as an electron collecting layer because the conduction band of ZnO (4.2 eV) is lower than LUMO of PCBM (3.7 eV) and higher than work function of FTO (4.4 eV), providing barrier-free junctions for charge transfer as shown in Fig. 3-1(b). Ohmic contact is possible at the interface between polymer and Au electrode since HOMO of P3HT (5.2 eV) is well matched with work function of Au (5.1 eV). The previous report [82] revealed that two-point electrical measurements of ZnO on FTO substrates gave linear current-voltage curve, demonstrating that ohmic contact is formed between ZnO and FTO.

3.3.2 Effect of sol concentration on device performance

First of all, devices were fabricated using 0.75 *M* sol by method A (see experimental section). The *J-V* characteristics of all fabricated devices showed short circuit behavior. This short circuit problem was also encountered by others [123] and attributed to the direct contact between hole conductor and back contact layer. This agrees with SEM image of ZnO film revealed in Fig. 3-4(a). It can be clearly seen from the Fig. 3-4(a) that ZnO colloids are not closely packed which creates nano-sized gaps on the film. These gaps are favorable for polymer to infiltrate the ZnO film and cause direct contact between polymer layer and FTO. It has been reported that spray pyrolysis was substituted with spin coating to avoid direct contact [123-124]. Herein, nevertheless, we modified the concentration of sol to eliminate this problem. Past study on sol-gel process discovered that the grain size of ZnO increases with increasing the concentration of sol because as the concentration increases, the amount of solute increases in the sol and therefore the electrostatic interaction between the solute particles becomes larger thereby increasing the probability of more solute to be gathered together forming a grain [119-120]. The next step was to prepare sols with 0.5 *M* and 0.3 *M* concentration in order to reduce grain size, consequently, forming closely packed colloid film. SEM images (refer Fig. 3-4) show that the grains from 0.5 *M* and 0.3 *M* sol are smaller than those derived from 0.75 *M* sol and the most closely packed and uniform in grain size is obtained from 0.3 *M* sol. The *J-V* characteristics of the devices using 0.5 *M* and 0.3 *M* sol do not show any short-circuit behavior but have photovoltaic effect. (The detail electrical parameters of the devices are shown in Table 3-1.)

Figure 3-4 FESEM images of ZnO films derived from (a) 0.75 *M* (b) 0.5 *M* and (c) 0.3 *M* sol. The nano-sized gaps on the film derived from 0.75 *M* are shown in circle.

ZnO Sol concentration	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
0.5 <i>M</i>	5.196	0.415	36	0.78
0.3 <i>M</i>	4.683	0.460	39	0.84

Table 3-1 The performance of devices with ZnO layer derived from 0.5 *M* and 0.3 *M*

3.3.3 Effect of sol-gel process on device yield

Figure 3-5 (a) Device Failure (%) due to short circuit Vs sol aging time for two different methods of sol-gel process (methods A and B). J - V characteristics of the devices fabricated from two-week aged (b) 0.5 M sol and (c) 0.3 M sol.

To investigate the stability of sol, we prepared 0.5 M and 0.3 M sols by method A and aged the sols for a few weeks before fabricating the devices. Ten devices were fabricated for each sol concentration and tested. It was found that some devices fabricated from aged sols malfunctioned due to short-circuit. The failure (%) of devices versus sol aging time is shown in Fig. 3-5(a). Although device failure was only 10% for both one-

week aged 0.5 *M* and 0.3 *M* sols, it was increased to 30% and 50% for two-week aged 0.5 *M* and 0.3 *M* sol respectively. All devices fabricated from three-week aged sol showed no photovoltaic effect due to short circuit. This shows that the sol prepared by method A is not stable after a few weeks. Therefore we modified the sol-gel process using method B and carried out the same experiment. We found that there is almost no difference in PCE due to modification of sol-gel process [Fig. 3-5 (b) and (c)] but tremendous positive effect on device failure (%). No device failure at all occurred for 0.3 *M* sol (method B) and only 10% for two-week aged 0.5 *M* sol (method B). However, this failure is probably due to human error in handling of samples during experiment and unlikely from instability of the sol. From the experimental result, it is significant that refluxing promotes the hydrolysis and condensation process during the formation of ZnO from precursors and hence the stability of the devices improves. The presence of the amine compounds from ethanolamine also increases the pH level, which should promote the formation of ZnO.

3.3.4 Effect of ammonia treatment on device performance

Despite the stability of sol by modified method, the performance of device was still low. We postulated that it is due to the impurity of ZnO film from sol-gel process. Previous studies on sol-gel process reported that zinc-oxo-acetate oligomers are formed during the hydrolysis and condensation of sol-gel process due to the presence of OH-group and acetate (CH_3COO^-) group from zinc acetate dehydrate [121]. These acetate-capped colloidal particles are transformed into crystalline ZnO film by high temperature

annealing. Nevertheless, as we employed low temperatures annealing which is more compatible with organic solar cell fabrication process, acetate (Ac) ions covering on the surface of the ZnO film were not completely removed, hindering the transport of electrons from active layer to bottom electrode. Therefore an additional room temperature surface activation method of ammonia treatment was applied to further remove the Ac ions. We immersed ZnO film in 0.3 M ammonia in distilled water for 15 min after sintering the film. Ammonia treatment can remove the ZnAc_2 coated on the surface of the ZnO film by forming dissolvable $\text{Zn}(\text{NH}_3)_4^{2+}$ ions [125]. The removal of Ac ions by ammonia treatment was verified with X-ray photoelectron spectroscopy (XPS).

Figure 3-6 XPS (a) wide scan spectra and (b) high resolution C(1s) spectra of as-deposited film, annealed film and annealed and ammonia treated film

Fig. 3-6 (a) and (b) are XPS wide scan spectra and high resolution C(1s) spectra of ZnO film respectively. The peak positions were referenced to carbon at 284.6 eV. The major peaks of Zn, O and a small peak of acetate are detected in wide scan spectra of as-

deposited film and no other impurity is spotted. Whereas the intensity of acetate peak is attenuated to negligible amount in the spectra of annealed and ammonia treated film. In high resolution C(1s) spectra, two distinct peaks are observed at binding energies around 288.6 eV and 284.6 eV for as-deposited film. The one at higher binding energy corresponds to the carbon atom bonded to carbonyl oxygen atom in the acetate group and the other peak associates with adventitious carbon atoms [126]. The intensities of both peaks are attenuated after low temperature annealing while the acetate group diminishes strongly and the intensity of carbon reduced to half after additional ammonia treatment.

Fig. 3-7 (a) and (b) show the J - V characteristics of devices with ammonia treated and pristine (only annealed) ZnO film for 0.3 M and 0.5 M respectively. With ammonia treatment, both V_{oc} and FF are improved in the device with ZnO film derived from 0.5 M sol, leading to the increase in PCE. All parameters are increased in the device with ZnO film derived from 0.3 M sol which yields $J_{sc} = 7.108 \text{ mA/cm}^2$, $V_{oc} = 0.548 \text{ V}$, FF = 40% and PCE = 1.55%. The J - V curves (in semilogarithmic scale) of the solar cells in the dark (Fig. 3-7 inset) show that device with ammonia treated ZnO film has higher current in forward direction and a lower leakage current in the reverse direction for both 0.5 M and 0.3 M cases.

Figure 3-7 J - V characteristics of the devices with ammonia treated and pristine ZnO film under light intensity 100 mW/cm^2 . ZnO films were derived from (a) 0.5 M sol [Method B] and (b) 0.3 M sol [Method B]. Inset: dark J - V curves of the respective devices in semilogarithmic scale.

3.3.5 Effect of the thickness of ZnO film

The performance of device was observed to be dependent on the thickness of ZnO film. We fabricated devices with different thicknesses of ZnO film, taking 0.3 M sol as a

reference. The J - V curves of the devices are shown in Fig. 3-8. The device fabricated from 120nm-thick ZnO film has $J_{sc} = 8.192 \text{ mA/cm}^2$, $V_{oc} = 0.563 \text{ V}$, $\text{FF} = 43\%$ and $\text{PCE} = 2.01\%$ while that fabricated from 200nm-thick ZnO film has only $J_{sc} = 6.498 \text{ mA/cm}^2$, $V_{oc} = 0.542 \text{ V}$, $\text{FF} = 42\%$ and $\text{PCE} = 1.46\%$. As evidence from J - V characteristics in Fig. 3-8(a), the series resistance (dV/dI at $V \geq V_{oc}$) of device with 200 nm ZnO film (28.4Ω) is higher than that of device with 120 nm (15.4Ω), demonstrating that the poor performance of device with very thick ZnO layer is due to a higher resistance of ZnO film.

The J - V characteristics of the solar cell in the dark [Fig. 3-8 (b)] show that the fabricated devices follow the diode characteristic with three distinctive regions: (1) a linear region at negative voltages and low positive voltages, (2) an exponential region at intermediate positive voltages and (3) a second linear region at high voltages. The current in the first and third region is limited by shunt resistance R_{sh} and series resistance R_s respectively. As the dark current equation without considering R_{sh} and R_s is

$$I = I_0 \left[\exp\left(\frac{qV}{nkT}\right) - 1 \right] \quad (3.1)$$

where I is the current through the diode, V is the voltage across the diode, I_0 is the dark saturation current, n is the diode ideality factor, T is the temperature in Kelvin, q is the elementary charge and k is the Boltzmann constant, the diode ideality factor of the device can be estimated from the slope of I - V or J - V curve in semilogarithmic scale. From the curves in Fig. 3-8(b), the diode ideality factor of the fabricated devices is close to 2. The fact that the slope of the curve between 0.5 V and 0.7 V (second region) is the same for different thicknesses of ZnO represents that the morphology of the bulk heterojunction is

similar [127]. However, the lower current in the first regime and higher current in the third region for the device with 120 nm ZnO film suggests that it has higher shunt resistance and lower series resistance, hence, showing the higher fill factor.

Figure 3-8 *J-V* characteristics of the devices with different thicknesses of ZnO films (120 nm and 200 nm) derived from 0.3 *M* sol [Method B] (a) under light intensity 100 mW/cm² (b) in the dark in semilogarithmic representation.

It was previously reported that bulk-heterojunction device without any electron collecting layer has PCE of 1.6% and with titanium oxide (TiO_x) electron collecting layer has PCE of 3.1% [128]. Although the performance of device with ZnO is not as high as that of device with TiO_x, it has higher efficiency than device without any electron collecting layer. Higher fill factor and efficiency, however, is achievable by optimizing the thickness of active layer and adding electron/exciton blocking layer which will be discussed in next chapter. This shows that colloidal ZnO film from sol-gel process is a

promising cost-effective material and process to be used as an electron collecting layer in bulk-heterojunction device.

3.4. Conclusion

We have demonstrated the charge collection of sol-gel derived ZnO film using bulk-heterojunction architecture. The performance of device is correlated with sol-gel process and thickness of the ZnO film. Sol with low concentration of precursors yields higher performance in device because of small grain size and uniform film. Ammonia treatment on ZnO film increases efficiency by removing residual acetate compound covering on ZnO film. The power conversion efficiency of 2.01% was achieved with ZnO optimized thickness of 120 nm using bulk-heterojunction architecture.

Chapter 4 An inverted organic solar cell employing a sol-gel derived ZnO electron selective layer and thermal evaporated MoO₃ hole selective layer

4.1 Why inverted structure?

The concept of bulk-heterojunction (BHJ), a blend of acceptor and donor materials, is typically implemented in the OSC, where the BHJ active layer is sandwiched between a PEDOT:PSS-coated ITO anode and a low work function (LWF) metal cathode. However, the conventional structure has drawbacks in the stability and lifetime of device. Neugebauer et al. demonstrated the rapid degradation of the device in air just after 8-12 h using MDMO-PPV/PCBM and C60 systems [129]. Schuller et al. developed devices with increased air-stability by encapsulation with a second glass. They showed that the performance of the OSC with a structure of ITO/PEDOT:PSS/MDMO-PPV:PCBM/Ca/Ag degrades less than 20% after more than 1000 h of operation under 1/3 sun at 85 °C [130]; however, at least 25,000 h of operation is needed for a viable product [131]. One limiting parameter associated with device stability is the LWF metal cathode. LWF metals, such as Li, Ca, and Al, are air-sensitive and can be easily oxidized, increasing the series resistance at the organic layer/electrode interface and degrading the device performance. Moreover, diffusion of oxygen into the active layer through pinholes and grain boundaries in the cathode causes the degradation of the active layer, leading to device instability in air [132]. Also, the interface between ITO and PEDOT:PSS is not

stable, owing to indium contamination into the polymer layer and the acidic nature of PEDOT:PSS which etches ITO [133-134]. The degradation of the ITO/PEDOT:PSS interface is faster upon exposure to air because water is absorbed by PEDOT:PSS film and an aqueous acid environment is formed due to the reaction between water and PSS [133].

To circumvent the problem associated with LWF metal electrode, a TiO_x layer was inserted between active layer and Al electrode, serving as a shielding and scavenging layer, preventing the penetration of oxygen and moisture into the active layer [135]. The lifetime of non-encapsulated devices exposed to air was improved by nearly two orders of magnitude. Such a buffer layer also acts as an optical spacer and helps increase the photo-generated current [136-137]. Despite a better structure for device stability, it still cannot avoid the ITO/PEDOT:PSS interfacial degradation. On the other hand, to overcome the ITO/PEDOT:PSS interface problem, Shrotriya et al. replaced PEDOT:PSS with transition metal oxides (MoO₃ and V₂O₅) as a hole-selective layer, demonstrating the PCEs of 3.1% and 3.33% for the devices with 3 nm V₂O₅ and 5 nm MoO₃ film thicknesses, respectively, comparable to that of the device (3.18%) with 25 nm PEDOT:PSS [138]. Unfortunately, this approach could not eliminate the usage of LWF metal (Ca). An intelligent way to address both top electrode and ITO/PEDOT:PSS interface issues is to construct an inverted structure, where the charge collection of electrode is opposite to that of conventional device structure. The reversed polarity of charge collection allows the use of a high work function (HWF) metal as top electrode as well as the removal of ITO/PEDOT:PSS interface. HWF metals such as Au and Ag are less sensitive to air, yielding prolonged interface stability between the active layer and metal electrode.

Moreover, HWF metals offer the possibility of using non-vacuum-processed techniques such as lamination [139-140], printing [141-142], and coating [143-144], which decreases production costs and brings closer the ultimate aim of roll-to-roll manufacturing. In addition, it has been reported that charge collection is also enhanced in the inverted geometry owing to inherent vertical phase separation with a donor-enriched top surface and an acceptor-enriched bottom surface in the blend polymer. Such a vertical concentration distribution of donor and acceptor disfavors charge transport in conventional geometry [141]. Another advantage of inverted structure is that if an n-type metal oxide with large surface area is employed with a BHJ, the interface between the metal oxide and light absorbing polymer can provide additional exciton dissociation sites and generate additional photocurrent [142]. Hence, inverted geometry contains the advantages of device stability, design flexibility, increased robustness, and higher photocurrents.*

4.2 Charge collection in conventional and inverted structure

The energy conversion process of incident photons into electricity in an inverted structure device is the same as that in a conventional OSC, as discussed in section (2.2.4). The only difference between two structures is the process of charge collection. Typically, a conventional structure device consists of ITO/PEDOT:PSS/polymer:fullerene blend/

* The advantages of inverted OSC are inspirational by the time of publication of this work but most of these advantages have been demonstrated now.

Figure 4-1 Schematic of charge carrier extraction in OSCs (a) without buffer layer, (b) with p-type buffer layer, and (c) with n-type buffer layer at the bottom electrode. The dashed lines in (b) and (c) refer to the Fermi level of the p-type and n-type buffer layers respectively.

