MAGNETIC NANOPARTICLES AND MAGNETIC EFFECTS INDUCED NOVEL ANODE BUFFER LAYER FOR POLYMER SOLAR CELLS

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ABSTRACT

Polymer Solar Cells (PSCs) have been attracting great attention in recent years due to their advantages such as flexibility, low cost, light weight, large area, clean, and processing simplicity, which make it possible to substitute its inorganic counterparts in order to finally circumvent the energy issues. Especially the low-cost fabrication and prospect for large-scale roll-2-roll production make it a promising candidate in the energy market. Even though PSCs with power conversion efficiency (PCE) over 12% has been achieved by tandem solar cell in 2013 and over 10% has been realized in single cell from our group in 2014, there still room for PSCs to further obtain higher PCE by designing and synthesizing novel materials in PSCs and optimizing premium device architectures.

In this thesis, we firstly overview the development of inverted PSCs which are described in Chapter I. In Chapter II, we address the stability issues for PSCs by applying \( \text{Fe}_3\text{O}_4 \) magnetic nanoparticles (MNPs) as the hole extraction layer (HEL). And an external magnetostatic field (MF) was further introduced as an experimental condition to see its influence on device performance. Consequently, enhanced stability and compatible PCE have been realized compared with the PSCs using poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) as anode buffer layer. However, the PCE of PSCs using this pure MNPs HEL is not satisfying. To further improve the device performance, we report in Chapter III a facial approach to realize both high efficiency and good stability of PSCs.
By using a thin film fabricated from the solution of PEDOT:PSS doped with Fe$_3$O$_4$ magnetic nanoparticles ((PEDOT:PSS):Fe$_3$O$_4$), and (PEDOT:PSS):Fe$_3$O$_4$ thin film aligned by an external magnetostatic field as an anode buffer layer, respectively, both enhanced efficiency and improved stability of polymer solar cells are observed. These achievements resulted from a combination of reduced acidity of PEDOT:PSS, enhanced electrical conductivity originated from generated counter ions and the paramagnetism of Fe$_3$O$_4$ magnetic nanoparticles by an external magnetostatic field. Our results certainly inspired a new approach towards the low-cost manufacturing polymer (organic) solar cells with both high efficiency and good stability. In Chapter IV, we conclude that by using MNPs into the anode buffer layer, both enhanced stability and device performance can be obtained. However, the complicated mechanism in the active layer is still unintelligible and the energy loss in recombination inside photovoltaic processing in the active layer still remains large. To further understand the operation mechanisms in PSCs, MNPs and external magnetostatic field is a good tool to unraveling the enigma.
PUBLICATIONS


7. Xiong Gong, Kai Wang and Chang Liu, provisional patent application for UA 1119, “Solution-Processed Perovskite Based Organic Inorganic Hybrid Photodetectors”. This application was filed 3/12/2014 and was assigned the following serial number by the USPTO: 61/951,567.

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CHAPTER I

INVERTED POLYMER SOLAR CELLS

1.1 Energy Source

Being the power source metric of all human civilization, the World Energy Consumption (WEC) has deep implications for humanity's social-economic-political sphere. Especially driven by strong economic growth, expanding global populations in recent decades, accompanied by rising living standards in developing countries such as China and India as well as energy demand in the fields of heavy industry and military, available energy supplies have been placed a huge strain. [1] Moreover, in the IEO2013 Reference case, based on historical values, the world energy consumption projection in future indicates an increase from 524 quadrillion Btu in 2010 to 630 quadrillion Btu in 2020 and 820 quadrillion Btu in 2040, a 30-year increase of 56 percent.[1] Although currently, worldwide consumption of existing petroleum and coal, which are the major sources for energy demand (fossil 81%) can balance the energy demand today, their short-term unrenewable nature and dismal environmental image (combustion of fossil will produce carbon dioxide and poisonous gas such as sulphur dioxide, contributing to “greenhouse effect” and acid rain respectively) turn down their sustainable application in the future.
To hedge against the eminent risk of global warming that could have disruptive effects on biological diversity, climate and world economies and to meet sustainable world energy demands in tomorrow, finding a novel e-friendly and renewable energy source is the most comprehensive insurance for long-term development of human civilization.

1.2 Solar Energy & Solar Cells

No doubt, direct solar energy is the world's greatest energy resource, delivering approximately $1.7 \times 10^{17}$ W upon the earth.\[^2\] While, the world’s total energy consumption in 2010 was around $5.6 \times 10^{20}$ J,\[^3\] which means that the solar energy hitting the earth in about one hour is sufficient to cover all the energy required for the humanity for a whole year. Mathematically, solar cells with efficiency of 10% covering 0.16% of Earth’s land would produce 20 Terawatts of energy about twice of that from fossil fuel consumption including numerous nuclear fission reactors,\[^4\] which have been labeled with unnecessarily radiation panic due to some historical tragedies such as Chernoby-nuclear-leak and recently Fukushima incident. However, the harness of solar energy today is still very low mainly due to the contradictory relationship between costs and power conversion efficiency. The commercially available inorganic silicon-based photovoltaic (PV) solar cells (85% market share) are still relatively expensive due to their highly demanding manufacture processing although the highest power conversion efficiency of inorganic solar cells can be reached as high as 43.5%. Alternatively, organic conjugated semi-conductors have shown their outstanding potential in cost-effective manufacturing due to their unique properties compared with their inorganic counterparts:

- Widely available compared with rare semiconductor materials;
• Low temperature solution-processable;
• Potential to be manufactured in continuous printing processings and large area coating techniques of roll-to-roll and packaged by lamination techniques;
• Easy integration in different devices;
• Environmentally friendly.

To be further commercialized, according to the module technology, costs regarding to the glass substrates, inverter (actually directly proportional to the power) and installation, among others\textsuperscript{[5]} should be considered. In conclusion, three key factors—efficiency, lifetime and costs (per $W_p$)—determine the competitive position of any solar cells in the energy market. Figure 1.1 demonstrates a critical triangle that summarizes the restrictions within which organic photovoltaics (OPVs) can be commercialized.\textsuperscript{[6]} Successful commercialization can be realized only if all three technology driving aspects are fulfilled at the same time, otherwise only niche markets can be addressed.


1.3 Device Structures for Polymer Solar Cells

For polymer solar cells, there are several types of device structures, in this context we only address on the conventional single junction polymer solar cells and inverted PSCs.

1.3.1 Conventional device structure

Since the concept of bulk heterojunction (BHJ) polymer solar cells (PSCs) with a conventional device structure as shown in Figure 1.2a was discovered in the University of California Santa Barbara in 1994[7], the power conversion efficiency (PCE) of BHJ polymer solar cells (PSCs) has been optimized up to 10.2% with a single active layer structure.[8] In a general conventional single structure PSCs, a bi-continuous interpenetrating composite is sandwiched between a low work function metal electrode (Al, Ca/Al) and a poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) coated transparent conducting metal oxide (Indium-Tin Oxide(ITO),

![Figure 1.2](image-url)

Figure. 1. 2 (a) Conventional and (b) inverted device structures for polymer PSCs. Fluorine doped Tin Oxide (FTO)) anode. However, the high vacuum evaporation of top metal electrodes makes the fabrication difficult to roll-to-roll processing in large scale and charge for extra energy consumption due to the vacuum thermal deposition. And
micropores are generally introduced within the ~100 aluminium electrode layer, allowing for both oxygen and moisture to diffuse though it and react with the underlying polymers, thus lowering the device performance.\[9,10\] On the other hand, the commonly used anode ITO can be etched over time upon directly exposure to the acidic PEDOT:PSS buffer layer (pH~1), especially at elevated temperature.\[11-14\] Furthermore, generally spin-coated PEDOT:PSS layer exhibit large microstructural and electrical inhomogeneities, including order-of-magnitude variations in morphological and electrical conductive gradient, especially from the region near surface to that in bulk.\[15\] Therefore, all of these considerations raise the question of whether an equivalent, transparent, nonacidic hole-transporting organic photovoltaic anode interfacial layer could be developed to replace the PEDOT:PSS to revolutionize the current device stability without sacrificing PCE or prices. The most representative example is a blend of 4,4'-bis [(p-trichlorosilylpropylphenyl) phenylamino]-biphenyl: poly[9,9-dioctylfluorene-co-N-[4-(3-methylpropyl)]-diphenylamine] (TPDSi₂:TFB). However, the high resistance nature makes it still inferior to PEDOT:PSS.\[16\] In fact, replacing the PEDOT:PSS layer with other hole-transporting layers (HTL) have been unsuccessful in maintaining high PCE so far.

Nonetheless still withal, an alternative solution is to eliminate such HTL at the ITO interface by totally revising the structure upside down. In addition, the reversed polarity of charge collection in inverted structure compared with conventional architecture allow the use of a more ambient stable and higher work function metal (Au, Ag, Cu) as the top anode,\[17,18\] and make it possible to fabricate air stable polymer photovoltaics based on process free from vacuum steps.\[19\] Consequently, by applying an inverted device
structure, both the acidic PEDOT:PSS and low work function, air instable, fabrication complex (thermal vacuum deposition required) metal (Ca, Al) are removed, giving rise to stability enhancement and cost reduction. Therefore, if the last principle triangle corner (efficiency) is enhanced, there will be a huge commercialization potential for inverted polymer solar cells.

1.3.2 The inverted device structure

The nomination of “inverted” primarily attributes to the reversed change in polarity of PSC. Figure 1.2 presents the inverted device structure for PSCs. In the inverted device structure, the buffer-I is termed as the electron extraction or hole blocking layer (EEL/HBL) and the buffer-II is termed as the hole extraction or electron-blocking layer (HEL/EBL), respectively. In detail, when illuminated in the sun, (1) specific photons are absorbed by active layer (for example, P3HT:PCBM); (2) electrons almost from HOMO level of donor materials (P3HT) are excited to higher energy level, with thermalization of the primary excitation, singlet excitons are mostly formed within donor materials (P3HT); (3) these excitons diffuse to the interface between donor (P3HT) and acceptor (PCBM) materials within their life-times, otherwise intra-molecular recombination will happen; (4) at the interface, charge-transfer (CT) states are firstly formed in the exciton-dissociation process, then dissociated into electrons and holes due to the chemical potential gradient there; (5) then electrons and holes are drifted into opposite directions driven by an external electric field offered by the asymmetrical contacts (electrodes with different work functions); (6) due to the proper energy level alignment, electrons and holes are selectively collected at top electrode (Al) and bottom ITO. (in general case of conventional BHJ PSCs, which use PCBM as the prevalent acceptor with a LUMO level
of 3.91 eV for PC₆₀BM and 4.3 eV for PC₇₀BM and P3HT as the donor with a HOMO of 5.0 eV, to furthest facilitate the electrons transporting from PCBM to cathode and sufficiently impede holes transporting from P3HT to cathode, a relatively low work function metal should be introduced as the cathode.) However, in the totally polarity “inverted” architecture in Figure 1.2b, ITO electrode is typically coated by a wide band gap metal oxide whose conduction level is aligned to LUMO of the acceptor in the BHJ layer to collect electrons while the other electrode (anode) is chosen to have a higher work function, e.g., Ag to collect holes. Nevertheless, from the optical perspective, in both architectures described above, the photodiodes are illuminated from the transparent substrate in the bottom and the surplus light are re-absorbed by active layer after reflection from the metal electrode on top, which are diagrammed in Figure 1.3a and b.