LWF metal from bottom to top, whereas an inverted structure device is composed of ITO/n-type material/polymer:fullerene blend/HWF metal. In principle, ITO is able to collect either holes or electrons from the polymer:fullerene network because its work function (from -4.5 to -4.9 eV) is between the HOMO and LUMO values of these organic materials (Fig. 4-1(a)). In the conventional device, ITO is modified by p-type PEDOT:PSS, which has a HWF so that electrons are blocked and only holes are collected

by ITO anode (Fig. 4-1(b)). Since the electrons must be extracted from the top electrode, air-sensitive LWF metal is applicable as the top cathode. On the other hand, if ITO is modified by n-type material with a LWF, the holes will be blocked and electrons will be exclusively collected by ITO electrode (Fig. 4-1(c)). Collecting the holes at the other side allows the usage of HWF metal as top electrode without losing the asymmetric electrode structure and concurrently eliminating the PEDOT:PSS/ITO interface issue. A hole-transporting layer can also be inserted between the active layer and the HWF electrode to effectively block the excitons and adjust the optical field distribution in the active layer.

4.3. Significance of the experiment

Previously, the inverted architecture with various electron-selective layers, Cs₂CO₃ [145], TiO_x [127] and ZnO [113] have been demonstrated. We also demonstrated the efficient collection of electron from polymer:fullerene by sol-gel derived ZnO layer, as in chapter 3. However, the performance of inverted cell is still lower compared to the conventional ones. On the other hand, PEDOT:PSS is traditionally used as the hole transport layer in inverted solar cell [128, 146]. However, PEDOT:PSS generally needs to be fabricated in an oxygen and moisture environment (outside the glove box) with baking, which is detrimental to the organic/polymer layer beneath [147]. Moreover, spin casting of aqueous solution of PEDOT:PSS on hydrophobic P3HT:PCBM is difficult [148].

There are other p-type-like metal oxides, such as NiO, MoO₃, V₂O₅ and WO₃ with high work function and good hole conductivity which have been demonstrated for hole

injection in organic light-emitting diodes (OLEDs) [149-150], anode buffer layer in conventional OSC [151-152] and intermediate layer in tandem OSC [153]. These oxide films can be deposited by thermal evaporation, which is compatible to thermal evaporation of anode (Au or Ag). However, there is a lack of study of inverted OSC with n-type metal oxide electron selective layer and p-type like oxide layer. Herein, we shall report an efficient inverted OSC employing a sol-gel derived ZnO electron selective layer and MoO₃ hole selective layer. We demonstrated that the PCE of inverted structure OSC is enhanced with a highly transparent sol-gel derived ZnO electron selective layer by controlling the concentration of sol. In addition, replacing commonly used PDEOT:PSS with MoO₃ helps to increase the V_{oc} and FF.

4.4 Experimental

In our inverted architecture, FTO/ZnO/P3HT:PCBM /MoO₃/Ag are stacked from bottom to top as shown in Fig. 4-2(a). The energy level diagram of the inverted cell is depicted in Fig. 4- 2(b). For the comparison of the stability, a conventional OSC was also fabricated with standard architecture (ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al). In our device architecture, we use FTO as bottom electrode instead of ITO which is used in conventional OSC. Since the work function of FTO (-4.4 eV) is higher than that of top electrode Ag (-4.5 eV), internal electric field due to unsymmetrical electrode is promoting the flow of charge carriers. However, the work function of ITO (in the range of -4.8 to -5.1 eV) is lower than that of Ag and the internal electric field is opposing the flow of

charge carriers. Therefore, for ITO bottom electrode, very high work function electrode such as Au is more suitable to be used as top electrode in inverted structure yet Au is much more expensive than Ag. Therefore we opt to use FTO and Ag as electrodes for our device. As the light enters from FTO side, the transmittance of ZnO is important in realizing high current density. The transmittance depends on crystal size of ZnO which in turn relies on the concentration of precursors in the sol. Therefore, we prepared sols with different concentrations of precursors using the method B described in previous chapter.

Figure 4-2 (a) Device structure of the inverted OSC with ZnO electron selective layer and MoO₃ hole selective layer, and (b) the corresponding energy diagram of the inverted cell

Throughout the device fabrication process, we fixed all the process parameters except the concentration of sol. Devices A, B, C and D were fabricated from 0.75 M, 0.5

M , $0.3 M$ and $0.1 M$ sol respectively. We also constructed an additional device E in the same condition as device D but without MoO₃ layer for comparison. In our typical device fabrication process, the prepared sols were spin-coated on the pre-cleaned FTO-coated glass ($15 \Omega/\square$). The thickness of ZnO films was controlled at ~ 120 nm except for device A where minimum thickness achievable was ~ 180 nm due to the large grain size. The synthesized films were sintered at 350°C for 1 h in the air to obtain ZnO films. Then, a 20 mg/ml solution of P3HT:PCBM (1:1 by weight) in chlorobenzene was spin cast on ZnO film to form an active layer of about 100 nm. Finally a 15 nm MoO₃ and 70 nm Ag was deposited under 3×10^{-4} Pa by thermal evaporation through a shallow mask. The fabricated devices were post-annealed at 150°C under N₂ ambient for 10 min. Photovoltaic measurement was conducted illuminating the devices under a solar simulator (Solar Light Co., Inc.) with AM1.5G filter. The J - V characteristics were examined using a Keithley 2400 Sourcemeter. The simulated light intensity was adjusted to 100 mW/cm^2 calibrated with a Thorlabs optical power meter.

4.5 Results and Discussion

The J - V curves of the devices are shown in Fig. 4-3 and the device operation parameters are summarized in Table 4-1. The variation in device performance is not significant in terms of V_{oc} and FF except for Device A with poor FF, which can be attributed to the recombination lost in ZnO film due to redundant thickness. However, it can be clearly seen that there is prominent changes in J_{sc} (comparing to device A, device

B and D showed 16 % and 47 % improvement respectively) due to different sol concentrations.

Device	V _{oc}	J _{sc}	FF	PCE
	(V)	(mA/cm ²)	(%)	(%)
A	0.604	5.986	47	1.71
B	0.607	6.945	53	2.24
C	0.620	8.086	57	2.84
D	0.616	8.858	57	3.09
E	0.56	8.687	47	2.30

Table 4-1 The summary of device operation parameters

The trend in J_{sc} is consistent with variation in transmittance of ZnO films used in the devices. The optical transmittance spectra of ZnO films derived from different concentrations of sol are shown in Fig. 4-4(a). The average transmittance of ZnO film obtained from 0.75 *M* is only 75%. The transmittance (Device A) of more than 80% is reached beyond 700 nm, but this region does not contribute much for photon current generation because the absorption spectrum of P3HT:PCBM is negligible beyond 700 nm. Therefore, the J_{sc} of device A is only 5.986 mA/cm². Although the transmittance of ZnO film derived from 0.3 *M* is slightly lower than the film derived from 0.5 *M* at the short wavelength region, it is higher at longer wavelength region, especially between 450 nm and 550 nm, where the absorption peak of P3HT:PCBM active layer is located. Hence, the J_{sc} of device is sharply increased from 6.945 mA/cm² to 8.086 mA/cm² by replacing the

0.5 *M* sol with the 0.3 *M* one. The optical spectrum of ZnO film derived from 0.1 *M* sol shows not only the highest transmittance (85% - 95%) at visible range but also a lower absorbance at ultraviolet region compared to other films and hence the J_{sc} of device D goes up to 8.858 mA/cm². The improvement in J_{sc} agrees with IPCE spectra of the fabricated devices [Fig. 4-4 (b)]. We can see that there is no blue shift in the IPCE curves but the device with higher transparency of ZnO film has a higher photocurrent. A sharp drop in IPCE below 400 nm is clearly seen due to the strong absorption of ZnO film near bandedge of ZnO. The spectrum beyond 700 nm is not a real response of the cells and it might be due to an artefact of the measurement.

Figure 4-3 The J-V characteristics of devices with ZnO films derived from different sols under simulated solar irradiation of AM 1.5G. ZnO films of Device A, B, C and D are derived from 0.75 *M*, 0.5 *M*, 0.3 *M* and 0.1 *M* respectively. Device E is the same condition as device D but without MoO₃ layer.

Figure 4-4 (a) The optical transmission spectra of ZnO films derived from different sols. The insert shows the relative absorption of various ZnO films near bandedge of ZnO. (b) The normalized IPCE spectra of the inverted cells.

It is possible that the improvement in device performance is due to better surface quality of the film which provides better wettability and adhesion with photoactive layer [128]. Therefore, surface morphology, roughness and contact angle analysis were carried out to investigate the surface quality of ZnO films. Fig. 4-5 shows the SEM images of ZnO film deposited from different concentrations of sols. The films are composed of nano-sized ZnO colloids and the grain size increases with the increase in sol concentration, as discussed in previous chapter. The grain size revealed from SEM image is consistent with surface roughness measurement and larger grain size results in rougher film. The surface roughness (rms) of the films obtained from 0.75 M, 0.5 M, 0.3 M and 0.1 M sol are 44.79 nm, 18.91 nm, 11.46 nm and 9.91 nm respectively and the water contact angles are 54.2 °, 64.7 °, 66.2 ° and 66.4 ° respectively. This result agrees with previous study that

the contact angle decreases with surface roughness for hydrophilic surface [154]. Based on contact angle measurement, the film derived from lower concentration of sol turns to be more hydrophobic, which is favorable for polymer film fabrication [155]. Hence, probably J_{sc} enhancement is partially contributed from surface property of the film.

Figure 4-5 SEM images of ZnO films derived from various sol concentrations of (a) 0.75 *M* (b) 0.5 *M* (c) 0.3 *M* and (d) 0.1 *M*.

In our device structure, MoO₃ has multi-functions of hole transporting, electron and exciton blocking. MoO₃ has been previously used as a hole-injection layer for OLEDs [149-150] and a replacement of PEDOT:PSS in conventional organic solar cell [151]. Therefore MoO₃ has very good hole transporting property. It also serves as electron/exciton blocking layer because conduction band of MoO₃ (2.3 eV) is much higher than LUMO of acceptor/donor (3.7 eV)/(3 eV) [Fig. 4-2(b)]. Due to these properties of MoO₃ layer, V_{oc} and FF of Device D (0.616 V, 57%) is higher than that of

the Device E (0.567 V, 47%) without sacrificing the J_{sc} , leading to improvement in PCE from 2.3% to 3.09% [Fig. 4-3]. It should be pointed out that V_{oc} and FF of our inverted OSC with MoO₃ is also higher than that of previously reported device without MoO₃ (0.493 V – 0.556 V, 47.5% - 51.8%) and the J_{sc} is similar (compare to the device with the same active layer thickness) [113]. Moreover, FF of our device (FTO/ZnO sol-gel/P3HT:PCBM/ MoO₃/Ag) is still higher than that reported in previous literature [146] where FF of the device (ITO/ZnO sol-gel/P3HT:PCBM/ PEDOT:PSS/Ag) is only 51.7% despite a similar V_{oc} .

Figure 4-6 Air-stability test of inverted and conventional cell

To investigate the air-stability, which is the major strength of inverted structure according to our design concept, we tested a series of spot test after elapsed periods of the storage time. The un-encapsulated cells were kept at room temperature, relative humidity

60% and under normal fluorescent light during the storage. The stability of the inverted cell in air was significantly improved compared to the conventional cell. Fig. 4-6 shows the change in the normalized PCE against the air-exposure time for the inverted and conventional cells. It can be seen that the shelf lifetime (the time when the PCE drops to half of its initial value) of the inverted cell is ~15 days, while the shelf lifetime for the conventional cell is only ~0.5 days. The longer air-stability can be attributed to the removal of ITO(FTO)/PEDOT:PSS interface and partial prevention from the penetration of moisture and oxygen by MoO₃ and high work-function metal.

Despite longer stability compared to conventional device, the degradation of inverted device was still observed upon exposure to environment containing oxygen and moisture. It has been known for a long time that diffusion of molecular oxygen and water into the devices leads to some of the most significant degradation mechanisms for OSCs. However, the degradation in OSCs comprises a complex range of mechanisms of which presumably not all have been identified. Some known mechanisms involve: degradation of interfaces, degradation of the active material, interlayer and electrode diffusion, electrode reaction with organic materials, morphological changes, and macroscopic changes such as formation of particles, bubbles and cracks.

Recently, a few studies were carried out on the comparison between degradation mechanisms in conventional and inverted geometry [156-157]. The materials used in the studies are [ITO/PEDOT:PSS/P3HT:PCBM/Al] for conventional geometry and [ITO/ZnO/P3HT: PCBM/PEDOT:PSS/Ag stripes] for inverted geometry. It was reported that the conventional geometry device has relatively long lifetime in a dry oxygen

atmosphere and relatively short lifetime in a humid (oxygen-free) atmosphere whereas the inverted geometry device showed the opposite behavior, i.e., short lifetime in the dry oxygen atmosphere and longer lifetime in humid atmosphere. The relatively short lifetime for the normal geometry device in a humid atmosphere could be related to the Al electrode because water diffuses through the Al grains, a process that unavoidably will lead to the formation of aluminum hydroxide/oxide, which is an insulator [158]. It has been also shown that the reactivity of Al toward dry oxygen is very low and the interface between polymer and Al is stable in the presence of dry oxygen but degrades quickly in the presence of water [159]. Thus, molecular oxygen preferentially diffuses through pinholes in the electrode that could be a slower diffusion mechanism as compared to diffusion of water in between the Al grains.

On the other hand, in inverted geometry, oxygen uptake (i.e., addition of oxygen) on the individual layers measured by XPS calibrated time-of-light secondary ion mass spectrometry (TOF-SIMS) data revealed that PEDOT:PSS reacts relatively efficiently with water but not with oxygen in the dark [156]. However, PEDOT:PSS reacts less with water during illumination probably due to a slightly higher temperature under illumination. Furthermore, it was observed that P3HT:PCBM reacts relatively efficiently with molecular oxygen when illuminated but almost not at all when stored in the dark. Thus, the most serious situation in regard to degradation in inverted geometry with ITO/ZnO/P3HT:PCBM/PEDOT:PSS/Ag stripes must be P3HT:PCBM reacting with molecular oxygen during illumination. Another degradation pattern in such structure is phase separation of PEDOT and PSS, which is more prominent in dry oxygen atmosphere than humid atmosphere. As a consequence of phase separation, PEDOT becomes less

shielded by PSS and susceptible toward oxygen environment. Thus phase separation deteriorates the barrier properties with respect to oxygen and favors transport of oxygen through the PEDOT phase with faster and selective oxidation at the interface. In contrast to PEDOT:PSS and P3HT:PCBM, the oxygen uptake on ZnO surface cannot be directly correlated to degradation because ZnO (like other oxides) exchanges oxygen easily.

In our device structure, because PEDOT:PSS is not used as a hole transport layer, the diffusion of oxygen molecule into P3HT:PCBM is likely to be the major degradation (the diffusion of moisture may not cause serious degradation for inverted geometry according to the reported literatures). Likewise ZnO, oxygen uptake on MoO₃ is not a serious degradation because of easy exchange of oxygen. Thus, lateral diffusion of oxygen molecule, i.e., diffusion through the sides of device, might be an important entrance channel in our device. Recently, the reversible degradation was found in inverted device with ITO/ZnO/P3HT:PCBM/PEDOT:PSS/Ag geometry [160]. The transient state is believed to be a result of the breakdown of the diode behavior of ZnO electron transport layer by O₂ desorption due to UV exposure from solar spectrum, followed by spontaneous recovery through successive re-adsorption of the O₂ on the ZnO during storing in the dark. Hence, desorption of O₂ in ZnO layer upon UV exposure will be a part of the degradation mechanism. Nevertheless, it is not a straightforward task to indentify the degradation mechanisms in OSC because some mechanisms are interrelated and take place at the same time, while some during operation of the cells and some during storage. More thorough and careful experimental studies are required to indentify the degradation patterns in inverted OSC.

4.6 Conclusion

In summary, we demonstrated relatively air-stable inverted OSC using a sol-gel derived ZnO and thermal-evaporated MoO₃ as electron-selective and hole-selective buffer layer respectively. The inverted-structure cell is much more stable in air than conventional cell. The performance of inverted cell can be significantly improved by modifying the transmittance and surface property of ZnO electron selective layer. Inverted OSC incorporating with MoO₃ has higher V_{oc} and fill factor than without MoO₃ due to hole transporting and electron/exciton blocking properties. Efficiency up to 3.09% has been achieved in inverted bulk-heterojunction solar cell by modifying the transmittance of sol-gel derived ZnO film to 95% and incorporating MoO₃. Finally, the degradation mechanisms in inverted OSC are briefly discussed.

Chapter 5 Improved inverted organic solar cells with a sol-gel derived indium-doped zinc oxide buffer layer

5.1 Introduction

As discussed in previous chapter, the polarity of an ITO (FTO) electrode should be reversed by modifying with an n-type functional buffer layer for the elimination of PEDOT:PSS/ITO interface and the replacement of low work-function metal with high work-function metal. However, the additional resistance that resulted from the collection of charges via functional buffer layer leads to high series resistance in the device and reduction in short-circuit current density. Hence, further improvement of inverted architecture can be expected by reducing the resistivity of the functional buffer layer and optimizing the energy alignment between acceptor/buffer layer interfaces [161].

Indium-doped zinc oxide (IZO), which has previously been applied as a channel layer in thin film transistor [162] and an interlayer for forming ohmic contact in UV-light emitting diode [163], is a suitable candidate to be used as an n-type functional buffer layer to overcome the limitation of inverted OSC due to the fact that its resistivity is lower and transmittance is higher compared to undoped ZnO [164]. Such IZO further offers several benefits: IZO can be deposited by low-cost solution-processing methods such as spray pyrolysis [165] and sol-gel techniques [166], which are compatible with solution-based-processing of BHJ solar cells. The amount of dopant is also tunable by controlling the amount of precursors within a reasonable accuracy. However, only ZnO [113], TiO₂[167],

TiO_x[127], and Cs₂CO₃[145] have been used as n-type buffer layers in inverted OSCs to date. Different from previous works in the literature, in this chapter, we reported on IZO as an n-type buffer layer of inverted OSCs and manipulated the doping concentration to optimize the device performance. It is worth mentioning that only small amount of dopant (1 at. % to 3 at. %) is required to make IZO film because it is used as a buffer layer and not necessary to be highly conductive film. In contrast, commercial ITO, which is generally used as a transparent electrode, requires large amount of indium (90% of In₂O₃ and 10% SnO₂ by weight) to become highly conductive film. Therefore, usage of indium as dopant is not a critical issue here although indium is a scarce material. We demonstrated that the performance of inverted OSC is enhanced, especially in the short-circuit current density, by replacing conventional ZnO with appropriately doped IZO buffer layer.

5.2 Experimental

5.2.1 Sol-Gel Preparation

We first prepared the IZO sol using zinc acetate dihydrate [Zn(CH₃COO)₂·2H₂O] (99.95% Fluka) as precursor, indium chloride [InCl₃] (98% Aldrich) as dopant source, ethanol [CH₃CH₂OH] (99.5+% Aldrich) as solvent and ethanolamine [NH₂CH₂CH₂OH] (99+% Sigma-Aldrich) as sol stabilizer [168]. Indium chloride contents used in the sol are 0, 1, 2 and 3 at.% of the precursor and the concentration of the sol was kept constant at 0.1 M. Zinc acetate dihydrate and indium chloride were first dissolved in ethanol and

rigorously stirred for 2-3 h at 80°C. Subsequently, ethanolamine was added to the solution followed by thorough mixing process with magnetic stirrer for 12-15 h at 60°C.

5.2.2 Device Fabrication

Figure 5-1 Device structure of the inverted organic solar cell, illustrating the flow of charge.

Numerical values inside the parentheses represent the thicknesses of corresponding layers.

The device architecture was FTO/buffer layer/ polymer:fullerene blend/MoO₃/Ag as shown in Fig. 5-1. In our typical device fabrication process, a functional buffer layer was spin-coated onto a pre-cleaned FTO glass with a sheet resistance of 15 $\Omega/\square$ from the sols in a low humidity environment (RH 13%). The coating step was repeated a few times to obtain desired thickness. As-deposited thin films were annealed at 350 °C for 1 h in air and colloidal thin films with a thickness of ~ 15nm were obtained. Then, the samples were transferred into a glove box and the active layer with a thickness of ~ 100 nm was fabricated by spin coating the blend solution, made of P3HT (Rieke Metals, Inc.) and PCBM (Nano-C) with a weight ratio of 1:1 in chlorobenzene (40 mg/ml), onto the buffer

layer previously deposited. Finally, a 15 nm MoO₃ and 70 nm Ag were deposited under 3×10^{-4} Pa by thermal evaporation through a shadow mask. The fabricated devices were post-annealed at 150 °C under N₂ ambient for 10 min.

5.2.3 Characterization and Simulation

Photovoltaic measurement was conducted as described in the previous chapter. X-ray Photoelectron Spectroscopy (XPS) measurements were performed with a Kratos ESCA (model AXIS Ultra) using a monochromated Al K α ($h\nu = 1486.7$ eV) x-ray source operated at 15 kV and 10 mA under 8.6×10^{-9} Torr. XPS data were collected after etching for 10 min with Ar⁺ to eliminate the contamination on the surface. X-ray diffraction (XRD) patterns of the films were obtained by a diffractometer (Siemens- model D5005) at 40 keV and 36 mA using Cu K α ($\lambda = 1.54056$ Å). Tapping mode atomic force microscopic (AFM) images of IZO films and active layers were taken with Nanoscope IIIa (Digital Instruments) scanning probe microscope. The sheet resistance of IZO-modified FTO film was extracted by Hall Effect measurement (BIO-RAD) with Van der Pauw geometry at room temperature. Al (80nm) deposited by e-beam evaporation was used as contacts for Hall Effect measurement. The optical transmittance and absorption spectra of the films were measured by UV-vis-NIR spectrophotometer system (PerkinElmer Lambda 950) with an integrating sphere to capture directly transmitted light and forward scattered light. External quantum efficiency (EQE) spectrum was measured using a Xenon-light source with 300mm focal length monochromator (Bentham).

Figure 5-2 A general multilayer structure having m layers between a semi-infinite transparent ambient and a semi-infinite substrate. Each layer j ($j = 1, 2, \dots, m$) has a thickness d_j and its optical properties are described by its complex refractive index. The optical electric field at any point in layer j is represented by two components: one propagating in the positive and one in the negative x direction, E_j^+ and E_j^- respectively.

Optical electric field simulation was carried out by matrix methods proposed by Pettersson et. al., using complex refractive index and thickness of individual layers as input parameters [169]. Assumptions made in the simulations are (1) layers included in the device are considered to be homogenous and isotropic, so that their linear optical response can be described by a scalar complex index of refraction; (2) interfaces are parallel and flat compared to the wavelength of the light; and (3) the light incident at the device can be described by plane waves. The outline of the simulation is as follow. Stratified structure with isotropic and homogeneous media and parallel-plane interfaces can be described by 2×2 matrices due to the fact that the equations governing the propagation of the electric field are linear and that the tangential component of the electric field is continuous. We consider a plane wave incident from left at a general multilayer structure having m layers between a semi-infinite transparent ambient and a semi-infinite

substrate as illustrated in Fig. 5-2. Each layer j ($j= 1,2,\dots,m$) has a thickness d_j and its optical properties are described by its complex refractive index $n_j = \eta_j + i\kappa_j$, which is a function of wavelength (energy) of the incident light. The optical electric field at any point in the system can be resolved into two components corresponding to the resultant total electric field; one component propagating in the positive x direction and one in the negative x direction, E_j^+ and E_j^- respectively.

The total system transfer matrix (scattering matrix) S , which relates the electric field at ambient side and substrate side by

$$\begin{bmatrix} E_0^+ \\ E_0^- \end{bmatrix} = S \begin{bmatrix} E_{m+1}^+ \\ E_{m+1}^- \end{bmatrix} \quad (5-1)$$

, can be calculated from two transfer matrices; an interface matrix and layer matrix. The former describes the propagation at each interface in the structure while the latter represents the propagation through the layer. The matrixes are constructed from the Fresnel complex reflection and transmission coefficients at interfaces, which can be calculated based on complex refractive index ($n_j = \eta_j + i\kappa_j$) and layer thickness d_j .

In order to calculate the internal electric field in layer j , the layer system can be divided into two subsets, separated by layer j , which means that the total system transfer matrix can be written as

$$S = S_j' L_j S_j'' \quad (5-2)$$

, where L_j is the layer matrix of layer j . The partial system transfer matrices for layer j are defined

$$\begin{bmatrix} E_0^+ \\ E_0^- \end{bmatrix} = S_j' \begin{bmatrix} E_j'^+ \\ E_j'^- \end{bmatrix} \quad (5-3)$$

where $E_j'^+$ and $E_j'^-$ refer to left boundary of layer j and

$$\begin{bmatrix} E_0^+ \\ E_0^- \end{bmatrix} = S_j'' \begin{bmatrix} E_j''^+ \\ E_j''^- \end{bmatrix} \quad (5-4)$$

where $E_j''^+$ and $E_j''^-$ refer to right boundary of layer j , as illustrated in Fig. 5-2. The complex refractive index (at 535 nm) and thickness used in the simulation for individual layers are shown in Table 5-1.

Layer	Thickness	Complex refractive index (at 535 nm)
Air	-	1
Glass	1.1 mm	1.5185
FTO	300 nm	1.8791 + 0.0026i
ZnO	15 nm	1.953 + 0.0032i
IZO (1 at.%)	15 nm	1.895 + 0.0017i
IZO (2 at.%)	15 nm	1.912 + 0.0021i
IZO (3 at.%)	15 nm	1.938 + 0.0029i
Polymer: fullerene	100 nm	1.9910 + 0.1105i
MoO ₃	15 nm	2.007 + 0.039i
Ag	70 nm	0.12918 + 3.2172i

Table 5-1 List of parameters used in the optical field simulation

5.3 Results and discussion

5.3.1 Properties of IZO film

Figure 5-3 XPS (a) wide scan (b) high resolution C (1s) and (c) high resolution Cl (2p) spectra of the films with various indium contents.

XPS scan was carried out to verify the incorporation of indium atoms in the doped films and to determine the elemental compositions of the films. XPS wide scan spectra, high resolution In (3d) and Cl (2p) spectra of various IZO films are depicted in Fig. 5-3(a), (b) and (c) respectively. XPS data fitting in Fig. 5-3 (c) was performed by FFT (fast fourier transform) filter smoothing in Origin software.

Indium	Zn	O	In	Cl
Dopant	(at. %)	(at. %)	(at. %)	(at. %)
0 at. %	51.66	48.34	NA	NA
1 at. %	51.07	48.46	0.47	~ 0
2 at. %	50.41	48.55	0.97	0.07
3 at. %	49.61	48.61	1.65	0.13

Table 5-2 The stoichiometry of IZO films with various indium contents calculated from XPS spectra

Since the binding energies of 1022 eV and 530 eV correspond to the $2p_{3/2}$ orbit of zinc and 1s orbit of oxygen respectively, it is verified that the films are composed of zinc and oxygen [170]. The incorporation of indium in the doped films can be clearly seen in high resolution scan. The chemical state of indium was detected in all doped films and corresponded to the binding energy of 443.9 eV and 451.4 eV for In $3d_{5/2}$ and In $3d_{3/2}$ peaks respectively [171-172]. A shifting of In $3d_{5/2}$ peak to 444.6-445.3 eV due to InCl_3 was not observed [172], suggesting that dopant InCl_3 is completely decomposed during sol-gel or annealing process. However, a small amount of chlorine was detected as elemental form at 199.5 eV in the narrow scan Cl (2p) spectra of highly doped films (Fig. 5-3(c)). The stoichiometry* of the films calculated from XPS spectra is shown in Table 5-2. From the stoichiometric data, it should be noted that the actual atomic concentrations of

* The stoichiometry was calculated by using build-in software provided from Kratos ESCA system (Model AXIS Ultra).

indium ($[\text{In}]/(\text{In}+\text{Zn})$) incorporated in the films coincide closely with expected values, $\text{In}_x\text{Zn}_{1-x}\text{O}$ where $x = 0, 0.01, 0.02, 0.03$ for 0, 1, 2 and 3 at. % indium doped films respectively. The data also reveal that the ratio of $\text{O}/(\text{Zn} + \text{In})$ is smaller than the stoichiometric ratio 1:1, meaning that oxygen vacancies exist.

Figure 5-4 XRD patterns of ZnO films doped with (a) 0 at. % (b) 1 at. % (c) 2 at. % (d) 3 at. % indium. The films were deposited at 13% RH.

Fig. 5-4 shows the XRD patterns of the films doped with various indium concentrations. As seen from the figure, all films show polycrystalline nature with a hexagonal wurtzite structure of ZnO, which was deduced from the XRD database comes along with Siemens diffractometer (Model D5005). The low intensity shown in the peaks is an expected result due to the small quantity of material in thin film and low

temperature annealing process. The three most prominent peaks occur at $2\theta = 31.77^\circ$, 34.42° and 35.25° ($d = 2.814 \text{ \AA}$, $2.605 \text{ \AA}$, $2.476 \text{ \AA}$) correspond to (100), (002) and (101) planes. No extra phase related to indium was observed in the doped films. The peak of (002) is higher than that of (101) in undoped ZnO film but (101) peak increases and it is comparable to (002) peak in doped films. The behavior of increasing (101) peak due to incorporation of indium in ZnO film was also reported in other works [173-174]. No significant change in the full peak width at half-maximum peak (FWHM) suggests that low level doping of indium does not cause too much variation in crystallite size.

Figure 5-5 Resistivity, carrier concentration and Hall mobility (with error bar $\pm 3\%$) of the films spin-coated at 13% RH as a function of indium contents. The lines are drawn as a guide for the eyes.

The electrical properties of the films characterized by Hall-effect measurement are shown in Fig. 5-5. The undoped ZnO film shows n-type conductivity with carrier

concentration of $4.676 \times 10^{17} \text{ cm}^{-3}$. The electrons formed by the ionization of zinc atom and oxygen vacancies cause the undoped ZnO to be n-type conductive. The carrier concentration of the film increases with increasing indium dopant and the carrier concentration up to $9.352 \times 10^{17} \text{ cm}^{-3}$ was obtained in 3 at.% indium doped film. The resistivity, however, decreases initially yet increases again with higher indium content. The resistivity decreases initially upon doping because indium dopant provides additional charge carrier and the mobility increases. An increase in resistivity with higher indium content can be attributed to an increase in chlorine content with higher doping. As revealed by XPS study, the chlorine content is negligible in 1 at. % indium doped film yet it increases to 0.13 at. % in 3 at. % indium doped film (Table 5-2 & Fig. 5-3 (c)). The chlorine may act as trap for carriers and cause impurity scattering, leading to a decrease in mobility. The lowest resistivity of $0.554 \text{ } \Omega\text{-cm}$ is achieved at 1 at. % doped film and corresponding carrier concentration and mobility are about $6.546 \times 10^{17} \text{ cm}^{-3}$ and $17.22 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ respectively. The trend in resistivity of the film due to indium doping is consistent with the previous reports [168, 175] although the values in this study are higher in order of magnitude as we are interested in semiconductor film rather than TCO. The difference in resistivity values arises from the difference in carrier concentrations which are much lower in former than latter film. In TCO, high temperature annealing at reducing atmosphere eradicates oxygen from ZnO crystal and increases oxygen vacancies, leading to higher carrier concentration [176]. As the films were annealed in air for this study, oxygen vacancies are suppressed and carrier concentration is an order of magnitude lower than a TCO film. Moreover, the mobility of TCO film tends to be higher due to improvement in crystallinity resulting from high temperature annealing.