1.3.3 Top-illuminated device structure

In comparison, a top-illuminated structure (shown in Figure 1.3c) has been developed by applying either a transparent conductive oxide or a thin metal or metal grid as the transparent top electrode, which means that the expensive ITO substrate can be replaced by the low-cost metal foil substrates or even plastic foils with opaque metal

![Figure 1.3](image-url)

Figure 1.3 Bottom-illuminated PSCs with (a) conventional device structure and (b) inverted structure and c) top-illuminated PSCs with an inverted device architecture.
coatings. Thus making it desirable to realize the PSCs integration with electronics such as image sensor arrays\textsuperscript{[21]} where the underlying electronics may reduce the luminous flux or be even opaque, e.g., a silicon IC or polysilicon on stainless steel.\textsuperscript{[22]} This architecture was firstly introduced by M. Glatthaar \textit{et. al.} by using a PSC device structure of: glass substrate/Al (80 nm)/Ti (20 nm)/photo active layer (150 nm)/PEDOT:PSS (250 nm)/Au-grid (50 nm),\textsuperscript{[23]} where the top-two-layer combination of highly transparent and conductive PEDOT:PSS (HTL) and thin Au-grid (anode) allow sufficient photons passing through to reach active layer and offer an ohmic contact between HOMO of P3HT and HTL to extract holes efficiently. And the thin titanium layer was inserted to prevent the formation of the highly insulating aluminum oxide at the surface of Al. An efficiency of (1.4 ± 0.3)% under AM 1.5 solar illumination was achieved by using such semi-transparent top electrode configuration with a BHJ composite of P3HT:PCBM in the year of 2005.

And in 2007, Takahito \textit{et. al.} fabricated a similar bi-layer organic solar cell using the concept of top light-harvesting with a structure of Si substrate/SiO\textsubscript{2} layer/cathode/organic layer/ semitransparent metal anode and a comparable PCE of 1.05% to that of conventional device.\textsuperscript{[24]} In addition, such top-illuminated inverted device was further rejuvenated to a superior mechanically flexible device with a higher PCE of \textit{ca.} 3% by Chen \textit{et al} in 2009. By applying a structure of stainless-steel (SS) foil/ photoresist/ SiO\textsubscript{x}/ Ag/ ITO/ Cs\textsubscript{2}CO\textsubscript{3}/ P3HT:PCBM/ MoO\textsubscript{3}/ Al counter electrode grid (10%)/ ITO, the flexible OPVs prepared on this SS substrates exhibited excellent mechanical flexibility and high air stability.\textsuperscript{[24]} Moreover, device engineering for highly efficient top-illuminated organic solar cells has been further developed recently. Particularly, optical
microresonant cavity system consisting of a photoactive layer sandwiched in two metallic electrodes, has received featured attention due to its low photon loss rate and functions of confining and storing optical energy in small volumes, thus making more photons captured by active layer. By coating a functional layer on a silver (Ag) electrode, not only the electrodes transmittance is improved but also electric field intensity in the photoactive layers was enhanced due to an induced microresonant cavity arising from fine-tuning-thickness of the capping layer.\textsuperscript{[25-28]}

As a result, PCE of 4.5\% was achieved by Hee-Tae Jung’s group using an architecture of PET/ Al/ PCDTBT:PCBM/ MoO\textsubscript{x}-Ag-MoO\textsubscript{x} (nanopatterned 3D microresonant cavity layer). And still applying the microcavity structures, Lin et. al. reported a similar top-illuminated small-molecule organic solar cells (SMOSCs) with PCEs exceeding 5\%.\textsuperscript{[29]}

Although all of these attempts disclosed a promising way to realize the top-illuminated OSCs with ITO-free architecture, their efficiencies were still inferior to their ITO-based counterparts. Meanwhile, other ideas of ITO-free OPVs have been developed recently, e.g. a top illuminated inverted organic photosensors with single layer graphene (SLG) electrodes were demonstrated by Michael L. Chabinyc’s group at UCSB.\textsuperscript{[30]}

In conclusion, the innovation of functional transparent electrodes, particularly the methodology of layered light-trapping or microresonant cavity, pushes the development of top-illuminated solar cell and (semi-) transparent polymer solar cells.\textsuperscript{[31]}

Representatively, PSCs using a semi-transparent Alloy/P3HT:PCBM/PEDOT: PSS/Ag structure with an efficiency of 2.6\% have been reported recently.\textsuperscript{[31]}
1.3.4 Bottom-illuminated device structure

In contrast to top-illuminated PSCs, its counterpart: bottom-illuminated structure shows a different device structure by changing the light coming direction from top to bottom. (Figure 1.3c) Specifically in bottom-illuminated inverted PSCs, a high work function (to match the HOMO of electron-donor materials, e.g. P3HT) metal is deposited or even printed on top of active layer to collect the holes from there, while a low work function material is used as the bottom electrode to effectively collect the electrons coming from the active layer and allow sufficient photons entering from the bottom to reach the active layer. Generally, the work function of the commonly used electrode ITO is -4.2 eV or even higher after oxygen-plasma treatment (-4.7eV), which is too high to from a barrierless ohmic contact with electron-acceptor, e.g. PC60BM (LUMO= -4.0 eV). And the sharp surface of ITO usually plays a negative role in forming premium morphology of the BHJ active layer, which essentially determines the device performance. Accordingly, a small electron affinity material is inserted between ITO and active layer to modify the sharp interface as well as effectively collect or extract the electrons from the donor material in active layer.

1.4 Electrode Buffer Layer

Typically in both conventional and inverted construction, interfacial layers serve a unique role in BHJ PSCs with the following main functions:\[32\]

1. photon transmission (e.g. PEDOT:PSS and some wide band-gap semiconductors)
2. charge injection (e.g. application in PLED)
3. “blocking” layers to filter specific charge carriers (e.g. inverted solar cells)

By inserting such the functionally interfacial layers between the active layer and the
electrodes, the device performance can be increased in different scales.\textsuperscript{[32]} Although various mechanisms were proposed for different cases, two dominating principles to clarify the PCE enhancement are that the interfacial layer can (a) reduce extraction barrier heights to increase photocurrent extraction and (b) act as “blocking” layers to reduce non-geminate recombination at the electrodes.

To realize such principles, in the inverted PSCs constructions, selection for the interfacial materials which are suitable energy band alignment with active layer materials become extremely important. Especially for commonly studied bottom-illuminated inverted PSCs, the bottom-layered electron transfer layer (ETL) should have (a) a suitable LUMO (lowest unoccupied molecular orbital) level same to or a little bit higher than that of PCBM (typical acceptor in BHJ) and electron extraction layer (EEL) should have (b) a relatively low HOMO (highest occupied molecular orbital) (much lower than that of donor materials in BHJ) to form a large Schottky contact to “block” hole transfer from the donor materials in BHJ. (c) Moreover, to ensure light pass through such ETL or EEL to reach the active layer, a large band gap and small thickness of the film should be addressed here. Also, (d) the electron mobility of the ETL should be high enough to transfer the electron efficiently and (e) the material stability should also be considered to maintain the device lifetime. On the other hand, to improve the charge selectivity and collection of holes, specific materials including various transition metal oxides (MoO\textsubscript{3}, WO\textsubscript{3}, V\textsubscript{2}O\textsubscript{5}) and solution processed conducting polymers (PEDOT:PSS, SPDPA) have been introduced as hole transporting or electron blocking layers or both.
1.4.1 Electron transfer/extraction layer

ETL and HTL were firstly introduced in OLEDs (organic light emitting diodes) to balance the charge carrier injection. And by applying such layers into other OPVs such as organic thin film transistors (OTFTs)\(^{[33]}\) and PSCs, device performance can be improved largely. Typically in PSCs, solution-processed transition metal oxide interfacial layer offer an additional opportunity to further decrease the fabrication price. By modifying the electrical and optical properties at the interface, enhanced device performance are expected for the device with such interfacial layers.

1.4.1.1 Transition metal oxides

For transition metal oxides used in PSCs, there are several types of utilization. And for the cathode buffer layer in inverted PSCs, two representatives are demonstrated below.

**ZnO**

ZnO is one of the transition metal oxides with suitable energy level as EEL, good transparency in whole visible region and good electron mobility,\(^{[34-36]}\) indicating a good choice for electron buffer layer in inverted PSCs. Together with TiO\(_2\), ZnO is claimed as n-type transition metal oxides (TMOs) to transfer electrons more efficiently. While TiO\(_2\) is widely applied in DSSC to collect the electrons excited from organic dyes and transfer them to electrode to be collected. The energy levels of these metal oxides have been reported around -4.4 eV and -7.6 eV for LUMO and HOMO, respectively. And the LUMO of typical acceptor PC\(_{71}\)BM is about -4.3 eV and typical HOMO for donor materials is around -5.0 eV, indicating that these materials can be a good electron selective layer and hole blocking layer in BHJ PSCs. Tomoki Shirakawa and Katsumi
Yoshino *et al.*, reported a sputter-deposited ZnO thin film (50-100 nm) as the ETL in the bi-layer structured photovoltaic cell. By using the structure of ITO/ZnO/C$_{60}$/PAT6/Au, a monochromic EQE of over 70% at the peak wavelength and a power conversion efficiency of 1.0% was obtained. To simplify the fabrication processing, White *et al* demonstrated a non-vacuum, solution processed thin ZnO film, which was inserted between the ITO and active layer (to extract electrons from the device). The corresponding PSCs with a ITO/ ZnO/ P3HT:PCBM/ Ag structure shows a equivalent performance with an enhanced $J_{SC}$ but alleviated $FF$ and a same $V_{OC}$. High quantum efficiency obtained in such devices imply that the electron mobility of the solution-cast ZnO layer is sufficiently large that electrons can be transferred fast from PCBM to ZnO.
to ITO and no electron buildup occur at the interface. Kelvin probe measurements show that the ZnO layer in air yielded a work function of -4.3 eV, closing to the conduction band at ~ -4.1 eV, indicating an inherently n-type characteristics. And a diode rectification in the dark of order of $10^5$ at ± 1.5V, showing such ZnO film is efficient to block holes.