The AFM images of IZO films coated at 13% RH are shown in Fig. 5-6. A significant change in morphology due to incorporation of In was not observed. The root mean square (rms) roughnesses of the films are 3.996, 2.537, 2.858 and 4.39 nm for IZO film with 0, 1, 2 and 3 at. % indium respectively. All IZO films with different indium contents show similar lateral grain size of 30-45 nm.

Figure 5-6 AFM images of buffer layers with (a) 0 at. % (b) 1 at. % (c) 2 at. % and (d) 3 at. % indium content. Scan size was $1\mu\text{m} \times 1\mu\text{m}$.

5.3.2 Analysis on performance of devices

Figure 5-7 *J-V* characteristics of devices, employing IZO films doped with various indium contents as the buffer layers, (a) under simulated solar irradiation of AM 1.5G (100 mW/cm²), (b) in the dark.

Fig. 5-7 (a) and (b) show the *J-V* curves of the resulting devices with different buffer layers and the extracted device parameters under illumination and in the dark

respectively. The variation in device performance is not significant in terms of open-circuit voltage (V_{oc}) and fill factor (FF). However, J_{sc} changes significantly due to buffer layer doping. J_{sc} of devices with IZO buffer layers containing 0, 1, 2 and 3 at. % indium contents are 8.392, 9.935, 9.307 and 8.924 mA/cm^2 , respectively. The maximum J_{sc} is achieved at 1 at. % indium content.

Figure 5-8 AFM images of active layers fabricated on buffer layer with (a) 0 at. % (b) 1 at. % (c) 2 at. % and (d) 3 at. % indium content. Scan size was $1\mu\text{m} \times 1\mu\text{m}$.

The photocurrent generation process in OSC involves five major steps: (1) light absorption and exciton generation, (2) exciton diffusion to acceptor-donor interface, (3) exciton dissociation at acceptor-donor interface, (4) free charge carriers transport to electrodes and (5) charge collection at electrodes. We can assume that exciton diffusion, exciton dissociation and charge carriers transport are the same for all devices, supposing that the morphology and phase separation of bulk heterojunction is the same for all

devices since we used the same acceptor and donor in the same solvent for all devices. This hypothesis can be verified with two experimental evidences. First, the morphology and roughness of the active layers fabricated on different buffer layers revealed by AFM measurement (Fig. 5-8) are nearly identical. The roughness (rms) values of the active layers on buffer layers with 0, 1, 2 and 3 at.% indium content are 0.381, 0.37, 0.37 and 0.394 nm respectively. Second, the slope of dark J - V curve in intermediate positive voltage region (between 0.5 V to 0.75 V) is the same, suggesting that internal bulk morphology (phase separation of donor/acceptor) is similar for all the devices [177].

Although the active layers were fabricated on different buffer layers, we observed that the thickness of all active layers was approximately controlled at 100 nm. In addition, the difference between the maximum and minimum roughness of buffer layers is only 1.85 nm which is extremely small compared to the thickness of active layer. All these evidences imply that the variation of active layers in the fabricated devices is negligible and changes in J_{sc} are not due to active layer. Hence, the enhancement in J_{sc} can be attributed to charge collection at electrode and/or the improvement in optical transmittance of buffer layer that increases the net absorption of light in active layer.

As the free electrons at acceptor/buffer interface pass through the buffer layer before being collected at electrode, the conductivity of buffer layer is important for charge collection process. The average sheet resistance of 0, 1, 2 and 3 at. % indium containing IZO-coated FTO is 42.3, 35, 37.2 and 40.2 $\Omega/\square$ respectively, suggesting that all IZO films are more favorable in transport of electron to FTO electrode than ZnO film and IZO with 1 at. % indium is the best among the buffer layers. The trend in sheet resistance of IZO-coated FTO is consistent with that in resistivity of IZO films mentioned in section 5.3.1.

Figure 5-9 Plot of $(\alpha h\nu)^2$ against $h\nu$ for calculating band gap of the buffer layers

Another factor responsible for charge collection is the energy alignment at acceptor/buffer interface. The work function of buffer layer can be precisely measured with ultraviolet photoelectron spectroscopy (UPS)[155]. However, due to constraint in equipment availability, we calculated the optical band gap of various IZO films by extrapolating the straight line of $(\alpha h\nu)^2$ plot to $h\nu$ axis (where α and ν are the absorption coefficient and frequency of photon, respectively which are extracted from absorption spectrum) as shown in Fig. 5-9 [178]. The observed band gap is increased from 3.198 eV to 3.218 eV with increasing indium concentration from 0 to 3 at. %. Moreover, theoretically, the Fermi level of an n-type semiconductor increases with carrier concentration. The increase in carrier concentration of IZO films with increasing dopant can be clearly seen from the Hall measurement (Fig. 5-5). Both facts suggest that the work function of buffer layer decreases with increasing indium concentration. A decrease in

work function of buffer layer reduces the energy barrier for electron to jump to the buffer layer, favoring the charge collection process. Hence, IZO buffer layer is better than pure ZnO buffer layer for charge collection process.

Figure 5-10 The optical transmission spectra of the combined layer (substrate, FTO and buffer layer) with different indium contents (Y-axis – left) in the buffer layer and absorption of P3HT:PCBM active layer (Y-axis – right) in the visible range. Inset: The normalized photocurrent generation factor due to the changes in indium content of IZO buffer layer

As the light is incident from the FTO electrode, the optical transmittance of FTO/buffer layer stack alters the net absorption of photons in the active layer. A few experimental works have been proved that J_{sc} is increased due to the high transparency of the under layer [179-180]. The transmittance of combined glass substrate, FTO and

buffer layer in visible range and the absorbance of the active layer are shown in Fig. 5-10. It can be seen that the transmittance of IZO with 1 at. % indium is higher than that of undoped buffer layer. However, it is hard to compare between IZO with 0, 2 and 3 at. % indium because of mixed high and low transmittance in different regions of spectrum. Therefore, we make use of the following equation to determine the effect of transmittance of buffer layer on J_{sc} ,

$$J_{ph} = \int \frac{q\lambda}{hc} \eta_A(\lambda) \eta_{int} S(\lambda) d\lambda \quad (5-5)$$

where J_{ph} , q , h , c , η_A , η_{int} , and S represent photocurrent density, the elementary charge, Planck's constant, the speed of light, absorption efficiency, internal quantum efficiency and spectrum of light from sun (simulator), respectively. Since q , h , c and S are constants, the term $\int \lambda \eta_A(\lambda) d\lambda$, defined as photocurrent generation factor, causes the variation in J_{sc} besides η_{int} . In order to take into account the effect of transmittance of buffer layer, we calculated η_A as the product of the absorbance of active layer and total transmittance (including substrate, FTO and buffer layer), with a spectral integration range from 350 nm to 700 nm. The normalized photocurrent generation factor is shown in Fig. 5-10 inset. Since the optical interference due to the reflection of light from the counter electrode is important for thin films with thickness comparable to the wavelength of incident light, we also simulated the optical field distribution inside the device for single wavelength illumination at wavelength 535 nm. Although there is no shift in peak of optical intensity (modulus squared of the electric field $|E|^2$), the maximum intensity $|E|^2$ in the active layer is observed in device with 1 at. % indium containing buffer layer (Fig. 5-11). The variation in optical electric field distribution inside the active layer follows the trend in

transmittance of electrode/buffer layer stack at 535 nm. From both transmittance of electrode/buffer layer stack and optical distribution simulation, it can be seen that J_{sc} is also affected by the optical property of buffer layer although the contribution is not very significant.

Figure 5-11 The simulated optical field distribution inside the devices with buffer layers containing various indium contents for single wavelength illumination at 535 nm. These devices have structure of glass (2.2mm)/FTO (300 nm)/IZO (15nm)/ P3HT:PCBM (100 nm)/MoO₃ (15 nm)/Ag (70nm)

Figure 5-12 Normalized EQE spectra of fabricated devices with different buffer layers containing various indium contents.

The combined factors of charge collection (transport in buffer layer and energy alignment) and light absorption (due to transmittance of buffer layer) contribute to J_{sc} of inverted OSCs in the experiment. Since IZO with 1 at. % indium is advantageous for all these factors, the device fabricated with this buffer layer shows the highest J_{sc} among the devices. Although IZO with 3 at. % indium is the most beneficial to the electron transfer from acceptor to buffer layer due to better energy alignment, J_{sc} of that device is lower than former due to the drawback in resistivity (carrier transport in buffer layer) and probably due to rough buffer layer that causes non-uniform electric field inside the buffer layer and disturbs current flow in device operation [181]. In Fig. 5-12, the trend of overall EQE spectra agrees well with that of J_{sc} . The variation in J_{sc} also correlates well with the change in series resistances (R_s) of devices, which are 9.85, 6.71, 8.95 and 9.5 $\Omega \cdot \text{cm}^2$ for the devices employing buffer layers with 0, 1, 2 and 3 at. % indium content, respectively.

The changes in R_s due to doping buffer layer can also be clearly seen in the dark J - V curves at high applied voltage region where shape of J - V curve is mainly dominated by R_s (Fig. 5-7(b)). The device with lowest R_s shows the highest dark current at high voltage region and vice versa.

We observed slight deterioration in FF due to indium incorporation (within 5%). A few groups reported that smooth buffer layer increases the FF of OSCs [180-181]. However, in the case of devices fabricated from IZO with 1 and 2 at. % indium, the FF is decreased despite a similar roughness. Therefore, some other reason must be responsible for low FF . Since R_s of devices with IZO buffer layer is lower than that of device with ZnO layer, a slight decline in FF is caused by decrease in shunt resistance (R_{sh}) which can be attributed to electron injection barrier. Since the buffer layer serves as electron collection in photocurrent generation process as well as electron injection under forward bias, a decrease in work function due to indium dopant not only increases the charge collection for solar cell but also facilitates the electron injection into diode under forward bias. The rise in electron injection capability increases the diode (leakage) current under forward bias, which is opposed to photocurrent direction. The leakage current due to electron injection barrier lowering can be observed in the dark J - V curves at negative and low positive voltage region (Fig. 5-7 (b)). Hence, in the case of devices fabricated from IZO with 1 and 2 at. % indium, we attribute low FF to the leakage current which reflects as low R_{sh} in J - V curve. For the device fabricated from IZO with 3 at.% indium, even lower FF can be ascribed to both leakage current and high roughness.

Although the work function of buffer layer is decreased, we observe that V_{oc} is not increased. According to the literature [182], the large concentration of electrons at the

cathode due to low electron injection barrier decreases V_{oc} . Hence, we suppose that the former effect compensates the latter one and V_{oc} is relatively stable in all devices. Despite slight degradation in V_{oc} and FF , due to significant increase in J_{sc} , overall power conversion efficiency (PCE) of devices fabricated from IZO with 1 and 2 at. % indium is higher than that of device with ZnO buffer layer. However, in the case of device fabricated from IZO with 3 at. % indium, slight increase in J_{sc} is offset by low FF and overall PCE is lower than ZnO based device.

5. 4 Conclusion

In summary, J_{sc} of inverted OSC is influenced by the n-type buffer layer due to the combined factors contributed from charge collection and light harvesting. A decrease in work function of buffer layer resulting from the increase in dopant is beneficial to the charge collection yet has slight negative impact on V_{oc} and FF due to electron injection barrier lowering. This kind of trend agrees well with previous findings in conventional OSCs in which J_{sc} is increased but V_{oc} and FF (or only V_{oc}) are declined due to high conductivity p-type buffer layer [181-182]. Based on previous findings and our observations, it can be concluded that, regardless of conventional or inverted OSCs, a buffer layer controls the tradeoff between J_{sc} and V_{oc} & FF , which can be compromised by manipulating doping level, in other word, the energy level and conductivity of the buffer layer. The doping level of the buffer layer must be well optimized to achieve the optimum power conversion efficiency of organic solar cell.

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Chapter 6 Top illuminated dye-sensitized solar cells with a room-temperature-processed ZnO photoanode on metal substrate and a Pt-coated Ga-doped ZnO counter electrode

6.1 Introduction

Dye-sensitized solar cells (DSSCs) provide a promising alternative to conventional silicon photovoltaic technology thanks to their high photon-to-electricity conversion efficiency (over 11%) [73], low-cost and environmentally friendly manufacturing from abundant and non-toxic materials such as TiO_2 and ZnO photoanode. Current state-of-the-art DSSCs are typically fabricated on a FTO glass, allowing the light to enter from the bottom of the glass substrate. However, it is estimated that conducting glass is the most expensive part of a DSSC and it incurs 60% of the total cost [183]. Moreover, a relatively high sheet resistance of the conducting glass compared to metal is another obstacle to produce large area solar cells. Therefore, alternatively, top-illuminated DSSCs are particularly attractive because they can be fabricated on inexpensive opaque substrates such as metal foils or plastic foils with metal coatings which may possibly lead to low-cost, light-weight and flexible DSSC fabrication through roll-to-roll manufacturing. Moreover, in the case of a DSSC with TiO_2 nanotube array grown from anodization of Ti metal, top-illuminated configuration allows to assemble the DSSC directly on Ti metal foil (Fig. 6-1 (a))[184], eliminating expensive and time-consuming sputtering process to

deposit Ti film on the conducting glass [185] or lift-off and attachment processes to transfer nanocrystalline film from the opaque substrate to FTO glass [186-187]. Because of these advantages, top-illuminated DSSCs with various metal substrates were demonstrated by several groups [188-191] and the highest efficiency of 7.2% has been achieved using a sintered nanocrystalline TiO_2 photoanode and a Pt-coated ITO counter electrode (Fig. 6-1 (b)) [191].

Figure 6-1 The schematic diagrams of some top illuminated DSSCs reported by other groups (a) DSSC with TiO_2 nanotubes directly fabricated on Ti foil [184], (b) flexible DSSC on Ti foil [191] and (c) flexible DSSC on stainless steel foil [188]

However, in such a top-illuminated DSSC, TiO_2 layer is sintered at high temperatures (450-500 °C) to improve the connection between TiO_2 particles. Despite a capability of withstanding high temperature, sintering at a high temperature oxidizes the metal substrate due to oxygen in the ambient air or diffusion of oxygen from metal oxide semiconductor, reducing the conductivity of the electrode. An additional sputtered indium tin oxide (ITO) layer on top of the metal substrate and a blocking layer (silicon oxide (SiO_x)) between ITO and metal substrate are required to further improve the efficiency (Fig. 6-1 (c)) [188]. Hence, a surface activation method which does not require high temperature sintering yet provides good interconnection between particles and substrate adhesion, is essential. A room-temperature fabrication not only facilitates the manufacturing of solar cells but also saves energy during fabrication. On the other hand, Pt-coated ITO or FTO glass is widely used as the counter electrode in the top-illuminated DSSCs [184, 188-191]. Nevertheless, the excessive use of ITO, especially for the production of transparent electrodes for large-area photovoltaic devices, is endangered by the scarcity and ever-increasing price of indium [192]. Similarly, the quality of FTO films available for industrial photovoltaic production is not ideal because high quality FTO is only available at a laboratory scale due to process restraints and low production volume [193-194]. This situation drives the search for alternative transparent conducting materials as the counter electrode to replace ITO and FTO.