Although initially realizing the solution-processed ZnO EEL in PSCs, White et al. still claimed the small grains in ZnO thin film evident in XRD (x-ray diffraction) spectra and AFM (atomic force microscopy) images may decrease the mobility in bulk. To further investigate the electron properties of ZnO thin film prepared in this sol-gel method, we fabricated the ~40 nm ZnO thin film by spin-coated a precursor solution (Zinc acetate and ethanolamine in the solution of 2-methoxyethanol with a concentration of 0.5 molL$^{-1}$) followed by 200°C annealing for 20 min. Then the ZnO thin films were ultrasonicated in isopropyl alcohol and subsequently dried in oven over four hours. Absorption spectra show a transparent characteristic from 400 nm to 1000 nm, indicating a prospective application in transparent OPVs. And the absorption is in good agreement with the large optical band gap of -3.19 eV. The morphological characterization shows that the ZnO thin film is quite uniform with nanoscale fibrils with a diameter of ~10 nm. Moreover, to explore the electric properties, we fabricated ZnO filed-effect transistors (FETs) to see the electron transporting properties. From the $I_{ds}$-$V_g$ curves in Figure 1.5, the electron mobility in the saturation regime was found to be $4.46 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$, which is compatible to the electron mobility from most of organic materials used as the ETL in organic electronics. Consequently, PCEs of 3.8% was observed from inverted PSCs with a device structure of ITO/ZnO/PSiF-DBT:PCBM/ MoO$_3$/Au.
In addition, to achieve a conformal and pinhole-free film, methods such as manipulating the concentration of sol have been developed.\cite{37} A concentration of 0.5 and 0.3 M can produce a conformal and closely packed films, while increase the concentration to 0.75 M, the produced ZnO film will show loosely packed colloids, causing polymer layer directly contacting with ITO and leading to a short-circuits in the device. Furthermore, conformal and pinhole-free film can also be achieved using layer-by-layer-deposition at atomic scale by introducing reactant gas into the reaction zone separately and sequentially at low temperature.\cite{38}
Regarding to the device performance, for P3HT:PCBM system, Hau et. al reported a PCE of 3.61% by using a structure of ITO-glass/ZnO sol-gel/ P3HT:PCBM/ PEDOT:PSS/ Ag and by changing the glass substrate into a flexible plastic substrate, the performance can also get 3.58%. On the other hand, all of the devices using inverted structure with ZnO as ETL or EEL show a much better stability compare with PEDOT:PSS based conventional structures.

**TiO\textsubscript{x}**

Another transition metal oxide TiO\textsubscript{x} is also a good alternative of interfacial layer in an inverted structure since its conduction band (-4.4 eV) is well matched with LUMO level of PCBM (-4.3 eV) and its valence band (-7.5 eV) is sufficiently low enough to effectively block the revised holes. Various methods have been demonstrated to prepare TiO\textsubscript{x} thin films such as atomic layer deposition (ALD) and traditional chemical processing. However, the time-consuming and high-cost nature of ALD procedure severely restricts such method in large-scale production. While for chemical processing, the preparation of TiO\textsubscript{x} films needs a high annealing temperature (> 200\degree C) or requires an extra procedure for the preparation of TiO\textsubscript{x} nanoparticles before film. In contrast, Bao et al reported single-step solution processed amorphous TiO\textsubscript{x} (a-TiO\textsubscript{x}) film as an ETL in inverted solar cell.[39] Using tetrabutyl titanate (TBT) as the Ti precursor to obtain TiO\textsubscript{x} by the traditional sol-gel method, a highest PCE of 4.65% was obtained using the TiO\textsubscript{x} film treated at 90 \degree C for 60 min as ETL between active layer and ITO. The author claimed that at low annealing temperature, the presence of OH in the α-TiO\textsubscript{x} film reduced the conductivity in a large scale. While the annealing temperature is increased over 90\degree C, the conductivity is increased to a saturation value of $7.4 \times 10^{-6}$ S cm\textsuperscript{-1}. 
Nanostructured transition metal oxides

As discussed above, the metal oxide layer inserted between ITO electrode and active layer, can transfer electrons and block holes owing to its proper energy level alignment. In addition to planar thin films, nanostructured metal oxide is usually applied to modify the interface between ITO electrode and the polymer: fullerene blend. By using nanostructures such as well-ordered, mesoporous TiO$_2$ and nano-wire ZnO, the interfacial area between metal oxide and the active layer is further enlarged, which also been named as double-heterojunction devices: one junction is between polymer and fullerene interface and the other one is between polymer and n-type metal oxide. In general case for BHJ PSCs, the active layer is a bi-continuous interpenetrating network of p-type polymer and n-type fullerene. After dissociation of photogenerated excitons into free charge carriers at D/A interface, holes and electrons are driven to the respective anode and cathode through the p-type polymer and n-type fullerene semiconductor, respectively.

However, in BHJ PSCs, the disordered bulk heterojunction of D and A makes it

![Figure. 1. 6 Four device architectures of conjugated polymer-based photovoltaic cells: (a) single-layer photovoltaic cell; (b) bilayer PV cell; (c) disordered bulk heterojunction; (d) ordered bulk heterojunction.](image)
possible for D directly contact with cathode buffer layer, indicating another interface between D and n-type buffer layer where photo-generated excitons can be dissociated (shown in Figure 1.6). On account of such angle, structured metal oxides applied as buffer layer can be utilized to offer another possibility for effectively dissociating excitons at the interface of metal oxide and polymer. Since TiO$_2$ can be patterned into a continuous network for electron transport,$^{[40-41]}$ if the conjugated polymers and TiO$_2$ can be structured in an ordered style with a pore size of 20-30 nm, which is comparable to the exciton diffusion length, the exciton can be dissociated effectively at the interface between n-type metal oxide and polymer. On the other hand, it is demonstrated that the charge carrier mobility of the polymer can be enhanced to 20-fold due to the vertical channel confinement in the pores along the direction perpendicular to the substrate$^{[42]}$, favoring the charge transfer in PSCs, although the size and orientation of pores may influence the packing pattern of polymer chains and result in different hole mobilities.$^{[43,44]}$ As a result, the concept of double-heterojunction, including the disordered BHJ in active layer and ordered heterojunction of metal oxide & polymer, not only optimizes ordered network morphology and mobility but also enlarges the exciton dissociation sites due to the large-surface area of the nanostructures, providing additional A-D junctions between polymer and n-type metal oxide. Recently, most work on conjugated polymer-TiO$_2$ PV cells has involved sintering TiO$_2$ nanocrystals and then trying to fill the conjugated polymer into the pores of the crystal by spin-coating the polymer solution. Furthermore, a method of casting a polymer and titania precursor solution to fabricated the film is also reported.$^{[45]}$ Moreover, other reasons to use TiO$_2$ are that it is nontoxic, many molecules can be attached onto its surface, such as organic dyes,
by using such characteristics, TiO$_2$ are widely used in dye-sensitised solar cells (DSSC). And the unique absorption at the UV region make it possible for TiO$_2$ film to serve as UV filters to further protect the photoactive materials from degradation.

The idea of double BHJ solar cell was realized by Gopal K. Mor et.al by using a vertically oriented TiO$_2$ nanotube arrays as the ETL, and infiltrating with P3HT and PCBM blend as shown below. The length of TiO$_2$ nanotube is 270 nm and the size of pores is chosen to be 50 nm, which is large enough to allow the subsequent polymeric layer to infiltrate the nanotubes and allow the polymer chains to coil, to be aggregated and had a more filmlike environment.$^{46}$ The well patterned P3HT due to the nanostructured TiO$_2$ nanotube was proved by the blueshift in the UV-visible absorption spectra because the blueshift relative to the rodlike chain in an unannealed neat film as shown below is indicative of a coiled configuration since the conjugation length is shorter on a coiled chain.$^{47}$ As a result, an additional BHJ at the TiO$_2$-P3HT interface induced enhancement of excitons dissociation sites and ordered nano-structure induced

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enhancement of hole mobility of polymers result in an enlarged $J_{sc}$ of 12.4 mA/cm$^2$ and high EQE (maximum 80% at 538 nm). Together with a $V_{oc}$ of 641 mV and $FF$ of 51%, the PCE was enhanced to 4.1%. (See in Figure 1.7) A similar work was done by Yu et. al using a structure of ITO/TiO$_2$/P3HT:PCBM/V$_2$O$_5$/Al. The self-organized TiO$_2$ nanotubes arrays were grown by anodizing Ti metal in glycerol electrolyte containing 0.5 wt% NH$_4$F and 1.0 wt% H$_2$O with 20 V potential, after annealing at 500 ℃ for 1h, the TiO$_2$ film shows an anatase phase with a diameter of 15-25 nm. The author claimed that in addition to the double BHJ interface, the enhanced electric conductivity of TiO$_2$ film due to the high-temperature processed crystalline all together result in an enhanced $J_{sc}$.

For ZnO, the nanofiber structured ZnO film has also been studied. Olson et. al fabricated vertically aligned ZnO nanofibers with respect to the substrate, and using polymer and the polymer: fullerene blend to fill in the ZnO film. The hybrid solar cells using ZnO nanofibers and P3HT show $V_{oc}$ of 440 mV, $J_{sc}$ of 2.2 mA/cm$^2$, $FF$ of 0.56, and PCE of 0.53%. And the double-BHJ device using ZnO nanofibers, P3HT and PCBM shows a $V_{oc}$ of 440 mV, $J_{sc}$ of 10.0 mA/cm$^2$, $FF$ of 0.43, and PCE of 2.03%. The author claimed that due to the large space between the ZnO fibers, the interface between ZnO and P3HT is insufficient large to dissociate more excitons, leading to a low $J_{sc}$ for hybrid solar cell compared to the ZnO/P3HT:PCBM solar cell. Interestingly, in this study, the $V_{oc}$ of 440 mV is less than that expected from the effective band gap of the donor-acceptor couple. In the case of P3HT-ZnO, the effective band gap is approximately 0.9 eV. Since the author did not give convincing evidence for explanation on the lower measured $V_{oc}$, but possible explanations are: the presence of mid-gap states on the surface of ZnO that pin the Fermi level; the electron mobility of ZnO nanofibers may be
so high that the recombination at the ZnO/P3HT interface is increased. In addition, the role of the ZnO nanorod was not clear, as there was no direct evidence to show the cascading electron transfer from PCBM to the ZnO nanorods. In this view of point, Kazuko Takanezawa et al studied P3HT:PCBM/ZnO nanorod photovoltaic devices with a thick hybrid layer up to 450 nm, (shown in Figure 1.8) The author demonstrated that by increasing the length of the ZnO nanorods, the $FF$ of the device can be increased from 38% to 50% by introducing the array of ZnO nanorods with an average length of 300 nm. Since the role of ZnO nanorod array in P3HT/PCBM/ZnO nanorod system is an electron collector/transporter, and the presence of the highly conductive ZnO nanorod (high electron mobility~ 1-5 cm$^2$ s$^{-1}$V$^{-1}$ along c-axis) makes the average distance from the generation point of the charge carriers to the ZnO surface become shorter. In conclusion, the device performance is improved due to the introduction of the nanostructured ZnO.

1.4.1.2 Alkali-metal compounds

In OLEDs, monolayers of insulating metal compounds such as LiF, CsF, Li$_2$O and Na$_2$O are utilized to function as desired interfacial chemistry and a desired trapped interface charge density, allowing an electron injection carrier to balance the hole
injection. Among them, LiF has also been reported to enhance polymer solar cell performance.\textsuperscript{[48]} Alkali metals or alkaline earth metals incorporated in organic molecules are also candidate materials for the electron injection layer (EIL). Alkali metal (Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Rb\textsuperscript{+}, and Cs\textsuperscript{+}) acetates and fluorides have been demonstrated to enhance electron injection in OLEDs.\textsuperscript{[49]}

A representative alkali-metal compound Cs\textsubscript{2}CO\textsubscript{3} as an interfacial layer was firstly reported by Canon group.\textsuperscript{[50]} The Cs\textsubscript{2}CO\textsubscript{3} as EILs in OLEDs was else introduced by Hasegawa in 2004.\textsuperscript{[51]} The application in PSCs was firstly demonstrated by G. Li, et al in 2006.\textsuperscript{[52]} Using a device structure of ITO/Cs\textsubscript{2}CO\textsubscript{3} (1 nm)/P3HT:PCBM/V\textsubscript{2}O\textsubscript{5} (10 nm)/metal, the $J_{sc}$ of 8.42 mA/cm\textsuperscript{2}, $V_{oc}$ of 0.56 V and PCE of 2.25\% under AM1.5G were obtained. The relatively low PCE is mainly due to the small thickness of active layer. In Yang’s group at UCLA, a low temperature annealed Cs\textsubscript{2}CO\textsubscript{3} interfacial buffer layer was reported in 2008, improving the PCE of the inverted cell from 2.3\% to 4.2\%, with short-circuit current of 11.17 mA/ cm\textsuperscript{2}, open-circuit voltage of 0.59 V, and fill factor of 63\% under AM1.5G 100 mW/cm\textsuperscript{2} irradiation were observed In general the decomposition temperature of Cs\textsubscript{2}CO\textsubscript{3} is near 550-600 °C,\textsuperscript{[53]} while during low temperature annealing, the Cs\textsubscript{2}CO\textsubscript{3} may decompose into low work function cesium oxide, indicating a n-type doped Cs\textsubscript{2}CO\textsubscript{3} thin film was realized after the annealing process.

Yang also demonstrated the thermal annealing can change the surface energy of the Cs\textsubscript{2}CO\textsubscript{3} thin film, making a transition from hydrophilic to hydrophobic, favoring the polymer film growth.\textsuperscript{[54]} Barbot also reported a C\textsubscript{60} doped Cs\textsubscript{2}CO\textsubscript{3} thin film as ETL, improving the efficiency from 3\% to 3.79\%.\textsuperscript{[55]}
Besides Cs$_2$CO$_3$, a number of other salts were also evaluated as the ETL in PSCs, including alkali carbonates from Li$_2$CO$_3$ to Cs$_2$CO$_3$, and cesium-containing salts such as CsF, cesium acetylacetonate [Cs(acac)]. The salts were firstly dissolved in water or polar organic solvent such as 2-ethoxyethanol to form dilute (0.2 wt %) solutions,$^{[57]}$ followed by the spin-coating process to form a 0.6-3 nm thick film. The function of the thin layer here is to lower the work function of ITO or FTO. With the addition of only a few monolayers of molecules, it is believed that strong dipole layer forms at the interface. As shown in Figure 1.9, a thin layer of Oxygen-Metal species is formed at the surface of ITO or FTO with metal ions in the vacuum side. The dipole here points from ITO to vacuum and reduces the ITO surface work function, and the interfacial charge transfer rate at cathode is enhanced, leading to a decrease of the series resistance. As a result, $J_{SC}$ increases due to the reduced series resistance and $V_{OC}$ increased due to a lower cathode work function before Fermi energy pinning.

![Figure 1.9](image_url)
1.4.1.3 Ultrathin layer

There are several ultrathin layers, and in this section, some examples are listed below to further explain such ultrathin layer for PSCs.

**Low-workfunction metals**

In the conventional PSCs, charge collection and built-in potential can be increased by introducing a layer of low-workfunction (Low-WF) metal such as Ca and Mg. Similarly, being sandwiched between the ITO electrode and the active layer in the inverted cell, low WF metals can serve as an interfacial layer that efficiently collects electron. The thickness should be thin enough to make enough light transport through such layer. Zhao et al reported an inverted organic solar cell using an ultrathin Ca layer (1 nm) as the ETL. With an optimal MoO$_3$ (3 nm) as the anode buffer layer, the inverted cell using P3HT:PCBM has a PCE of 3.55\% under simulated 100 mW/cm$^2$ illumination. The work function of Ca is -2.9 eV, which lowers the work function of ITO, thereby increasing the $V_{OC}$ of the device due to Fermi level pinning between Ca and PCBM via surface states, result in an Ohmic contact between Ca and PCBM. While on the other hand, the energy level alignment of Ca and P3HT also make it form a rectifying contact to block the hole collection on the ITO side.

**Conjugated polymers**

Similar to alkali-metal compounds, the main mechanism for using organic interfacial modifiers is the formation of an interface dipole layer that leads to a substantial reduction of the work-function of the electrode. Organic interfacial modifiers such as polyethylene oxide (PEO),$^{[58]}$ polyethyleneimine based structures$^{[59, 60]}$ or polyvinylpyrrolidone$^{[61]}$ has been reported recently. Especially, Tang et al. utilized a thin (<10 nm) cathode interlayers
of conjugated polymer poly(3,3’-([9’,9’-dioctyl-9H,9’- H-[2,2’-bifluorene]-9,9-diyl) bis(1,4-phenylene)])bis(oxy))bis(N,N-dimethylpropan-1-amine)) (PFPA-1) to increase the device performance. As a result, an increase of approx. 20% was obtained in $J_{SC}$ and FF. Moreover, Cao’s group also reported high efficiency OSCs using interlayer of poly [(9,9-bis(3’-(N,N-dimethylamino) propyl)-2,7- fluorene)-alt-2,7-(9,9–dioctylfluorene)] (PFN) processed from an alcoholic solution.

In addition, recently conjugated polyelectrolytes (CPEs) which consist of a conjugated backbone with side groups that carry ionic functionality have been identified as a very promising approach to lower the work-function of a cathode material in organic solar cells. For example, a CPEs of poly[(9, 9-bis((60-(N,N,N-trimethylammonium)hexyl)-2,7-fluorene)-alt-(9,9-bis(2-(2-(methoxyethoxy)ethoxy)ethyl)-9-flu-orene))dibromide (WPF-6-oxy-F) was directly layered on top of ITO to change the work-function to facilitate the extraction of electrons. Similar work has also been done by Kirill Zilberberg et al, who reported on inverted polymer:fullerene solar cells using the conjugated polyelectrolyte P3ImHT as ultra-thin cathode interlayer to reduce the work-function of ITO. By using UV exposure treatment, an efficiency of 4.8% is achieved due to a suitable electron selective cathode result from the dipole induced WF lowering in ITO.

1.4.2 Hole transfer/extraction layer

There are several HT/E layers, and in this section, some examples are listed below to further explain such layers for PSCs.
1.4.2.1 n-type transition metal oxides

In comparison to the cathode buffer layer (EEL & ETL) in the inverted architecture, a layer of n-type semiconductor metal oxides (MoO$_3$, WO$_3$, NiO$^{[68]}$, and V$_2$O$_5$, etc.) have also been used to modify the interface between active layer and top metal electrode. Transition metal oxides (TMOs) were firstly introduced in the field of organic electronics by Tokito et al in 1990’s. They demonstrated a significant increase in hole-injection when using thin films of vanadium, molybdenum and ruthenium oxides as interlayers between the anode and the organic material in organic light emitting diodes (OLED)$^{[69]}$. The motivation to study such materials predominantly stemmed from their reported high work function, semiconducting properties and good transparency, characteristics that are all very important for electrodes or for charge generation/ recombination materials.$^{[70]}$

Figure 1.10 The energy level diagram of state-of-art photovoltaic polymers, electron accepting fullerene derivatives and transition metal oxides.
Particularly in the inverted PSCs, such metal oxides can be used as the anode buffer layer, which is crucial in improving the device performance. For example, Heegar et al. have reported the effectiveness and stability of MoO$_3$ as an anode interfacial transition metal oxide layer in BHJ devices as compared to highly conductive PEDOT:PSS. In terms of principle, similar to EEL & ETL, if appropriate materials and configurations are chosen, such buffer layer will optimize PSCs by modifying surface properties to promote a higher degree of ordering or to tune the effective WF of electrodes,\textsuperscript{[71]} keeping excitons away from electrodes\textsuperscript{[72]} and preventing undesired recombination.\textsuperscript{[73]}

In particular, the WF of the metal oxides interlayer need to be large enough so that the Fermi levels of the interlayers match the HOMO levels of photovoltaic polymers. Otherwise, the WF of general high-WF metal (WF (Ag)~4.64 eV) is not high enough to form an Ohmic contact with conjugated polymers because general HOMO energy of such polymers in BHJ is even higher (e.g. HOMO (P3HT)~5.3 eV). And the electrons may transfer from metals to absorber, creating an interface dipole and reducing the device built-in potential, which not only increases the series resistance under forward bias but also decreases the extraction field at short circuit condition. As a result, in order to enhance the performance of PSCs, the anode buffer layer requires higher-WF to form better contact with conjugated polymers.\textsuperscript{[74]}

Based on different mechanism for the hole extraction, both n-type and p-type semiconductor metal oxides have been utilized as anode interfacial layers in PSCs.