In order to address the limitations discussed above, herein we report on a new class of FTO/ITO-free top-illuminated DSSCs employing room-temperature-processed porous ZnO films as the photoanode and Pt-coated Ga-doped ZnO (GZO) films as the counter electrode. The photoanodes were prepared at room temperature by squeegee-

printing the paste of ZnO nanoparticles (NPs). Zinc acetate assisted inter-particle connection and ammonia activation ensure the good interconnection between particles and substrate adhesion, avoiding the need for high temperature sintering. Instead of typical FTO/ITO counter electrode, GZO which has been applied as transparent electrode in organic solar cell [195] and conventional DSSC [196], is adopted in this work for its low cost, natural abundance, non-toxicity and high thermal/chemical stability [197-198]. We demonstrated that the performance of these DSSCs with GZO is comparable to that of DSSCs with FTO counter electrode. The photovoltaic characteristics of these bottom- and top-illuminated devices were compared and the differences were discussed in terms of optical transmittance spectrum, incident photon-to-current efficiency (IPCE) and energy band diagram. The influence of metal substrate on the photovoltaic properties of the resulting devices was also investigated.

6.2 Experimental

Figure 6-2 Illustration of the squeegee printing method used in fabrication of porous ZnO film.

The thickness of the ZnO film is determined by the thickness of the tape.

In our experiment, ZnO NPs were synthesized from zinc acetate dihydrate (99.95% Fluka) precursor in methanol [199]. ZnO NPs were then transformed into ZnO paste similar to the previous report [125]. Briefly, 5.0 g ZnO NPs were mixed with 8 ml acetic acid (HAc) (0.1M) aqueous solution by mortar grinding. After being aged at room temperature, ZnO NPs were converted to ZnO paste. The various metal (Ti, Al, Ag, Ni) substrates were prepared by e-beam evaporation of metals on glass under high vacuum. The porous ZnO films were fabricated by squeegee-printing the ZnO paste on metal substrates, as illustrated in Fig. 6-2. For a bottom-illuminated DSSC, the ZnO porous film was fabricated on the commercial FTO glass (Nipon Sheet Glass). After being dried at room temperature, the ZnO films were immersed in 0.3 M ammonia for 15 min for surface activation^{*}. The activated films were cleaned with ethanol and dried in a laboratory oven. For dye loading, the ZnO films were immersed in an ethanol solution containing 0.3 mM Ru-metal complex dye (*cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium)) (from Everlight as a free sample) for 2 h. The transparent conducting GZO films as the counter electrode were deposited on glass substrates by a metal-organic chemical vapor deposition (MOCVD) system equipped with a home-made shower-head injector. Trimethylgallium (TMGa), dimethylzinc (DMZn) and oxygen were used as precursors and nitrogen was employed as a carrier gas for the metal-organics. The flow rates of N₂ and O₂ were controlled at 500 and 200 standard cubic centimeter per minute (sccm), respectively, while those of TMGa and DMZn were controlled both at 2 sccm. The GZO films were grown at a relatively low temperature of 300°C with a chamber pressure of ~25 Torr. The counter electrode was

^{*} The surface activation will be discussed in details on page 120.

completed by sputtering Pt on GZO film under mild condition (20 mA) for 30 s. Some counter electrodes were also prepared on FTO for comparison. The two electrodes were bonded together by a $\sim 60\ \mu\text{m}$ thick thermal plastic. Finally, the electrolyte composed of 0.1 M I_2 , 0.1 M LiI, 0.5 M terbutylpyridine and 0.6 M 1-hexyl-3-methylimidazolium iodide in methoxy-acetonitrile was introduced between the electrodes by capillary action, as illustrated in Fig. 6-3. The capillary action, in opposition to gravity, enables uniform spreading of the electrolyte between the electrodes.

Figure 6-3 Illustration of filling up electrolyte between two electrodes

Photovoltaic measurement was conducted illuminating the devices under a solar simulator (Model 16S-002, Solar Light Company Inc.) with AM1.5G filter. The current-voltage (J - V) characteristics were performed using a Keithley 2400 sourcemeter. All devices were tested in ambient condition and simulated light intensity was adjusted to 100

mW/cm² calibrated with a Thorlabs optical powermeter. The incident photon-to-current efficiency (IPCE) was measured by an IPCE measurement kit (Newport – Model QE-PV-SI) in DC mode. The SEM images of ZnO porous film were recorded using a JEOL FESEM and the tapping mode AFM images of GZO film were taken with Nanoscope IIIa (Digital Instruments) scanning probe microscope. X-ray diffraction (XRD) patterns of the films were obtained by a diffractometer (Siemens- model D5005) operating at 40 keV and 36 mA using Cu K α ($\lambda = 1.54056 \text{ \AA}$). The thickness of the films was measured by a surface profiler (KLA Tencor P-15). The sheet resistance and resistivity of GZO films were extracted using Hall effect measurement system (BIO-RAD) with van der Pauw method at room temperature. The optical transmittance and absorption spectra of the films were measured using UV-vis-NIR spectrophotometer system (PerkinElmer Lambda 950) with an integrating sphere to capture directly transmitted light and forward scattered light.

6.3 Results and discussion

6.3.1 Material Characterization

Fig. 6-4 (a) and (b) show the SEM images and XRD patterns of porous ZnO film after surface activation. The average crystalline size of ZnO NPs both revealed from SEM image and calculated from XRD pattern using Scherrer formula is about 20 nm. The typical pore size as measured from SEM image is in the range of 10 to 100 nm. The thickness of the porous film was controlled at 8 μm . The film shows polycrystalline nature and all the diffraction peaks can be indexed to hexagonal wurtzite structure of ZnO. There

are two underlying mechanisms that promote the linkage between ZnO NPs as well as adhesion to the substrate: surface charge effect and binder effect [125]. During grinding the ZnO NPs in diluted HAc solution, the acid etches the surface of the ZnO NPs. The Ac^- ions screening on the surface of ZnO easily attract Zn^{2+} ions which come from etching ZnO by HAc. The etching process also generates ZnAc_2 which acts as binder to connect ZnO NPs together as well as anchor to the substrate. After the film has been dried, ammonia activation removes ZnAc_2 covered on the surface of the ZnO NPs easily without heating up to high temperature by forming dissolvable $\text{Zn}(\text{NH}_3)_4^{2+}$ and the ZnO surface was changed to hydroxyl termination which facilitates the dye adsorption on the porous film.

Fig. 6-4 (c) and (d) show the AFM image and XRD patterns of GZO film deposited by MOCVD. From AFM analysis, the roughness (rms) of GZO film is $\sim 25\text{nm}$. This nanoscale rough film also acts as an efficient anti-reflection coating due to the refractive index grading at the rough electrolyte/GZO interface [193]. Likewise ZnO porous film, hexagonal wurtzite structure of ZnO can be clearly seen in the resultant GZO film but no phase related to Ga is observed probably due to low Ga content ($\sim 5\text{ at. } \%$). A strong diffraction peak at $2\theta = 34.4^\circ$ indicates the preferential orientation along (002) direction and high-quality crystallinity of the film. The resistivity of GZO film measured by Hall effect system is as low as $8.01 \times 10^{-4} \Omega\text{-cm}$. At the film thickness of $\sim 750\text{ nm}$, the sheet resistance of the film reaches $10.68 \Omega/\square$.

Figure 6-4 SEM image of ZnO porous film fabricated on Ti substrate (a) and its XRD pattern (b). AFM images of GZO counter electrode deposited on glass substrate by MOCVD (the unit of scale bar is μm .) (c) and its XRD pattern (d).

6.3.2 Comparison between top-illuminated and bottom-illuminated cells

Figure 6-5 Schematic of bottom-illuminated cell (a) and top-illuminated cell (b)

Figure 6-6 J - V characteristics of the bottom- and top-illuminated DSCs under illumination (filled symbols) and in the dark (open symbols). Devices are named in the format of working electrode – counter electrode. (*) denotes the bottom-illuminated device.

The device architectures of a bottom-illuminated cell (conventional) and top-illuminated cell used in the experiment are illustrated in Fig. 6-5. The J - V characteristics

of DSSCs with various working and counter electrodes, both in the dark and under AM1.5G illumination (100 mW/cm^2) are shown in Fig. 6-6. In our discussion, we denote DSSCs based on their working and counter electrodes, e.g., Ti-GZO refers to the DSSC with Ti working electrode and Pt-coated GZO counter electrode. All devices, except conventional FTO-FTO device, are top-illuminated. The J_{sc} of Ti-GZO is similar to that of Ti-FTO, however it drops about 25 % compared to FTO-FTO bottom-illuminated device. The variation in J_{sc} can be understood by optical transmittance spectra of various electrodes and IPCE measurement (Fig. 6-7). The absorption edge of FTO is observed at 350 nm while that of GZO is shifted to 400 nm. The transmittance of GZO is, therefore, lower than that of FTO in the spectral region below 500 nm but the difference above 500 nm is smaller. The transmittance of both FTO and GZO films is slightly reduced upon Pt-coating. Although a red shift in absorption edge occurred in GZO compared to FTO, this shift does not affect much the performance of top-illuminated device due to the absorption edge of electrolyte is at 480 nm. Hence, the transmittance of combined GZO/Pt/electrolyte is comparable to that of FTO/Pt/electrolyte and J_{sc} of Ti-GZO device (4.756 mA/cm^2) is quite close to that of Ti-FTO device (4.966 mA/cm^2). It is also observed that the IPCE spectrum of Ti-GZO is similar to that of Ti-FTO device. The IPCE spectra of top-illuminated devices are not much different from those of bottom-illuminated device at long wavelengths because of negligible absorption of electrolyte in this region. However, the transmittance of GZO/Pt/electrolyte and FTO/Pt/electrolyte is much lower than that of FTO in the region below 500 nm due to the sharp absorption edge of the electrolyte around 480 nm. Therefore, in contrast to the bottom-illuminated device, the spectral responses of top-illuminated devices sharply drop below 500 nm and there is almost no

observable response below 450 nm. The IPCE peaks of top-illuminated devices are also affected due to this strong absorption of the electrolyte near its absorption edge. From IPCE and transmittance spectrum, we can conclude that the strong absorption of the electrolyte at the absorption edge (~ 480 nm) is mainly responsible for 20-25% drop in J_{sc} of the top-illuminated device.

Figure 6-7 (a) Transmittance spectra of FTO and GZO with/without Pt and 60 μm -thick electrolyte (left vertical axis) and absorption spectrum of D719 dye (right vertical axis). (b) IPCE spectra of the fabricated devices.

Figure 6-8 Schematic of top-illuminated DSSC showing energetics of individual layers (a) before contact, (b) after contact in dark and (c) after contact under strong illumination when open circuit. The vertical axis is the electron energy versus vacuum level (VAC) on the left scale and versus normal hydrogen electron (NHE) on the right scale. E_{FM} , E_C , E_{FS} , LUMO, HOMO and E_{redox} stand for Fermi level of metals, conduction band and Fermi level of ZnO (semiconductor), lowest unoccupied molecular orbital and highest occupied molecular orbital of dye and redox potential of electrolyte, respectively. E_F , E_{Fn}^* and E_{Fp}^* represents Fermi level of the system (in the dark, equilibrium condition) and the quasi-electron and quasi-hole Fermi levels (under illumination, non-equilibrium condition). The vertical arrow in (c) indicates V_{oc} can be attained from the system. The energy levels are approximately drawn to scale. Dash-arrows A, B and C represent the recombination of injected electrons at ZnO/D⁺, ZnO/ I_3^- and Ti/ I_3^- interfaces, respectively.

The V_{oc} of the fabricated devices are similar to each other but the FF of the devices with Ti substrate (without anneal) (66%) is higher than that of the bottom illuminated device with FTO substrate (60%). Generally, FF of a solar cell is determined by two components: shunt resistance (R_{sh}) $[(dV/dI)_{V=0}]$ and series resistance (R_s) $[(dV/dI)_{V \geq V_{oc}}]$. It can be seen from $J-V$ curves that R_{sh} of these devices are similar but Ti-FTO and Ti-GZO devices have smaller R_s than FTO-FTO device. Therefore, higher FF of Ti-GZO and Ti-FTO devices can be attributed to a reduction in R_s , which can be explained by energy band diagram at ZnO and electrode interface. Fig. 6-8(a) shows the energy levels of individual layers in DSSC before contact.

Figure 6-9 Schemes of electron energy at (a) Ti/ZnO contact and (b) FTO/ZnO contact. Left diagrams illustrate the energy level of individual layers before contact, centre ones show the band

bending at the interface in the dark, and right diagrams show the formation of ohmic and Schottky contact for Ti/ZnO and FTO/ZnO, respectively, under strong illumination when open circuit.

The work functions of metals are taken from the literature [200]. The electron affinity of ZnO is about 4.3 eV [201-202], and the work function of ZnO nanostructure, which is nearly independent of the geometrical size [203], was measured to be 5.2 – 5.3 eV [203-205]. In our analysis, the conduction band (E_C) and the Fermi level of ZnO semiconductor (E_{FS}) are taken to be -4.29 eV and -5.2 eV with respect to the vacuum level, respectively. A redox potential of I/I_3^- electrolyte (E_{redox}) of -4.85 eV (with respect to the vacuum level) is extracted from the previous reports [16, 79, 101]. After ZnO is made contact with liquid electrolyte in the dark, E_{FS} is aligned to E_{redox} as well as Fermi level of metals (E_{FM}) of the two electrodes under equilibrium condition (Fig. 6-8(b)). Band bending at the interfaces, which will be shown in detail in Fig. 6-9, is neglected in this figure for simplicity. Under strong illumination when open circuit, this equilibrium condition is disturbed and E_{FS} moves up to the electron-quasi Fermi level (E_{Fn}^*), which is close to the conduction band minimum of ZnO due to the accumulation of photogenerated electrons in the E_C of ZnO (Fig. 6-8(c)). Likewise, E_{redox} is shifted to the hole-quasi Fermi level (E_{Fp}^*) owing to virtual hole injection into electrolyte. The potential difference between E_{Fn}^* and E_{Fp}^* dictates the operating V_{oc} of the system.

Next we take a closer look at the energy levels across the interface between the electrodes and ZnO (Fig. 6-9 (a)). The left diagram illustrates the energy level of Ti metal and ZnO semiconductor before contact. Upon contact and in the dark, the Fermi levels of Ti and ZnO are adjusted to I/I_3^- redox couple (-4.85 eV). Hence, the band bending of 0.87

eV and the band off-set of 0.04 eV appear at the interface. No band bending is formed at the metal side. The shift of E_C due to the solvation effects, which arise from immersion in the solvent [16], and Helmholtz layer dipole owing to the cation adsorption on the ZnO surface, which comes from the carboxylate group of the dye [16, 91], are ignored to simplify the discussion. Under strong illumination when open circuit, E_{FS} is shifted to E_{Fn}^* which aligns with the Fermi level of Ti and an ohmic contact is then formed at the semiconductor and metal junction. On the other hand, the energetics of FTO and ZnO are different, as shown in figure 6 (b). The work function of FTO is reported to be varied from 4.7 to 4.9 eV [16, 101, 206]. In our analysis, the work function of FTO is taken as 4.9 eV. Like the interface between Ti and ZnO, the Fermi levels of FTO and ZnO are aligned to -4.85 eV upon contact with electrolyte in the dark condition. The band bendings of 0.3 eV and 0.61 eV are formed at the ZnO and FTO sides, respectively. Under strong illumination when open circuit, E_{FS} of ZnO is shifted to E_{Fn}^* which is close to the conduction band of ZnO. Thus, in contrast to Ti substrate, the misalignment of the Fermi levels of FTO and E_{Fn}^* makes a Schottky contact at the metal and semiconductor junction, which obstructs electrons to be injected into the electrode. This Schottky barrier accounts for the increase in R_s of FTO-FTO device whereas an ohmic contact is formed at the semiconductor/metal interface in Ti-FTO/Ti-GZO devices and hence R_s decreases. In addition to the ohmic contact, a very low sheet resistance of Ti film ($\sim 1.5 \Omega/\square$), which is nearly an order of magnitude lower than that of FTO ($14 \Omega/\square$), also further reduces R_s , and in turn increases FF.