The n-type semiconductor metal oxides such as molybdenum oxide, tungsten oxide and vanadium oxide, are commonly used for anode Ohmic contacts for OPV devices. Even though early reports presented MoO$_3$, V$_2$O$_5$ and WO$_3$ as conducting p-type
materials, with electron affinity (EA) and ionization energy (IE) of MoO₃ often quoted in literature to be on the order of 2.3 and 5.3-5.4 eV, respectively, they were recently unambiguously demonstrated to be n-type materials with very deep lying electronic states.

The combined UPS/IPES spectra taken from MoO₃, V₂O₅ and WO₃ layers shows similar deep lying electronic states, with a VB edge around 2.5-3 eV below the Fermi level and a CB edge very close to the Fermi level, indicating a highly n-type material. And the n-type conducting properties mainly result from the slightly non-stoichiometric composition, with some oxygen deficiency proven by XPS.

The application of these TMOs as the HEL in PSCs has been widely studied although they are n-type semi-conductors. Because of the large WF of the TMOs film relative to the IE of the organic film, electrons transfer from the organics to the TMO to

Figure. 1. 11 (a) Energy level alignment and band bending at the MoO₃/CBP interface, as deduced from the UPS; (b) proposed hole-injection and hole-extraction mechanisms.
establish thermodynamic equilibrium across the interface, resulting in Fermi level at the interface pinning closely to organics’ HOMO edge. Such similar band bending occurrences have been reported already.\cite{85} For example, Figure 1.11 (a) summarizes the energy level alignment and band bending determined for the MoO$_3$/CBP interface as well as the mechanisms for charge injection and extraction at the interface. The deeply large ionization energy of MoO$_3$ (9.7 eV) precludes holes transporting via the valance band. While the energy difference between the bottom of CB of MoO$_3$ and HOMO of CBP is so close that electron may transfer between these two materials. Under positive bias, hole-injection into the organic film can take place due to the electron transfer from HOMO of CBP to the CB of MoO$_3$, which has already applied as interconnect in stacked OLEDs. While in inverted PSCs, mainly take advantages of the hole-extraction process. As shown in Figure 1.11b, at the interface between MoO$_3$ and the organic layer in PSCs, the photo-generated hole in electron donor polymers recombines with an electron from MoO$_3$, leaving a hole in the MoO$_3$, which is equivalent to “hole extraction”.

MoO$_3$

Among all the TMOs, MoO$_3$ shows premium performance in PSCs. Because of its low melting temperature (795 °C), the film of molybdenum oxide can be processed by thermal evaporation (deposition), which allows accurate thickness control at a nanometer scale. For e-MoO$_3$, the oxygen deficiency results in the defect band, which lifts the Fermi level closer to CB.\cite{86, 87} The WF of MoO$_3$ is 6.7± 0.2 eV and strongly depends on the stoichiometry and highly sensitive to surface contamination. Particularly, under oxygen or air, the WF decreases to 5.3-5.7 eV\cite{88-90}, but still sufficient to yield good Ohmic contacts with organic hole transporting materials, giving that the optimum HOMO level
of the photovoltaic polymers generally resides between -5.2~5.6 eV considering the trade-off relationship between $V_{OC}$ and optical absorption band.

Small et al showed that compared with the conventional bottom MoO$_3$ p-contact, enhanced Ohmic contacts can be made when MoO$_3$ and silver are sequentially evaporated onto organic materials as a top p-contact. By using MoO$_3$ as an anode buffer layer in the inverted PSCs, our group also achieved high PCE of ~8.4%. Moreover, compared with PEDOT:PSS, MoO$_3$ shows better stability, indicating prospective lifetime for PSCs. However, the processing of thermal evaporation limits its application in large-scale production. To overcome such short slab, our lab contributes a solution-processed MoO$_x$ (s-MoO$_x$) to simply the fabrication process and lower the processing cost. To note, we use a rather simple way to prepare the MoO$_x$ precursor solution: drop-wisely add H$_2$O$_2$ (30%) into Molybdenum powder in ice-water bath followed by further purification and then dried by heating, and use methanol to dissolve the solid to get a precursor solution with a concentration of 10 mg/mL. In comparison, Liu et al. prepared the precursor solution by dissolving ammonium molybdate [(NH$_4$)$_6$Mo$_7$O$_{24}$] into a mixture of hydrochloric acid and de-ionized water before spin-casting.$^{[91]}$ Girotto et al. C.$^{[92]}$ prepared precursors by dissolving MoO$_3$ powder into H$_2$O$_2$. Zilberberg et al.$^{[93]}$ presented a precursor based on bis(2,4-pentanedionato) molybdenum(VI) dioxide and isopropanol. For s-MoO$_x$, several factors need to be considered: (1), the film roughness should be lower enough to avoid the pin-hole at the interface causing current leakage; (2), the processing simplicity should be small enough to ensure the value of such processing; (3), the WF for general s-MoO$_x$ tends to be lower than that of e-MoO$_3$, which will affect the quality of the resulting Ohmic contacts. Taking consideration of all the three points above,
our group demonstrated a room-temperature, solution-processed molybdenum oxide (MoO₃) as a hole extraction layer to substitute PEDOT/PSS in polymer solar cells. With a smoother surface, better transparency, and high electrical conductivity of MoO₃, enhanced efficiency of PSCs was achieved.

**WO₃**

Similar to MoO₃, WO₃ is another n-type semi-conductor with a rather low WF, which is closely relative to the stoichiometry, the crystalline structure and thus the processing conditions. Evaporated films of amorphous WO₃ are generally deficient in oxygen which gives rise to the gap states and n-type semiconductivity. And further oxygen deficiency result from e.g. thermal annealing in vacuum will lead to metallic properties like WO₂.

The application of WO₃ in inverted PSCs has been reported by Chen Tao et. al, claiming that the high WF of WO₃ (~4.8 eV) will enhance the hole collection at the photoactive layer/Ag intereface. By using a device structure of ITO /nc-TiO₂ /P3HT:PCBM /WO₃ /Ag, the devices display a $V_{OC}$ of 0.6 V and a $FF$ over 0.60. The thickness of WO₃ layer is about 10 nm, which is thick enough to segregate the active layer to be contacted with Ag electrode, thereby decreasing the recombination rate of photogenerated charges. However, the author also claims that a thicker layer of WO₃ will generally contribute to a larger series resistance, resulting in low current. Seungchan Han, Seunghyup Yoo et. al also reported that by using thermal deposition, the WO₃ thin film could obtain a notably small RMS of 0.88 nm, which contribute to the good contact with active layer and thereby enhancing the $FF$ to over 70%. Even though they claim that in the same condition the RMS of MoOx is large of 7.2 nm, which is unbelievably high, the small RMS of WO₃ seems prospective in interfacial engineering in PSCs. On the other
hand, solution processed WO$_3$ (s-WO$_3$) has also demonstrated in conventional devices, indicating the possibility for using the low-cost solution processed WO$_3$ in inverted PSCs.

**V$_2$O$_5$**

The third widely used n-type metal oxide as the anode buffer layer is the V$_2$O$_5$, whose band gap is 2.8 eV confirmed by the UPS and IPES. To point out, the WF of V$_2$O$_5$ is extremely high with a value of 7.0 eV (using thermal deposition processing in ultra-high-vacuum conditions <10$^{-10}$ Torr), offering excellent Ohmic contact to organic semiconductors even with low HOMO levels. Vacuum evaporated V$_2$O$_5$ has been reported as an effective anode buffer layer. Shrotriya et al. previously reported that vacuum evaporated V$_2$O$_5$ layers function as anode buffer layers both in devices with conventional ITO/V$_2$O$_5$/organic layer/Al configuration and devices with “inverted” ITO/Cs$_2$CO$_3$/organic layer/V$_2$O$_5$/Al configuration.

Similar to other n-type TMOs, the WF of V$_2$O$_5$ is significantly depended on the environment and processing method. Especially, for sol-gel prepared TMO layers, the WF is relatively lower than those prepared from vacuum evaporation. And in past few years, TMOs layers obtained by solution processing from nano-particles (NPs) dispersions were reported. However, the RMS of the TMOs thin film by using this method is generally larger than that of the e-TMOs, indicating the contact between TMOs and active layer will cause energy loss and inferior PCE. And for the TMOs prepared by sol-gel deposition, routinely high temperature processing (>300 °C) is needed to achieve a certain microstructure or crystalline phase. However, in inverted PSCs, such high temperature will cause the decomposition of the active layer materials. As mentioned
before, solution processed TMOs offer a cheaper way to fabricate PSCs compared with
e-TMOs. And in this concern, in the past few years, solution processed TMOs have been
studied. Kirill Zilberberg and Thomas Riedl et al have demonstrated that a 10 nm thick
$V_2O_5$ layer can be obtained by spin-coating from isopropanol solution of vanadium (V)
oxitiisoproposide followed by stored at ambient air for 1hour for hydrolysis at room
temperature. And similar PCE can be achieved for inverted PSCs compared with the
e-$V_2O_5$.\textsuperscript{104}

1.4.2.2 p-type transition metal oxides

Different from n-type TMOs, the p-type characteristics of NiO originated from
positive charge compensation at the thermodynamically favored $Ni^{2+}$ vacancies\textsuperscript{105-107}
And the WF of NiO strongly depends on its chemical and physical properties such as
surface chemistry, crystal orientation and processing conditions. The surface of NiO film
may adsorb surface contaminants (nitric oxide, carbonaceous & hydroxyl species) upon
exposing in ambient air, leading to decreasing in WF.\textsuperscript{108-110} Interestingly, Ratcliff et al.
reported that $O_2$ plasma treatment may increase the WF from 4.7eV to 5.3 eV due to the
dipolar nickel oxyhydroxide (NiOOH) formed on the NiO surface.\textsuperscript{111} The typical
HOMO level for polymers such as P3HT is about 5.3 eV and the LUMO of PCBM is
nearly 4 eV, while the affinity of NiO is relatively small of $\sim$2.1 eV, together with its wide
band gap, NiO acts as an effective hole transfer layer and electron blocker by ohmic
contact from at NiO/P3HT interface and energy barrier formed at NiO/PCBM
interface. The first NiO used in PSCs was introduced by Irwin et al in a conventional
structure. An optimized $\sim$10 nm NiO layer was inserted between active layer and ITO by
using pulsed laser deposition (PLD). With P3HT:PCBM system, the over 5 % PCE was
obtained. Recently, solution-processed NiO was also reported for polymer photovoltaics.\textsuperscript{[112-114]}

Since the pure stoichiometric NiO is an excellent insulator, with conductivity on the order of $10^{-13}$ S cm\(^{-1}\) at room temperature,\textsuperscript{[115]} while after stoichiometric changes such as different processing method, the NiO\(_x\) becomes a wide bandgap p-type semiconductor. For inverted PSCs, the NiO acts as both HTL & EBL on top on active layer, and high temperature processing for NiO seems impossible due to the damage of the active layer. Proper methods for preparing premium NiO layer in the inverted PSCs are still needed to be studied.