In our experiment, we also further deliberately annealed the working electrode (Ti substrate together with ZnO) at 450° C in air to investigate the effect of high temperature

annealing. FF of Ti(anneal)-GZO device is dropped to 55% and J_{sc} is also slightly reduced. It was also observed that sheet resistance of Ti film increases to $>300 \Omega/\square$ (by two orders of magnitude) upon annealing due to oxidation of Ti. Therefore, we attribute this decrease in FF to a high sheet resistance of the annealed film which increases R_s of the device. This clearly shows that we should adopt a low-temperature process for top-illuminated DSSC to avoid oxidation of metal (especially for low-work-function metals which are easy to be oxidized) although metal substrate withstands high temperature.

From J - V curves of the fabricated devices, we observed that V_{oc} is relatively constant despite electrode change. Generally the Fermi level shift in the semiconductor due to the accumulation of photogenerated electrons in the conduction band (in other words, the electron-quasi Fermi level shown as E_{Fn}^* in Fig. 6-8(c)) mainly determines V_{oc} of the resultant DSSC although some other limiting factors including large negative flat band potential of electrode (FTO) [101], and band edge displacement [94] are suggested. As E_{Fn}^* depends on the electron concentration in the semiconductor, V_{oc} should be related to the recombination of injected electrons with oxidized dye (D^+) or I_3^- ions – either at the interface of ZnO/dye (A), ZnO/electrolyte (B), or Ti(FTO)/electrolyte (C), as shown in Fig. 6-8(a). Since the net current flow at V_{oc} is zero, V_{oc} can be worked out by equating the electron injection current density and recombination current density at bias $V = V_{oc}$ [94]. Mathematically it can be expressed as

$$V_{oc} = \frac{kT}{q} \ln \left(\frac{AI}{n_0 k_1 [D^+] + n_0 k_2 [I_3^-] + n_{e0} k_3 [I_3^-]} \right) \quad (6-1)$$

where k is the Boltzmann constant, T denotes the temperature, q represents the fundamental charge; k_1 , k_2 and k_3 are the kinetic constants of recombination for A, B and C, respectively; n_0 and n_{e0} are the concentrations of electronic states in semiconductor and electrode in the dark (equilibrium); $[D^+]$ and $[I_3^-]$ are the concentrations of oxidized dye and oxidized redox couple; and A and I are the area of electrode and incident photon flux, respectively. Unlike previous reports [94, 207-208], we include the recombination at the electrode/redox couple interface in our expression and ignore the reaction order for I_3^- and electron as it is close to 1 [79]. Because the recombination processes A and B are the same for both top- and bottom-illuminated devices and V_{oc} is relatively constant for all devices, it can be concluded that the recombination between the electrode and I_3^- is not worsened by replacing FTO with Ti. This hypothesis can be supported by the J - V curves of which the inverse slopes at zero bias are similar for the top- and bottom-illuminated devices. This observation also refutes the previous suggestion that large negative flat band potential of FTO limits the maximum attainable V_{oc} because an increase in V_{oc} was not observed although negative flat band potential is reduced by replacing FTO with Ti [101].

6.3.3 Effect of metal substrates on top-illuminated DSSC

We also investigated the effect of metal substrate on the performance of top-illuminated DSSC by employing various metals with different work functions (from low to high). We used Al, Ti, Ag and Ni (whose work functions are 4.18 eV, 4.33 eV, 4.74 eV and 5.35 eV, respectively) [200], as the working electrode and Pt-coated GZO as the

counter electrode. J - V characteristics of the fabricated devices are depicted in Fig. 6-10(a). Only very small photovoltaic effect is generated from Al-device (inset of Fig. 6-10(a)) although a favorable ohmic contact between Al and ZnO was reported [209]. Therefore, we suppose that an oxide layer has formed between Al and ZnO owing to the easily oxidized nature of Al. The oxidation process makes the work function of Al even lower than pristine Al [210]. The work function of Al is reported to be reduced to -3.7 eV after being exposed to air in 1 h [210], and the work function of its oxide film is reported to be as low as -1.6 eV [211]. This low-work-function oxide layer creates a huge barrier for electrons at the conduction band of ZnO to flow to Al electrode, and hence only small amount of photocurrent is extracted. However, Ag and Ni-devices have reasonable photovoltaic effect despite a lower performance than Ti-device. As seen from the J - V curves, R_{sh} of Ti-device is much higher than that of Ag and Ni-device, suggesting that there is less recombination in Ti-device compared to Ag and Ni-devices. Because the same materials, except for the bottom electrode metal, are used in all devices, the recombination rates of A and B (refer to Fig. 6-8(a)) are the same in all devices. A poor performance of Ag and Ni-devices can, therefore, be attributed to the recombination of injected electrons with oxidized I_3^- ions at the metal/electrolyte interface (recombination C). To confirm this hypothesis, we investigated the catalytic activity for redox reaction of the metals by fabricating bottom-illuminated DSSC with these metals as the counter electrode and Pt-counter electrode as a reference (Fig. 6-10(b) inset). The J - V characteristics of these devices are shown in Fig. 6-10(b). When Ti is used as the counter electrode, no photovoltaic effect is observed, meaning that Ti exhibits very little or no catalytic activity. However, we observed photovoltaic effect when Ag and Ni are used as

the counter electrode. Hence, Ag and Ni exhibit catalytic activity although their effect is not as strong as Pt. When Ag and Ni are used as the working electrode in top-illuminated device, the catalytic property of these metals enhances the reaction $I_3^- + 2e^- \rightarrow 3I^-$ at the working electrode/electrolyte interface and increases the recombination by reducing I_3^- with injected electrons. As Ni has a higher catalytic effect than Ag, FF of Ni-device is lower than that of Ag-device. The recombination current has also a negative impact on the photogenerated current and hence J_{sc} of Ag and Ni-devices are smaller than that of Ti-device. As discussed previously, V_{oc} of DSSC depends logarithmically on the inverse of kinetic constant of recombination; the increase in recombination also reduces V_{oc} . Therefore, we observed the descending order of V_{oc} from Ti to Ni-device. Another factor for inferior performance of Ag and Ni-devices is the high work function of the metal. Like FTO, high-work-function Ag and Ni result in a Schottky barrier at the ZnO/metal junction under strong illumination when open circuit, hence increasing R_s . When the device operates as a diode in the dark, high work-function Ni creates a higher barrier than Ti or Ag does. The turn-on voltage of Ni-device is, therefore, higher than that of Ti and Ag-device in the dark J - V curves. In fact, Ag is not practical to be used as an electrode because we noticed that Ag film is corroded within an hour after injecting liquid electrolyte (as it is vulnerable to the corrosive iodide/triiodide redox electrolyte). However, we did not observe any corrosion on Ti metal by visual inspection even after few weeks. These findings reveal that Ti is a more appropriate metal to be used in top-illuminated device.

Figure 6-10 (a) J - V characteristics of top-illuminated devices with various metal substrates (Al, Ti, Ag and Ni) under illumination (filled symbols) and in the dark (open symbols). Inset- J - V curve of Al-device at low scale to show the small photovoltaic effect. Pt-coated GZO is used as counter electrode in these devices. (b) J - V characteristics of bottom-illuminated devices with various counter electrodes (Ti, Ag, Ni and Pt) to investigate the catalytic effect of the metals. Inset: device architecture used to test the catalytic effect.

6.4 Conclusion

We demonstrated FTO/ITO-free, top-illuminated DSSCs with room-temperature-processed ZnO photoanodes on Ti substrates. The efficiency of such a top-illuminated DSSC with the GZO counter electrode (1.91%) is comparable to that of conventional DSSCs with the commercial FTO counter electrode (1.99%). Although the efficiency of the top-illuminated DSSC is about 20% lower than the conventional bottom-illuminated DSSC (2.37%), it reduces the cost of DSSC by eliminating the usage of conventional conducting glass (FTO/ITO), which is the most expensive part of DSSC. Our room-temperature-processed photoanode yields a higher fill factor than high-temperature-processed photoanode without sacrificing the good interconnection between nanoparticles and adhesion to the substrate. We also showed that Ti is more suitable to be used in a top-illuminated DSC architecture than other metals because of minimum catalytic activity on redox reaction and high resistance to corrosion.

Acknowledgment

The transparent conductive GZO films are fabricated by Dr. Zhao Junliang from our group. His contribution to this work is greatly appreciated.

Chapter 7 Dye-sensitized solar cell with a titanium-oxide-modified carbon nanotube transparent electrode

7.1 Introduction

Common TCOs such as ITO and FTO are ubiquitously used as window electrodes in optoelectronic devices. However, there exist major technical issues associated with the usage of TCOs as the window electrodes due to their inherent limitations: (1) high cost for large-scale fabrication by vacuum-process, (2) scarcity of their material sources, (3) diffusion of dopants into active materials, (4) limited usage on flexible substrates due to brittleness, (5) chemical instability, and (6) limited transparency in the near infra-red region [20, 192, 212-214]. A recent success in the fabrication of optically transparent and electrically conducting thin film from carbon-based materials using carbon nanotubes* (CNTs) and graphene has attracted significant attention [215-216]. In comparison to traditional TCOs, these carbon-based materials may allow for substantially reduced costs because of the abundant material source and potentially scalable fabrication from solution process [217]. They are mechanically strong and flexible as well as chemically stable [218-219]. More interestingly, they remain transparent in the near infra-red region, in contrast to TCO [214-215].

As such, CNT and graphene have been demonstrated as the window electrode in a wide range of solid-state applications [220-224]. However, it has not been possible to

* Single-walled CNT with mixture of metallic and semiconducting nanotubes

integrate carbon-based materials as a working electrode in liquid-type DSSC to date because of their well-known catalytic property to redox reaction. Thus, it has been appropriate to use them as a counter electrode in DSSC to replace expensive Pt [225]. When they are used as a working electrode, however, their catalytic property allows the collected electrons at the working electrode to recombine with I_3^- ions in the electrolyte by the reaction $I_3^- + 2e^- \rightarrow 3I^-$, at the electrolyte/working electrode interface. Hence, despite the fact that CNT and graphene have similar work functions (4.7 – 4.9 eV and ~ 4.6 eV, respectively)[226-227] to that of conventional TCOs, electrically conductive and optically transparent, no liquid-type DSSC with a carbon-based working electrode could be realized so far.

To circumvent this problem, we proposed and employed a facile method for surface modification with thin oxide layer, suppressing the recombination of electrons with I_3^- , as illustrated in Fig. 7-1, while maintaining the electrical and optical properties of the working electrode made of CNTs. Although this approach would solve the problem, the prerequisites for an ideal oxide used in the modification limits the choice of available materials. First, the oxide layer must convey electrons from the conduction band of TiO_2 to the CNT electrode; i.e., the conduction band of oxide must lie between the work function of CNT and the conduction band of TiO_2 . Second, the layer must be optically transparent within the solar spectrum. Third, it must be chemically stable (inert to acid and base), especially in the electrolyte. Last, the layer must be compact and pinhole-free to avoid direct contact with the electrolyte and CNT film. For example, a sol-gel processed ZnO film has been proven as a highly transparent, electron-transporting layer in an organic solar cell [179]. However, ZnO is not compatible with acid-containing anatase

paste and dye solution. Alternatively, a compact TiO_2 layer by spray-pyrolysis is able to withstand the acid [228], but heating/pre-heating the substrate at high temperature during film deposition oxidizes the CNTs. Thus, herein, we have modified the CNT film with sol-gel-processed titanium sub-oxide (TiO_x) at low temperature (150°C). By modifying CNTs with TiO_x , we demonstrated that the efficiency can be tremendously improved.

Figure 7-1 Schematic of (a) recombination of electrons with I_3^- at the CNT/electrolyte interface in the case of bare CNT electrode, (b) inhibiting the charge-transfer kinetics at the interface by using a thin TiO_x layer, (c) unidirectional flow of electrons in the liquid-type DSSC with the TiO_x -modified-CNT working electrode, showing the energetics of the individual components used in the cell.

7.2 Experimental

Figure 7-2 Schematic diagram to show the air gun spray method used in printing CNT films

The transparent, conductive CNT films were produced by air-gun spray method (as illustrated in Fig. 7-2) from the solution containing 0.2 mg/mL single-wall CNT dispersion (Carbon solution Inc., the ratio of metallic to semiconducting nanotubes is 1:2) and 0.5 wt% sodium dodecylbenzene sulfonate (SDBS) surfactant in distilled water [229]. Prior to spraying, the mixture was probe-sonicated at 120 W to make a homogenous mixture. The SWCNT solution was then centrifuged at 8000 rpm for 30 minutes and the supernatant was collected. The supernatant was directly sprayed using air spray gun (Badger) onto glass substrates. Manual operation method is used to spray CNT solution, i.e., the air-gun sprayer is held by an operator, about 6 to 10 inches from the glass substrate, and moved back and front over the surface, each stroke overlapping the previous to ensure a continuous coat. The regulator on the compressor was adjusted to 20 PSI (pounds per square inch). During the spraying process, glass substrate was put on a hot plate with a temperature at around 80-90°C. After the film deposition, the surfactant

was removed by immersion in distilled water for 24 h. Some CNT films were immersed in 98 wt% sulfuric acid for 30 min to yield *p*-type doped CNT films. TiO_x sol-gel was prepared by refluxing 1 mL of titanium (IV) isopropoxide, 5 mL of 2-methoxyethanol and 0.5 mL of ethanolamine in a three-necked flask under argon environment at 80°C for 2 h and 120°C for 1 h [230]. The prepared sol-gel was spin-coated onto the CNT film at 3000 rpm. The thickness of the film was controlled by diluting the sol solution with 2-methoxyethanol. Subsequently, the samples were heated at 150°C for 1 h in air. The precursor was hydrolyzed and converted to TiO_x during heating in air.

For the fabrication of DSSC, porous TiO_2 film was deposited by screen-printing the TiO_2 paste on bare/ TiO_x -modified-CNT. For a standard DSSC, the porous TiO_2 film was fabricated on the commercial FTO glass (Nipon Sheet Glass, $15\Omega/\square$). TiO_2 film was sintered at 450°C for half an hour in air. After being cooled down to 80°C, the working electrode was immersed in an ethanol solution containing 0.3mM cis-diisothiocyanato-bis(2,2'-bipyridyl-4,'-dicarboxylato)ruthenium(II) bis(tetrabutylammonium) (Solaronix, N719) overnight for sensitization. Then, the sensitized photoanode was cleaned with ethanol to remove excess dye. A Pt-coated-FTO layer is used as the counter electrode. The two electrodes were bonded together by a ~60 μm thick thermal plastic. Finally, the electrolyte composed of 0.1 M LiI, 0.1 M I_2 , 0.5 M *tert*butylpyridine and 0.6 M 1-hexyl-3-methylimidazolium iodide in methoxy-acetonitrile was introduced between the electrodes by capillary action. The cell was immediately tested without sealing.

The photovoltaic measurement of the cells, the transmittance spectra, XPS spectra and thickness of the films were conducted as described in the previous chapters. All

electrochemical measurements were carried out with Autolab system. Ag/AgCl (KCl-saturated) and Pt coil were used as reference electrode and counter electrode, respectively. NOVA software provided from Autolab electrochemical system was used to fit the impedance data for the charge-transfer resistance calculation. The sheet resistance was measured with a four-point-probe system.

7.3 Results and discussion

Figure 7-3 (a) SEM image of a typical CNT film deposited by air-gun spray. (b) The sheet resistance vs. optical transmittance of the doped and undoped CNT film.