1.5 Interfacial Modification Layer

As aforementioned, metal oxides such as ZnO, MoO\(_x\) are widely used as ETL and HEL in inverted PSCs, respectively. However, poor electrical coherence at the organic/inorganic interfaces,\textsuperscript{[116-119]} might result in the inferior device performance. This poor contact originates from the hydroxyl groups on the surface of the metal oxide, which will cause charge trapping and high charge carrier recombination at the interface,\textsuperscript{[120]} thus leading to limited FFs in inverted solar cells compared to their conventional counterparts. Therefore, the electrical contacts need to be appropriately controlled to minimize the resistance across the interfaces, fulfilling the efficient collection of charges at the electrodes. On this concern, several modification materials are thereby introduced to further improve the device performance.
1.5.1 Non-cross-linkable self assembled monolayers

Apart from the poor contacts between metal oxide/BHJ interface, another factor that restricted the performance of inverted solar cells is the morphology of the BHJ layer. Since non-appropriate phase separation will lead to geminate and non-geminate recombination, causing losses in device performance.\textsuperscript{[121-124]} Therefore, it is imperative to decrease the series resistance across the interfaces and control the phase distribution in the bulk-heterojunction layer at the same time. One approach to simultaneously solve the two problems is inserting SAM between metal oxide and BHJ active layer.\textsuperscript{[125-130]} Through the chemical reaction between the anchoring group (usually carboxylic acid and phospholic acid) and the hydroxyl groups on metal oxide, a corresponding ester linkage can be formed.\textsuperscript{16} The SAM cannot only protect the metal oxide layer from organic solvent destruction through the immobilized function group.
Hau et al. demonstrated four kinds of SAMs with four different functional groups: fullerene derivative (C$_{60}$-SAM), terathiophene SAM (TT-SAM), benzoic acid SAM (BA-SAM) and lauric acid SAM (LA-SAM), and studied their application in modifying TiO$_2$ inorganic/BHJ organic interface in inverted solar cells.$^{[127]}$ Molecular structures of four SAMs were shown in Figure 1.12. An overall enhanced performance was observed from PCE 2.8\% for the pristine device, to PCE 3.0\% for LA-SAM modified device, 3.2\% for BA-SAM modified device, 3.4\% for TT-SAM modified device and 3.8\% for C$_{60}$-SAM modified device. The overall increased efficiency suggested the contact was improved by the introduction of SAMs, which was proved by the measurement of contact angle. The contact angle increased from 5$^\circ$ (to DI water) to 40$^\circ$–80$^\circ$ for SAMs modification, verifying SAMs improves the hydrophobicity of metal oxide. The greatest improvement was obtained through C$_{60}$-SAM modification as expected. Due to the outstanding electron-withdrawing property of C$_{60}$ molecule under illumination, the photoinduced charge transfer between C$_{60}$-SAM and organic BHJ activelayer is anticipated to be much larger than other SAMs, with decreased back charge recombination at the interface.$^{[132]}$ $J$-$V$ curves from pristine P3HT:TiO$_2$ heterojunction based inverted PSCs (in which device structure the influence of PCBM can be avoided) testified this conjecture, showing largest $J_{SC}$ and $FF$ for devices with C$_{60}$-SAMs modification. However, other three kinds of SAMs also showed different degree of enhancement. Another factor demonstrated to be accounting for the PCE improvement is the influence on the phase distribution of the upper layer. Increased crystallinity and better ordering of P3HT chains were demonstrated to be formed in blend films with SAMs modification. Therefore the charge recombination will be decreased in BHJ activelayer, resulting in a better performance.$^{[133]}$
Moreover, organic field effect transistors (OFET) measurement proved that the C\textsubscript{60}-SAM facilitated the accumulation of PCBM to the bottom TiO\textsubscript{2} interface, with the evidence that higher electron mobility was obtained on the TiO\textsubscript{2} side. Furthermore, from the capacitance-voltage (C-V) measurement, low capacitance was observed under positive gate voltage, implying no significant n-mode accumulation. This demonstrated that the C\textsubscript{60}-SAM can facilitated the nucleation of PCBM and provided a better percolation conduction pathway of PCBM at the interface, consequently improving the overall distribution of phases, morphology and crystallinity of the blend.

For mass production, however, the inverted PSCs should have an acceptable PCE even processed in ambient atmosphere. Therefore Haul et al. studied the influence of ambient atmosphere on performance of inverted PSCs with/without C\textsubscript{60}-SAM (same structure as shown previously) modification.\textsuperscript{[126]} In this work, C\textsubscript{60}-SAM was used to modify ZnO-Nanoparticles (electron-selective layer), and PEDOT:PSS as hole-selective layer. PSCs without C\textsubscript{60}-SAM experienced 11\% decrease from 3.7\% (inert processing) to 3.3\% (ambient processing), while with C\textsubscript{60}-SAM modification, it underwent only 2\% from 4.54\% to 4.45\%. The comparative insensitivity of the C\textsubscript{60}-SAM modified devices to
ambient process was likely attributed to the passivation of ZnO surface with C$_{60}$-SAM, which diminished the O$_2$ absorption and thus improved the interfacial properties.$^{[134, 135]}$ Aside from different functional groups as demonstrated before, different anchoring groups and linkages will exert drastic different PSCs performance as well. Hau et al. conducted a series of experiment to systematically investigate the effect of the binding groups (catechol, carboxylic acid, and phosphonic acid) on the performance of inverted solar cells.$^{[136]}$ In addition, different linkage geometry of the carboxylic acid anchoring group to C$_{60}$ and different functionalization of a carboxylic acid anchoring group onto PCBM were also investigated. Molecular structures of five SAMs were shown in Figure 1.13. It was found that the C$_{60}$-SAMs with either the carboxylic acid or catechol end-group can be formed onto the surface of ZnO by a simple solution spin-coating process, whereas the formation of phosphonic acid end-group onto ZnO needs solution immersion technique. It’s worthy mentioned that solution immersion technique can also facilitate the formation of catechol, carboxylic acid end-groups onto ZnO. However, it raised a problem that ZnO could be degraded by C$_{60}$-COOH and C$_{60}$-PA, due to the acidic nature of carboxylic acid and phosphonic acid molecules.$^{[137]}$ Therefore, to reduce the potential etching of ZnO, the utilization of less acidic bind terminal units is more attractive, such as catechol-based C$_{60}$ (SAM[2]). Both weak diprotic acid nature and ability to form bidentate bonding with metal oxides make it a fascinating candidate to modify the ZnO surface.$^{[138, 139]}$ SEM images confirmed the expectations above, as shown in Figure 1.14. The unmodified ZnO-NPs showed relatively smooth and dense film morphology, in contrast, the surface of the phosphonic acid C$_{60}$-SAM modified ZnO-NPs showed large number of voids, indicating significant etching into the ZnO-NPs layer. The
carboxylic acid C$_{60}$-SAMs also displayed slight signs of etching as can be seen by the initial stage of void formation in the SEM images, with a much less severity than the phosphonic acid C$_{60}$-SAM. In clear contrast with SAM[1] and SAM[3], C$_{60}$-CAT (SAM[2]), showing weakly acidic nature, however exhibited similar surface profile to that of unmodified ZnO-NPs, which demonstrated the minimum degradation.

Heterojunction solar cells based on ITO/ZnO-NPs/C$_{60}$-SAM/pure P3HT/PEDOT:PSS/Ag were fabricated to understand the effect of the different C$_{60}$-based SAMs at the ZnO-NP interface. When modified with the C$_{60}$-SAMs, the devices showed an overall improvement in FF, $J_{SC}$, and PCE, which manifested surface charge traps of ZnO-NPs were passivated by C$_{60}$-SAMs, furthermore, the back charge recombination was suppressed. However, $V_{OC}$ showed different degree of decreasing. Pristine device showed $V_{OC}$ of 0.66 V, which value reduced to 0.57 V after modified with carboxylic acid anchoring group (SAM[1]). It was attributed to the interfacial dipole formed from the
carboxylic acid anchoring to surface of the ZnO-NPs.\textsuperscript{[140]} An even lower $V_{OC}$ of 0.48 V was observed for catechol anchoring group (SAM[2]) modification, which was ascribed to the formation of a strong interface dipole because of catechol forming bidentate bonding. It resulted in an intramolecular ligand to metal charge transfer transition.\textsuperscript{[141-144]} For phosphonic acid anchoring group (SAM[3]), it showed similar $V_{OC}$ to that of SAM[1] modification when processed from spin-coating and solution immersion technique for a short time of period. However, the devices lost photodiode property after immersing in phosphonic acid solution for a long time of period, which was in agreement with the previous results (degradation and etching of the ZnO-NPs layer because of the acidic nature of the phosphonic acid SAM). It’s interesting to point out that, SAM[4], possessing the same binding group with SAM[1], showed much larger $V_{OC}$ of 0.64 V than that of SAM[1]. It was demonstrated to be account for the bifunctionalization of the C$_{60}$, which led to a lower-energy LUMO and helped to compensate the interfacial dipole effect caused by the binding at the surface. Changing the linkage to the C$_{60}$ molecule (SAM[5]) showed a slight decreased $V_{OC}$ (0.52 V) compared to SAM[1]. Unlike the huge discrepancy of $V_{OC}$ from the five SAMs, variations in $J_{SC}$ and $FF$ from the different SAMs are minimal except for the C$_{60}$ phosphonic acid anchoring SAM (SAM[3]). The lower $J_{SC}$ and $FF$ compared to that of the other C$_{60}$-based SAMs were likely attributed to the slower electron-transfer process of the phosphonic acid anchoring group, as previously reported.\textsuperscript{[145, 146]} However, the influences of the C$_{60}$-SAMs on the $V_{OC}$ are less remarkable in BHJ devices, because the interface for the exciton dissociation is primarily from the donor/acceptor interface. Consequently, $V_{OC}$ varied in a small range between 0.61 V to 0.62 V for these PSCs. Efficiency was improved from 3.47% (without
modification) to $\sim 4.4\%$ (with the carboxylic acid C$_{60}$-SAMs), 4.19$\%$ (with the catechol C$_{60}$-SAM), and 3.96$\%$ (with the phosphonic acid C$_{60}$-SAM).

In conclusion, self-assembled monolayers, as described above, exert multi-positive effects on the interface, including enhancement of exciton dissociation, reduction of charge recombination, decrease of interface contact resistance, passivation of surface electron traps on metal oxide, and controlling the upper layer phase distribution.

### 1.5.2 Cross-linkable self-assembled monolayer

However, there’re still some drawbacks of these SAM layers that’ll limit further enhancement of inverted PSCs performance. The primary considerations are their insufficient coverage at the molecular scale and probable desorptions of the molecules during wet processing, which will create localized defects at the interlayer.$^{[147]}$ It would be a great potential to develop a fullerene material that can be readily undergo chemical cross-linking to form a robust and immobilized layer. To realize such target, several groups of cross-linking SAMs were synthesized and characterized.

The first we will introduce is styrene group. Styrene group was used because of its outstanding thermally curable property, due to the fact that polystyrene can be formed through rapid polymerization in the solid state without any initiators, through thermal annealing, two styryl groups can be formed as cross-linkers.$^{[148, 149]}$ Based on the favorable thermo-property of styrene group, a fullerene derivative material [6,6]-phenyl-C61-butyric styryl dendron ester PCBSD (Figure 1.15), with a small dendron functionalized with two thermally crosslinkable styryl groups, has been synthesized and characterized.$^{[147]}$
PCBSD cross-linked network (C-PCBSD) was formed by solution spin-coating on top of the ZnO surface, followed by thermal curing at 160 °C for 30 min, which served as a robust and adhesive thin film with sufficient solvent resistance. Therefore, it supported the sequential solution processing of multilayers in the device structure of ITO/ZnO/C-PCBSD/P3HT:PC_{61}BM(1:1,w/w)/PEDOT:PSS/Ag.\cite{1147} PSCs experienced a dramatic improvement after C-PCBSD modifying ZnO surface. PCE enhanced from 5.9% to 6.2%, with $V_{OC}$ increased from 0.58V to 0.60V, $J_{SC}$ increased from 11.6 mA/cm$^2$ to 12.8 mA/cm$^2$, $FF$ increased from 52% to 58%. Two reasons are responsible for the simultaneously enhancement of $V_{OC}$, $J_{SC}$ and $FF$. Firstly, the utilization of the C-PCBSD interlayer provides an extra P3HT/C-PCBSD interface for exciton dissociation, which is more efficient than the P3HT/ZnO interface.\cite{150,151} Furthermore, C-PCBSD with LUMO energy level (3.8 eV) located between the LUMO of P3HT (3.3 eV) and the conduction band of ZnO (4.4 eV), served as an energy gradient intermediate. It facilitated the electrons transporting to ZnO through an energetically downhill cascade pathway.\cite{152}

Device stability was also explored to further convince the favorable functionality of C-PCBSD. Pristine devices with bare ZnO showed degrading rate of 6.6×10$^{-3}$ day$^{-1}$, while after incorporating C-PCBSD, it sharply decreased to 4.1×10$^{-3}$ day$^{-1}$. Since device

Figure. 1. 15 Molecular structures of fullerene derivatives.
degradation was like to be attributed to leakage current caused by the formation of hot spots in bulk or at the interface.\textsuperscript{[153]} The hot spot could be passivated by coverage of a three-dimensional C-PCBSD network on ZnO, which in turn suppressed the leakage current and consequently improved the operational lifetime. In addition, long-term mutual penetration between ZnO and active layer would occur without this dense and robust interlayer, which might alter their chemical or physical properties.

This interface modification strategy was also applied to inverted PSCs based on P3HT as donor polymer and indene-C$_{60}$bis-adduct (ICBA) as the acceptor.\textsuperscript{[154]} Without C-PCBSD interlayer, PSCs exhibited an exceptional PCE of 4.6\%, with a high $V_{OC}$ of 0.82 V due to the higher-lying LUMO level of ICBA. With C-PCBSD incorporation, PCE significantly increased to 6.22\%, showing simultaneously enhancement of $J_{sc}$ (12.4 mA/cm$^2$), $V_{OC}$ (0.84 V) and $FF$ (60\%). However, $FF$ of 60\% is still too low to restrain the efficiency of PSCs. This is primarily due to the unfavorable BHJ phase distribution, which resulted in higher charge recombination and in turn limited $FF$. In order to provide a direct path for charge transport so as to decrease the charge carrier recombination, the ideal architecture of the donor and acceptor is the periodic, vertically aligned, and interpenetrating ordered bulk heterojunction (OBHJ).\textsuperscript{[155-158]} Therefore, anodic aluminum oxide (AAO) template-assisted approach\textsuperscript{[159-161]} was employed to construct C-PCBSD layer with vertically oriented nanorods, which created a well-organized nano-structured interface to facilitate charge transfer.\textsuperscript{[162]} PSCs devices were fabricated based on the structure of ITO/PEDOT:PSS/C-PCBSD nanorods/P3HT:ICBA/PEDOT:PSS/Ag (as shown in Figure 1.16), which showed a decent PCE of 7.3\%, with a large $FF$ of 72.3\%, $V_{OC}$ of 0.84 V, $J_{sc}$ of 12.07 mA/cm$^2$. As control group, devices with planar C-PCBSD as
interlayer were also fabricated, which exhibited a much inferior PCE of 6.2%, with a dramatically decreased $FF$ (66%) and slightly diminished $J_{sc}$ (11.17 mA/cm$^2$). The tremendous enhancement can be ascribed to the several reasons. Firstly, extra P3HT/C-PCBSD interfacial areas offered by the vertical structure of C-PCBSD nanorods ensured sufficiently exciton dissociation, generating higher photocurrent which supported by steady-state photoluminescence (PL) measurement.$^{[162]}$ Secondly, the incorporation of C-PCBSD nanorods layer raised electron mobility from $9.4 \times 10^{-4}$ cm$^2$V$^{-1}$S$^{-1}$ to $2.6 \times 10^{-4}$ cm$^2$V$^{-1}$S$^{-1}$ while maintaining the hole mobility, facilitating a more balanced charge carrier transport.

Aside from styryl functional group which can form cross-linkers through thermal annealing, oxtane functional group has also been an attractive alternative as effective cross-linker in organic electronics.$^{[163-167]}$ Favorable to radical polymerization of styryl group, which is sensitive to air and needs to be carried out in glovebox, the cationic polymerization of oxtane is much stable in air ambient. Moreover, since the ring-opening
polymerization process of oxtane features low volume shrinkage of surface layer and excellent adhesion on a substrate, the film can be formed homogeneous without microcracks or defects. Last but not least, in sharp contrast to carboxylic acid, phosphonic acid, or chlorosilane serving as anchoring groups for SAM, which may etch and degrade the surface of metal oxide in long term, neutral oxetane does not have an acidic nature and consequently gains much higher stability for PSCs devices.\textsuperscript{[168]} Based on these theories, PCBM-based n-type material, [6,6]-phenylC61-butyric oxetane dendron ester (PCBOD) was synthesized, with a small dendron containing two oxetane groups as the crosslinkers (shown in Figure 1.15).\textsuperscript{[168]} Oxtane groups in PCBOD were shown to be thermally inert from the DSC measurement, exhibiting no exothermic transition at Tg. A catalytic amount of photoacid generator (PAG) was utilized to generate acidic protons upon UV irradiation, so as to incur the cationic oxetane ring-opening polymerization. Infrared spectroscopy revealed the occurrence of cross-linking of oxetane groups after heating at 140°C for 30 min accompanied with exposure to UV light for 40 s. TiO\textsubscript{x} was chosen as electron selective and hole-blocking layer, on top of which the anchoring of oxetane groups may take place by nucleophilic attack of the hydroxyl groups on the TiO\textsubscript{x} surface to open the protonated oxetane rings, followed by the possible bidentate anchoring through the etherification condensation. Finally, a vertically multimolecular interlayer can be formed through ring-opening polymerization between oxetane groups.

As a consequence, inverted solar cell devices based on the configuration of ITO/TiO\textsubscript{x}/C-PCBOD/P3HT:PC\textsubscript{61}BM(1:1,w/w)/MoO\textsubscript{3}/Ag exhibited a decent PCE of 4.5\%, with a $V_{OC}$ of 0.61 V, a $J_{SC}$ of 12.25 mA cm\textsuperscript{-2}, and an $FF$ of 61.26\%. In clear contrast,
devices without C-PCBOD interlayer showed a much inferior PCE of 3.57%, with simultaneously diminished $V_{oc}$ (0.58 V), $J_{sc}$ (10.65 mA cm$^{-2}$) and $FF$ (57.76%). The results were in consistent with the favorable properties of C-PCBOD, demonstrating that C-PCBOD, containing two oxetane groups and simultaneously undergoing cross-linking interlayer on TiO$_x$ surface, provided a dense, robust, and pinhole-free multimolecular interlayer to address the interfacial problems in traditional inverted solar cells and improve the PSCs performance.

The last group of SAMs we will introduce is trichlorosilane functionalities. Since all the self-assembled and cross-linking fullerene derivatives described above need thermo assistance or UV illumination to trigger the reaction thus creating cross-linkers. However, the thermo or UV treatment will complicate the process of SAMs formation on top of metal oxide. Therefore, trichlorosilane functionalities, which can readily undergo facile hydrolysis to produce polysiloxane in ambient air became attractive. Due to its high reactivity and wide availability, it has been widely used in self-assembled and cross-linked monolayers for interface modification.$^{[169-175]}$ On account of the advantageous property of trichlorosilane functionalities, Liang et al. presented a new fullerene material bis(2-(trichlorosilyl)propyl)malonate C$_{60}$ (TSMC) (shown in Figure 1.15),$^{[176]}$ which can spontaneously form self-assembled and cross-linked monolayer (SA-C-TSMC) on TiO$_x$ surface upon spin-coating, without external thermal heating or UV illumination. In this SAM, Si-O-Si serves as a cross-linker between TMSC molecules. Although the process of SAM formation on metal oxide is simplified, cross-linked TSMC retained all the excellent properties its counterparts possessed: passivating the metal oxide surface, reducing the contact resistance, hindering back charge recombination at
inorganic/organic interface, controlling the upper layer phase distribution, etc. Moreover, AFM and TEM images revealed nanostructures on surface of SA-C-TSMC layer with a RMS of 5.26 nm. The vertically grown semispherical nanoaggregates comprising the cross-linked TSMC aggregates are ca. 10-30 nm in height and ca. 20-60 nm in diameter, which provided extra charge generating-interfacial area and more efficient electron transport pathways. In contrast, TiO\textsubscript{x} showed a much smooth morphology with a RMS of 3.49 nm. Therefore, inverted solar cell devices based on the configuration of ITO/TiO\textsubscript{x}/TSMC/P3HT:PC\textsubscript{61}BM(1:1,w/w)/PEDOT:PSS/Ag demonstrated an enhanced PCE from 3.2% (without interlayer) to 3.9% (with TSMC interlayer). \(V_{OC}\) raised from 0.58 V to 0.60 V, \(J_{sc}\) raised from 9.87 mA cm\textsuperscript{-2} to 10.42 mA cm\textsuperscript{-2}, \(FF\) raised from 55% to 61.7%.