SEM image of a typical CNT film produced by the spray method is shown in Fig. 7-3(a). A number of well-entangled and interconnected CNTs with a general diameter of 10-25 nm were observed. The relationship between the sheet resistance and the optical transmittance of the doped and undoped CNTs at the optical wavelength of 600 nm is

shown in Fig. 7-3(b). Generally, the doped CNT film yields higher transmittance compared to the undoped one at the same sheet resistance. The optimum combination of sheet resistance and transmittance occurs for $400\text{--}450\ \Omega/\square$ while the corresponding transmittance is around 75–78%. Hence, the doped CNT film with a sheet resistance $400\pm 20\ \Omega$ was chosen for our device fabrication.

Figure 7-4 (a) AFM image of TiO_x coated CNT film ($8.0 \times 8.0\ \mu\text{m}^2$) (b) Typical optical transmittance spectra of the bare CNT, TiO_x and TiO_x -modified-CNT films. Photograph of TiO_x film (c) and TiO_x -modified-CNT film (d) on the glass substrate.

AFM image of sol-gel processed TiO_x film deposited on CNTs is shown in Fig. 7-4(a). The resulting TiO_x film is composed of myriad nano-sized colloids, completely covering the underlying CNT bundles. The elemental composition of Ti and O, cross-checked by X-ray photoelectron spectroscopy, is 41.9% and 56.6%, respectively. Since

the ratio of O to Ti is between 1 and 2, the film is considered as titanium sub-oxide, rather than titanium dioxide. The modification of CNT film with ultra-thin TiO_x layer slightly affects the sheet resistance of the overall electrode. The sheet resistance of TiO_x -modified-CNT film increases only to $550 \pm 20 \, \Omega/\square$ with a 10-nm-thick TiO_x film from $400 \pm 20 \, \Omega/\square$ for the bare CNT film. More interestingly, TiO_x film is highly transparent in visible region as well as the near infra-red range and, hence, the transmittance spectra of bare and modified CNT films are nearly the same (Fig. 7-4(b)).

Figure 7-5 J - V characteristics of liquid-type DSSC with the bare CNT electrode and the TiO_x -modified-CNT electrode under simulated solar irradiation of AM1.5G (1 sun)

	$J_{sc} \text{ (mA/cm}^2\text{)}$	$V_{oc} \text{ (V)}$	FF (%)	PCE (%)
Bare CNT	0.281	0.057	23	~ 0%
TiO_x-modified-CNT	6.221	0.613	45	1.7

Table 7-1 The electrical characteristics of the devices

The J - V characteristics of the cells with the bare CNT electrode and the TiO_x -modified-CNT electrode ($\text{TiO}_x \sim 10$ nm) under illumination of AM1.5G simulated solar light (100 mW/cm^2) are shown in Fig. 7-5. The PCE of the cell using the bare CNT electrode is nearly 0%, and the cell is therefore almost nonfunctional. By modifying CNTs with TiO_x , however, the PCE of the cell significantly improves to 1.7%. The detail electrical characteristics of the devices are listed in Table 7-1.

Figure 7-6 (a) Cyclic voltammograms of the bare CNT and TiO_x -modified-CNT in 0.1M KCl solution containing 5.0 mM $\text{K}_3\text{Fe}(\text{CN})_6$ at a scan rate of 10 mV/s. (b) the Nyquist plots of a three-

electrode system with the bare CNT and the TiO_x -modified-CNT working electrodes in an electrolyte containing 0.05M I_2 and 0.5M LiI in aqueous solution with a bias of 300 mV. The frequency range was from 0.1 to 100 kHz with the frequency decreasing from left to right. Inset is the equivalent circuit used in fitting data.

To further understand the role of TiO_x in the CNT-electrode-based DSSC, we studied the electron-transfer properties of the electrodes using cyclic voltammetry (CV). Fig. 7-6(a) shows the CV response of the electrodes in 0.1M KCl solution containing 5.0 mM $\text{K}_3\text{Fe}(\text{CN})_6$ at a scan rate of 10 mV/s. The bare CNT electrode shows a quasi-reversible characteristic with a cathodic peak of 0.56 mA/cm^2 at a reduction potential 0.026 V and an anodic peak of 0.35 mA/cm^2 at an oxidation potential 0.86 V, suggesting that there is electron-transfer between the CNTs and the redox system. In contrast, neither cathodic nor anodic peak was observed in CV response of TiO_x -modified-CNT electrode, indicating that the electron transfer between the CNTs and the redox species is blocked by TiO_x . Since the catalytic activity can also be evaluated with charge-transfer resistance (R_{CT}) at the electrode/electrolyte interface, we also conducted electrochemical impedance spectroscopy (EIS). EIS data for electrochemical cells such as fuel cells and DSSCs are most often presented in Nyquist plot. A complex plane or Nyquist plot depicts the imaginary impedance, which represents the capacitive and inductive character of the cells, versus the real impedance of the cell. Fig. 7-6(b) shows the Nyquist plots of a three-electrode system in an electrolyte containing 0.05M I_2 and 0.5M LiI in aqueous solution. The plots were fitted with the equivalent circuit model (inset Fig. 7-6(b)). R_{CT} indicates the electron transfer resistance between the electrode and electrolyte. The Nernst diffusion impedance (Z_{N}) describes the diffusion of I_3^- in electrolyte while R_s stems from the ohmic

resistance of the electrolyte and electrodes [207, 231]. From the fitted data, R_{CT} of the bare CNT electrode was found to be only $311.4 \Omega \cdot \text{cm}^2$ while that of TiO_x -modified-CNT was $2.513 \text{ k}\Omega \cdot \text{cm}^2$. Because R_{CT} varies inversely with the I_3^- reduction activity of the electrode [232], the larger R_{CT} of TiO_x -modified-CNT film suggests that the reduction of I_3^- at the CNT/electrolyte interface is largely suppressed by TiO_x .

Based on the observed data, we proposed a mechanism of electron collection at the carbon- based-working electrode in DSSC. Without any modification, almost all the electrons collected at CNTs reduce I_3^- to I^- at the CNT/electrolyte interface and, thus, almost no photovoltaic effect is observed in the cell. When TiO_x -modified-CNT is used, the TiO_x layer effectively blocks redox species from CNTs and retards the electron-transfer kinetics at the CNT/electrolyte interface, ensuring the unidirectional flow of electrons in the cell. The injected electrons from the excited state of dye molecules are then collected at the CNT electrode in two steps. First, the electrons percolated along the TiO_2 porous network are transferred to TiO_x whose conduction band (4.2 - 4.4 eV) is close to that of TiO_2 (4.2 eV). Then the electrons at the conduction band of TiO_x are injected to CNTs since the work function of CNT is lower than the conduction band of TiO_x .

7.4 Conclusion

In conclusion, we proposed and demonstrated the feasibility of carbon-based transparent, conductive film made of CNTs as the working electrode in a DSSC containing redox solution, enabled by surface modification of CNTs using TiO_x , which

serves as a retardation medium to electron-transfer kinetics at the CNT/electrolyte interface without degrading the electrical and optical properties of CNTs. TiO_x -modified-CNT electrodes used in the experiment were fabricated by solution process at room temperature and thus it could be potentially used on plastic substrate for flexible DSSC. Certainly, this is an initial attempt towards the direction of carbon based transparent, conductive film as working electrode in liquid-type DSSC. As a result, the power conversion efficiency (1.7%) is still lower than that of our DSSC with FTO electrode (4.49%), primarily due to lower transmittance and higher sheet resistance of CNT films. With further optimization in the sheet resistance and transmittance, carbon based window electrode could become a viable alternative to TCO in both solid-state and liquid-type optoelectronic devices.

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The transparent conductive CNT films were fabricated by Hosea Tintang from Prof Zhang Qichun's group. His contribution on this work is greatly appreciated.

Chapter 8 Dye-sensitized solar cell with all carbon electrodes

8.1 Introduction

The high cost of DSSCs comes mostly from their electrodes, namely FTO (ITO) glass, as discussed in chapter 6 and 7. On top of this, the counter electrode is made of FTO (or ITO) with a thin layer of Pt as a redox catalytic layer. This Pt catalytic layer is extremely important in DSSCs for the regeneration of the dyes after excitation, but, it is very expensive. Although there is a counter argument that Pt does not contribute significantly to the overall price per peak-watt due to very small amount of Pt (proximately 50 mg/m²), another problem associated with Pt is its stability in electrolyte. There are also some reports of corrosion of Pt in triiodide-containing solutions generating platinum iodides such as PtI₄ [233-234]. In order to reduce the Pt-related negative factors, many studies have been done to find the alternatives to replace the Pt catalytic layer. Popular materials are multiwalled CNT, single walled CNT, carbon black, poly-aniline, and graphene [225, 235-238]. In fact, carbon-based transparent electrodes as the replacement of conventional FTO/ITO have been widely used in several solid-state optoelectronic devices such as organic thin film transistor, organic light emitting diode, organic solar cell and solid-state DSSC [220-224, 239-240]. However, to our surprise, there are fewer examples that consider replacing ITO (or FTO) together with the catalytic layer. Although Aitola *et al* reported that CNT-based films can be used as both conductive and catalytic layer, the fill factor of their DSSC is only 21.2% under one sun light due to

poor catalytic activity [241]. In another paper, a higher fill factor was achieved using vertically aligned N-doped CNT [242], but FTO is still required as the working electrode due to its excellent light transparency.

Figure 8-1 Schematic of (a) DSSC with TiO_x -modified-CNTs as the working electrode and bilayer CNTs as the counter electrode, in which the recombination at the working electrode is inhibited by TiO_x layer while the charge transfer kinetics at the working electrode is accelerated by carbon black (b) the energetic diagram of the individual components used in the cell.

Therefore, it came to our attention that the dramatically-reduced cost and the high stability of DSSCs could be achieved if FTO/ITO and Pt in DSSCs are replaced by all carbon electrodes. In addition, carbon-based electrodes have other advantages over

conventional FTO/ITO electrodes such as the abundance of material source, potentially scalable fabrication from solution process, non-brittleness, chemical stability, and optical transparency in the near infra-red region, as discussed in the chapter 7. However, in practice, the liquid-type DSSCs with all carbon electrodes face two problems: (1) CNT and graphene show very good conductivity but their catalytic activity is much worse than lower-conductivity carbon black in use as a counter electrode; and (2) the recombination is inevitable if they are used as bare working electrodes (this issue was discussed in chapter 7). By addressing these two problems, we here reported a significant improvement in the replacement of all DSSC's electrodes with carbon-based materials. In our FTO/ITO and Pt-free DSSCs, transparent conductive CNT films, which are modified with titanium-sub-oxide (TiO_x) for suppressing the charge transfer kinetics, are used as the working electrode, and the CNT films with thick carbon black layers are used as the counter electrode to increase both conductivity and catalytic activity, as illustrated in Fig. 8-1.

8.2 Experimental

The preparation of transparent conductive CNT films and TiO_x -modified CNT films for working electrode is the same as described in the chapter 7. As the optical transparency of the counter electrode is not critical, the CNT film of the counter electrode, however, was made thicker than that of working electrode to obtain a lower sheet resistance ($\sim 90\Omega/\square$). The carbon black layers for the counter electrode were simply collected from a candle light. N-doped CNT for the comparison of catalytic activity was obtained from Prof. Hu Zheng group in Nanjing University, China. The fabrication of DSSCs, the photovoltaic measurement and the electrochemical test were also carried out

using the same methods described in the chapter 7. Raman spectra were collected using a WiTec confocal Raman system equipped with 488 excitation laser source. The photograph of DSSC with all carbon electrodes is shown in Fig. 8-2.

Figure 8-2 The photograph of DSSC with all carbon electrodes

8.3 Results and Discussion

Prior to the fabrication of DSSC with all carbon electrodes, we separately made two DSSCs with one-side carbon electrode, respectively. First, DSSC with carbon-based counter electrode was fabricated using FTO as a working electrode and conductive CNT film with sheet resistance of $90 \Omega/\square$ as a counter electrode since the optical transmittance is not important for the counter electrode. Despite good conductivity, the conductive CNT film does not show strong catalytic activity, which was evaluated with charge-transfer resistance (R_{CT}) at electrode/electrolyte interface, using electrochemical impedance

spectroscopy (EIS). R_{CT} was calculated by fitting the Nyquist plot of a three-electrode system in an electrolyte containing 0.05M I_2 and 0.5M LiI in aqueous solution (Fig. 8-3 (a)). The Nyquist plot was fitted with the equivalent circuit model (inset Fig. 8-3(a)) which consists of R_{CT} in series with the Nernst diffusion impedance (Z_N) and in parallel with a double layer capacitance C . All of the above are in series with the series resistance (R_s). R_{CT} of conductive CNT electrode is $311.4 \Omega \cdot \text{cm}^2$, which is very large compared to that of Pt-coated-FTO electrode ($15.57 \Omega \cdot \text{cm}^2$). R_{CT} represents the resistance for electron transfer kinetic between the electrode and redox species in the electrolyte. Thus, a larger R_{CT} implies less electrons transfer from the electrode to the electrolyte and a poor catalytic activity of the electrode. It was reported that when CNTs are doped with electron-rich nitrogen, their catalytic activity increases due to the formation of metallic CNTs through band gap reduction [242]. We also found marginal improvement in catalytic activity of nitrogen-doped-CNT electrode, whose R_{CT} is about $271.8 \Omega \cdot \text{cm}^2$. A substantial increase in catalytic activity was observed when thick carbon black (10 μm) was added on the conductive CNT film (we shall call this combination as bilayer CNT). R_{CT} of the bilayer CNT electrode significantly reduces to $54.36 \Omega \cdot \text{cm}^2$, which is comparable to that of Pt-coated-FTO electrode.

The Raman spectroscopy was also performed to characterize the CNT film and carbon black. In the Raman spectrum, the G-band which is observed around 1580 cm^{-1} is a characteristic feature of the graphitic layers and corresponds to the vibrations of sp^2 carbon atoms. In CNT, this band transforms into two bands as a result of the confinement of wave-vectors along the circumference. The lower frequency component (G^-) is

Figure 8-3 (a) The Nyquist plots of a three-electrode system with various electrodes of interest (CNT, Bilayer CNT and Pt). Inset (left) shows the experimental setup of three-electrode system.

Ag/Ag(Cl) and Pt wire were used as a reference and counter electrode respectively in the system. Inset (right) shows the equivalent circuit used in fitting data. Solid lines represent the fitted curves. (b) The Raman spectroscopy of CNT and carbon black films. Inset is the detail spectroscopy of a typical carbon black film. (c) SEM image of a typical carbon black film.

associated with vibrations along the circumferential direction and the higher frequency component (G^+) is attributed to vibrations along the direction of the nanotube axis. The D-band, which is usually located between 1330 and 1360 cm^{-1} , involves scattering from a defect which breaks the basic symmetry of the graphene sheet. It is observed in sp^2 carbon containing porous, impurities or other symmetry-breaking defects. Thus, the comparison of the ratios of the two peak intensities of these two bands gives a measurement of the amount of defect densities or impurities on the carbon materials [243-244]. A low G/D ratio indicates high defect density or impurity of the material whereas a high G/D ratio represents low defect and high purity. The Raman spectroscopy study showed that the as-prepared CNT films have a good quality with high G/D ratio (>20) (Fig. 8-3(b)). On the other hand, carbon black films have very high resistance and low G/D ratio, which might be due to the presence of defects in carbon black. Because the active sites for catalysis in carbon materials are located at the crystal edges, carbon black with defects which create additional edges is probably more active than highly orientated CNT [236]. In addition, the thick layer with porous morphology may create additional active sites due to the large surface area (Fig. 8-3(c)).

Figure 8-4 J - V characteristics of DSSCs with carbon-based counter electrode and standard cell.

The current density-voltage (J - V) characteristics of DSSCs with carbon-based counter electrodes and standard cell under illumination of AM1.5G simulated solar light (100 mW/cm^2) are shown in Fig. 8-4. The electrical parameters of these DSSCs are listed in Table 8-1. For simplicity, we shall denote the name of DSSCs according to the electrodes used in the cell. For example, FTO/Pt cell stands for the DSSC with FTO working electrode and Pt counter electrode. The J_{sc} and V_{oc} of FTO/CNT and FTO/bilayer CNT are not too different while the fill factor increases substantially from 30% to 54% when CNT film is replaced by bilayer CNT film. The electron transfer kinetics between bilayer CNTs and electrolyte is fast enough to reduce triiodide (I_3^-) in electrolyte. This fast process prevents the undesirable recombination between the collected electrons at the working electrode and I_3^- anions from electrolyte and hence FF increases. The FF of CNT/bilayer CNT cell, however, is still lower than that of FTO/Pt cell (65%). From J - V curve, the shunt resistances (R_{sh}) [dV/dI at $V = 0$] of FTO/bilayer CNT cell and FTO/Pt cell are similar but the series resistance (R_s) [dV/dI at $I = 0$] of FTO/bilayer CNT cell is

larger than that of FTO/Pt cell. This suggests that lower FF of FTO/bilayer CNT is mainly caused by large R_s of the cell due to the larger sheet resistance of bilayer CNT film compared to Pt-coated-FTO film ($15 \Omega/\square$), rather than catalytic activity.

Cell	J_{sc} [mA/cm ²]	V_{oc} [V]	FF [%]	PCE [%]
FTO/Pt	9.186	0.708	65	4.22
FTO/CNT	7.835	0.684	30	1.63
FTO/bilayer CNT	8.037	0.688	54	2.98
CNT/Pt	0.281	0.057	23	0.001
TiO _x -modified-CNT/Pt	6.221	0.613	45	1.70
TiO _x -modified-CNT/CNT	5.534	0.599	25	0.84
TiO _x -modified-CNT/bilayer CNT	6.164	0.607	37	1.37

Table 8-1 The electrical parameters of DSSCs with various electrodes

A kink in the J - V curve is observed in FTO/CNT device. It was reported that the kink in the J - V curve close to open circuit voltage occurs in molecular photovoltaic devices when large interfacial energy steps are present at the electrode(s) (> 0.4 eV) or carrier mobilities are low [245]. However, the work-function of CNT (4.7 eV) is very close to redox potential of electrolyte (4.85 eV) and there is almost no energy step. Low mobility is also not responsible for the kink in this case because the hole mobility in DSSC is determined by the diffusion of redox species and the same electrolyte was used in all devices. In a separate literature reported by other group, a kink in J - V curve in DSSC was also observed when thin layer of multi-wall CNT was used as a counter electrode whereas the kink disappeared when thick layer of CNT was used. Thus, we

suggest that the kink is related to the electron transfer kinetic between the electrolyte and the counter electrode in this particular case. When the electron transfer kinetic is slow, insufficient amount of electrons are supplied from the counter electrode for the reduction of I_3^- ions. Thus, there is a higher chance of recombination of electrons at the working electrode with I_3^- ions, resulting in a s-shape in the J - V curve and low FF.

Figure 8-5 J - V characteristics of DSSCs with carbon working electrode and DSSCs with all carbon electrodes

The DSSCs with carbon-based working electrode has already been discussed in chapter 7 and will not be elaborated here. After verifying the feasibility of DSSCs with one-side carbon electrode, we fabricated DSSCs with all carbon electrodes. The PCE of TiO_x -modified-CNT/CNT cell is 0.84% and could be improved to 1.37% in TiO_x -modified-CNT/bilayer CNT cell due to stronger catalytic activity of bilayer CNT counter electrode. Compared to the TiO_x -modified-CNT/Pt cell (one side carbon electrode), the

TiO_x-modified-CNT/bilayer CNT cell (all carbon electrodes) gives similar J_{sc} and V_{oc} . Only the FF drops to 37% because the CNT film, which is less conductive compared to FTO, loads the additional series resistance on the cell. This can be clearly seen by comparing the J - V curves of the TiO_x-modified-CNT/Pt cell and the TiO_x-modified-CNT/bilayer CNT cell (Fig. 8-5).

Certainly, this is an initial attempt towards the direction of DSSCs with all carbon-based electrodes. Although the efficiency of the current cell with all carbon electrodes is still somewhat lower than that of our standard DSSC with FTO working electrode and Pt counter electrode (the efficiency is 4.22%), we still have enough room to enhance it. As mentioned above, low transmittance of CNT film reduces the photocurrent, leading to a lower J_{sc} . Moreover, we also observed the reduction in V_{oc} when FTO is replaced with the carbon-based working electrode. Generally, the V_{oc} of DSSC is logarithmically inversely proportional to the kinetic constant of the recombination of the collected electrons at the electrode with I₃⁻ anions [94, 207]. Therefore, some electrons are lost at CNTs/electrolyte interface although mass recombination is suppressed by TiO_x. Low conductivity of CNT film also incurs additional series resistance in the cell and hence lowers FF. All these problems will be addressed in our future research and the enhanced properties is anticipated. For instance, incorporation of CNT film on the top of a metal grid will reduce the sheet resistance considerably without much sacrificing the optical transmittance, yielding a larger FF.

8.3 Conclusion

In conclusion, we demonstrated that carbon-based materials can be used as both working and counter electrodes in DSSC to eliminate expensive conventional electrodes completely. The conductive CNT film is modified with ultra-thin TiO_x at the working electrode to slow down the electron-transfer kinetics while thick carbon black is added on conductive CNT film at the counter electrode to increase the catalytic activity. These implementations make all-carbon-electrode-DSSCs feasible with reasonable efficiency. To our best knowledge, this is the first demonstration of DSSCs with all carbon electrodes. The efficiency is mainly limited by the low conductivity and transmittance of CNT films. With further optimization in the conductivity and transmittance of CNT films, DSSCs with all carbon electrodes can make the leap to emergence of truly cost-effective and flexible DSSCs.

Chapter 9 Conclusions and Future outlook

9.1 Conclusions

The role of solar cells for energy harvesting is more and more important in 21st century due to increasing energy demand, depletion of oil and climate change issues. Driven by the demand for inexpensive solar cell with moderate efficiency, the interest in using XSCs is growing as a result of their potential low cost, ease of processing, and compatibility with flexible substrates. In this thesis, we have proposed alternative design of XSCs with new combination of materials for the improvement in efficiency, stability and cost-effectiveness, and also demonstrated the feasibility of our design concept. First of all, the efficient charge collection of electrons from polymer:fullerene bulk-heterojunction was demonstrated with sol-gel derived ZnO film. This observation is an initial step towards fabrication of highly efficient inverted structure OSC which has advantage in device stability in air. Based on that concept, we developed air-stable inverted structure OSC using sol-gel derived ZnO as an electron selective layer and thermal-evaporated MoO₃ as a hole selective layer. The hole-selective MoO₃ layer renders higher efficiency due to the exciton blocking property. We also demonstrated that the efficiency of inverted OSC is improved by replacing ZnO with appropriately doped IZO as an electron selective layer. It was observed that J_{sc} of inverted OSC is enhanced by IZO due to low resistivity and low work-function which improves charge collection process, and high transmittance that promotes light harvesting in active layer. A decrease in work function of buffer layer resulting from doping is beneficial to the charge collection yet has

slight negative impact on V_{oc} and FF due to electron injection barrier lowering. An electron selective buffer layer controls the tradeoff between J_{sc} and V_{oc} & FF , which can be compromised by manipulating doping level, in other word, the energy level and conductivity of the buffer layer. The inverted OSC using 1 at.% indium doped ZnO electron selective buffer layer and MoO_3 buffer layer has yielded the maximum power conversion efficiency of 3.3%.

In the rest of the thesis, we reported our designs of DSSCs to replace traditional TCOs which are expensive and scarce for large-scale production of solar cells. We developed top-illuminated structure DSSC in which bottom FTO electrode is replaced with metal substrate and top FTO electrode is replaced with GZO electrode. Despite lower J_{sc} due to partial loss of light in electrolyte, this design gives higher FF due to lower series resistance from formation of ohmic contact if low work-function metal like Ti is used as electrode. We also examined various metals for this structure. Ti is an appropriate metal because of minimum catalytic activity on redox reaction and high resistance to corrosion. We also developed DSSC with transparent and conductive CNT as working electrode. However, the efficiency of DSSC with bare CNT working electrode is extremely small because the collected electrons at the working electrode recombine with triiodide in electrolyte through the redox reaction. To circumvent this problem, we proposed and employed a facile method for surface modification with TiO_x layer, suppressing electron-transfer kinetics at the CNT/electrolyte interface while maintaining the electrical and optical properties of the working electrode made of CNTs. As a result, the power conversion efficiency of 1.8% has been realized using CNT as counter electrode. Because

CNT and other carbon materials possess catalytic property, finally, we fabricated DSSC with all-carbon-electrodes to completely eliminate traditional TCOs.

9.2 Future outlook

9.2.1 Inverted structure OSC

It has been shown that the stability of OSC can be improved by inverted structure without additional encapsulation. Many efforts have been attempted so far to understand the charge carrier extraction behavior in inverted structure and to improve efficiency by employing various interfacial layers between organic active layer and electrodes. It was speculated that the spontaneous vertical phase separation of the BHJ blend results in a donor-enriched top surface and an acceptor-enriched bottom contact, which accounts for the enhancement of the charge collection efficiency [141]. Therefore, manipulating the orientation of vertical segregation in acceptor-donor blend is an alternative promising technique to further improve the efficiency of inverted cell. The segregation in the blend can be manipulated by the careful control of driving forces such as entropic and enthalpic forces [246], crystallization [247], and surface energy of the materials [248]. Utilizing surface energy as a driving force, Wei et al. reported self-organized buffer layers for conventional OSCs, in which a small amount of PCBM with a fluorocarbon chain (F-PCBM) is mixed in P3HT:PCBM solution. Owing to the low surface energy of fluorocarbon, F-PCBM spontaneously migrates to the surface of organic layer during spin-coating, forming a monolayer of F-PCBM on the surface, which serves as a buffer

layer for the electron extraction. This self-organized F-PCBM layer also creates a dipole moment pointing away from top Al electrode, which further reduces the work function of Al top electrode, resulting in an increase in FF and J_{sc} . Mimicking this approach and adopting the technologies for the segregation of the blend materials, the manipulation of segregation of BHJ blend to obtain a donor-enriched top surface and an acceptor-enriched bottom contact is achievable, leading to further efficiency improvement of inverted cells.

Moreover, incorporating nanostructure metal oxides as the buffer layer can further increase efficiency owing to the additional heterojunctions between nanostructure and donor. However, it has to overcome the charge carrier recombination at the surface of metal oxides via charge trapping sites created by hydroxyl groups, leading to low contribution to the final photocurrent. Therefore, the passivation of trap states on the surface of nanostructure by self-assembly monolayer (SAM) or other methods will enhance the performance of such inverted cell. Through manipulating the segregation in BHJ blend, and incorporating passivated nanostructure metal oxide, inverted OSCs with better air-stability and higher efficiency could be achieved.

9.2.2 DSSC

Without considering dye loading and molar extinction coefficient of dye, a simple way to increase photocurrent in DSSC is to extend the absorption spectrum as much as possible, i.e. to absorb the photons in near infra red region. The optical gap of ruthenium dye which gives the highest efficiency is 1.8 eV, limiting the photoresponse of the cell to

~ 700 nm. Hagfeldt and Grätzel suggested that the photocurrent close to 920 nm absorption threshold would increase the J_{sc} from currently 20.5 mA/cm² to about 28 mA/cm², leading to overall efficiency to over 15% [249]. Thus, from molecular engineering perspective, the optical gap of sensitizer must be narrow down by either lower the energy level of LUMO or raise the energy level of HOMO to increase J_{sc} . As the entire donor distribution function must lie above the conduction band edge of semiconductor, the lowering the LUMO of dye to extend the light absorption will be limited by the efficient charge injection from dye to semiconductor. Fortunately, the ultra fast charge injection rate (femosecond range) and slow excited-state decay time (nanosecond range) would seem to have enough room for lowering the LUMO of dye before injection efficiency are considerably deteriorated. The raising the HOMO of dye, an alternative route to increase J_{sc} , is limited by the minimum potential difference between the redox potential and HOMO of dye necessary for efficient dye regeneration. This potential difference is approximately 550mV in a current typical DSSC and there is much room for improvement.

The V_{oc} is another major component that can boost the efficiency of DSSC. It was proposed that even a relatively small increment of 200mV in V_{oc} would allow the overall solar conversion yield to be raised from currently 10-11% to nearly 15%.[249]. The V_{oc} is determined by the difference between the redox potential of electrolyte and the quasi-Fermi level of semiconductor. Thus, raising the quasi-Fermi level of semiconductor or lowering the redox potential is a possible route to increase the V_{oc} . Theoretically, an approximately 200mV can be increased if we can lift up the quasi-Fermi level close to maximum level, i.e. the conduction band of semiconductor. Unfortunately, it is unlikely to

raise the quasi-Fermi level to the conduction band of semiconductor because according to previous studies, an order of magnitude increase in injection rate or reduction in recombination is required to just increase 60mV.[94-95] Thus, more feasible way to increase V_{oc} is to lower down the redox potential of electrolyte. Similar to the J_{sc} case, the lowering the redox potential is limited by the minimum potential difference between the redox potential and HOMO of dye necessary for efficient dye regeneration.

Based on this discussion, we can increase the efficiency of current DSSC by either: (1) raising the HOMO level of dye or (2) lowering the redox potential or (3) simultaneous action of (1) and (2). Assuming that the minimum overpotential of 200mV is necessary between the HOMO of dye and redox potential to ensure efficient dye regeneration, Hamann et al. estimated the possible efficiencies of DSSCs by shifting the HOMO level of dye and redox potential in various combinations [250]. Efficiencies beyond 16% are reasonably attainable with various combinations of dyes and redox couple, modified according to the above methods.

Increasing the surface area of semiconductor (dye loading) and molar extinction coefficient of dye are another two aspects to increase J_{sc} . Upon intensive investigations of various morphologies of TiO_2 and ZnO photoelectrode, TiO_2 nanocrystalline film seems to be the best optimization between surface area and charge collection. The molar extinction coefficient can be increased with organic dye but suffers in spectral response. Thus, an alternative route to boost the efficiency is tandem cell or dye cosensitization concept. Tandem cell or cosensitization with high-molar-extinction-multi-dyes allows for the extension of absorption spectrum as well as increase in light absorption. The

development of new materials or modifying the existing materials to fulfill the energetics as outlined above and constructing tandem cell or cosensitization of multi-dyes with complimentary absorption spectrum will lead to DSSC with efficiency exceeding 15%.

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List of publications

Book Chapter

1. A. K. K. Kyaw, M. F. Yang and X. W. Sun (2011) “Solar Cell as an Energy Harvesting Device”, a book chapter in “Electrochemical Technologies for Energy Storage and Conversion”, Edited by Lei Zhang, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany. DOI: 10.1002/9783527639496.ch11
2. D. W. Zhao, A. K. K. Kyaw and X. W. Sun (2011) “Organic Solar Cell with Inverted and Tandem Structures”, a book chapter in “Energy Efficiency and Renewable energy through Nanotechnology”, Edited by Ling Zang, Springer London. DOI: 10.1007/978-0-85729-638-2_3

Journal

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Conference/Workshop

1. Photonics Global Conference 2010, Singapore, 2010, oral presentation: *Effect of post-annealing hydrothermal-grown ZnO nanorods on the electrical parameters of dye-sensitized solar cells*
2. The Complex Interaction & Mechanisms in Organic Photovoltaics (CIMOPV) workshop, Brisbane (Australia), 2010, oral presentation: *Interfacial modification of cathode for an efficient inverted organic solar cell*