1.5.3 Water/alcohol soluble polyelectrolytes

Based on the discussions in the previous context, we are familiar that most of the metal oxide or metal carbonate interlayers (ZnO, TiO\textsubscript{x}, Cs\textsubscript{2}CO\textsubscript{3}, etc) need thermal evaporating or post-annealing at high temperature, which becomes the primary limitation for the inverted PSCs due to their incompatibility with mass production. To make it compatible with the roll-to-roll processing technique, novel interlayers are in dire needed to replace the traditional metal oxide/carbonate interlayers.

In recent years, water/alcohol polyelectrolytes have been widely used as ITO surface modifier, not only due to their unique solution processing property, but also their orthogonal solubility in commonly used organic solvents for photoactive materials.\textsuperscript{[177-179]} The favorable solubility, which originates from the hydrophobic polymer back bones and hydrophilic ionic functionalities, ensures the ITO surface modifying layer would not be
destroyed by upper organic activelayer and thus realizes all solution processed PSCs. Moreover, the additional layer creates a dipole alignment at the interface, due to the specific functional groups (such as ethylene oxide, phosphonate, amino or ammonium, etc). This interfacial dipole will give rise to an increased built-in potential (and hence $V_{OC}$), at the meantime, electron transport and collection are facilitated by lowering the workfunction of cathode, which result in a better energy alignment and minimized contact resistance.

In 2010, Na et al. demonstrated highly efficient inverted solar cells by interfacial tuning via a water-soluble conjugated polymer\cite{180}. As ITO interface modifier, poly[(9,9-bis((6-(N,N,N-trimethylammonium)hexyl)-2,7-fluorene)-alt-(9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9-fluorene)) dibromide (WPF-6-oxy-F)\cite{181} was employed (the molecular structure is shown in Figure 1.17). Based on the device structure of ITO/WPF-6-oxy-F/P3HT:PCBM/MoO$_3$/Ag, dramatically raised $V_{OC}$ was observed from

![Figure 1.17 Molecular structure of WPF-6-oxy-F, PTPA-EP, PCP-NOH, PCP-EP, PC-P, P3ImHT, P3(TBP)HT$^+$Br$^-$, PFN, PFEN-Hg and PFN-OX.](image)
0.35 V to 0.655 V was reported, with enhanced $J_{sc}$ from 8.05 mA/cm$^2$ to 8.83 mA/cm$^2$, $FF$ from 37% to 59% and a corresponding PCE from 1.04% to 3.38%. The enhanced $V_{OC}$ was attributed to the favorable interfacial dipole formed by WPF-6-oxy-F interlayer, which was confirmed by kelvin probe study. Workfunction of ITO raised from 4.66V to 4.22V after modifying, which increased the built-in potential for maximizing $V_{OC}$ and minimizing contact resistance.\cite{182, 183}

Due to the excellent application of triphenylamine based cationic conjugated polyelectrolytes in PLEDs,\cite{184} Xu et al first employed triphenylamine based polyelectrolyte in inverted PSCs as electron injection layer.\cite{185} PTPA-EP (shown in Figure 1.17), comprising diethyl phosphonate end groups on side chains, shows good solubility in hydrophilic solvents. Based on the structure of ITO/(PTPA-EP)/PCDTBT:PC71BM/MoO3/Ag, efficiency exhibited significantly enhanced after PTPA-EP modified ITO surface, from 2.57% to 4.59%. In agreement with previous researches, most prominent improvement was presented in $V_{OC}$. However, efficiency is still lower than 5.13% for inverted solar cells with ZnO interlayer on ITO. Therefore, more effective electron interlayers are in urgent to replace the conventional metal oxide and metal carbonate interlayers. In 2012, Zhu et al went a breakthrough with polycarbazoles interlayer, which was motivated by the previous successful utilization of polycarbazoles as cathode interlayer in PLEDs.\cite{186} 2,7-carbazole-1,4-phenylene copolymers PCP-NOH and PCP-EP\cite{187} comprising surfactant-like diethanolamino and phosphonate end groups on the side chains of the both main chain blocks, respectively, exhibited good solubility in alcohol. By employing these two interlayers as ITO surface modifier, inverted PSCs based on poly(2,7-carbazole) (PCDTBT) as the polymer

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donor$^{188}$ and [6,6]-phenyl C$_{71}$-butyric acidmethylester(PC$_{71}$BM) as the acceptor showed improved PCE from 1.63% to 5.39% for PCP-NOH and 5.48% for PCP-EP, respectively. Later on, the same group investigated another 2,7-carbazole based polyelectrolyte as ITO surface modifier.$^{189}$ PC-P, a homopolymer of 2,7-carbazole with hydrophilic phosphonate side chains, raised PCE from control devices (bare ITO as cathode electrode) of 2.62% to 6.04% for devices with ITO/PC-P as bilayer cathode. As comparison, ZnO modified ITO surface exhibited a lower PCE (5.53%) than that of PC-P modified. The HOMO and LUMO levels of PC-P are -5.27eV and -2.39eV, respectively.$^{190}$ It is an interesting observation that PC-P could efficiently extract electrons despite the up-lying LUMO. Workfunction of ITO measured from Kelvin probe was shown to shift from -4.7eV to -4.3eV, ensuring a good electron extraction capability from PCBM to ITO. The 0.4eV vacuum level shift, caused by the interfacial dipole of 10 nm PC-P, was in agreement with the 0.38eV increment of $V_{OC}$. Moreover, the polycarbazole main chain of PC-P created a good organic−organic contact with the PCDTBT donor in activelayer, contributing to the enhancement of $J_{SC}$ and $FF$.

Aside from poly(triphenylamines) and polycarbazoles based polyelectrolytes aforementioned, another group of polyelectrolytes (polythiophene) have also been widely studied in recent years. Several kinds of cationic polythiophene derivatives have been studied in conventional PSCs as electron selective layer.$^{191-194}$ Based on such results, cationic polythiophene derivatives were utilized as ITO surface modifier in recent years. Zilberberg et al presented a conjugated polyelectrolyte poly(3-[6-(N-methylimidazolium)hexyl]thiophene) bromide P3ImHT (shown in Figure 1.17) as ultra-thin cathode interlayer.$^{195}$ Interestingly, this CPE also exhibited a similar
property with TiO$_x$ (and ZnO). UV illumination was found to be a requisite condition to avoid S-shape in $J$-$V$ curves.\textsuperscript{[196-198]} The reason for the elimination of energy barrier between interface of ITO and TiO$_x$ (and ZnO) upon UV illumination has been well studied before.\textsuperscript{[199]} The negatively charged oxygen chemisorbed at the TiO$_x$ (and ZnO) surface leads to a band bending in TiO$_x$ (and ZnO) and a depletion layer at TiO$_x$ (and ZnO) surface. Oxygen desorption at TiO$_x$ (and ZnO) surface upon UV illumination and a simultaneously lowered work function result in increased electron selectivity and $FF$. For the ITO/CPE cathode, UV illumination was shown to lead to a reduction of the ITO WF together with WF lowering due to the dipole of the CPE leads to an effective electron selective cathode. Consequently, bare ITO based inverted PSCs showed a limited PCE of 2\%, while for CPE and TiO$_x$ modified ITO based inverted PSCs, elevated PCEs were shown to be 4.8\% and 4.9\%, respectively.

In another work conducted by Worfolk et al, a cationic and water-soluble polythiophene, poly[3-(6-\{4-tert-butylpyridiniumyl\}-hexyl)thiophene-2,5-diyl bromide] P3(TBP)HT$^+$Br$^-$ (shown in Figure 1.17), combined with anionic PEDOT:PSS, serve as a versatile cathodic buffer layer through electrostatic layer-by-layer (eLBL) assembly.\textsuperscript{[200]} The cathodic interfacial buffer layer was fabricated by submerging cleaned ITO in cationic P3(TBP)HT$^+$Br$^-$ solution for 5 min, followed by immersing in anionic PEDOT:PSS solution for 5 min with intermediate rinsing steps. P3(TBP)HT:PEDOT:PSS films of $n$ bilayers was then completed by iterating the above cycle for $n$ times. Workfunction of ITO can be decreased to as low as 3.8eV after several cycles of eLBL assembly. Interestingly, the workfunction of ITO was found to oscillate between 3.8eV and 4.0eV regardless of repeated cycles, which was likely attributed to the modulation of
Another highlight for this study is the improved stability of inverted PSCs even under air ambient condition. The normalized PCE of the devices maintains 97% of its original performance after 1080 h, and even after 1500 h it remained 87% of the original performance. The presented stability was superior to other reported cathodic buffer layers studied under similar conditions. The outstanding stability was ascribed to the combination of the improved architecture of the modifier and the deeply-lying HOMO energy of the donor polymer poly({4,8-di(2-ethylhexyloxy)benzo[1,2-b:4,5-b’]dithiophene}-2,6-diyl)-alt-({5-octylthieno[3,4-c]pyrrole-4,6-dione}-1,3-diyl) (PBDTTPD).[202-207]

The last group of water/alcohol soluble polyelectrolytes we are going to present is poly[(9,9-bis(3’-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9–dioctylfluorene)] (PFN) and its derivatives. It has been reported that PFN can be incorporated into PLED to

![Figure. 1. 18 Band alignment of inverted device structure.](image-url)
enhance electron injection from high-work-function metals such as aluminum.\textsuperscript{[208, 209]} Based on such favorable property for electron transporting, PFN and its derivatives are utilized as ITO surface modifiers in inverted PSCs in recent years.\textsuperscript{[210-212]}

The most inspiring result was obtained by He et al, reaching the PCE of 9.2\% with inverted structure, which was the highest certified PCE reported by now.\textsuperscript{[210]} PFN was used as cathodic buffer layer, polythieno[3,4-b]thiophene/benzodithiophene (PTB7) as donor polymer\textsuperscript{[213]} and [6,6]-phenyl C\textsubscript{71}-butyric acid methyl ester (PC\textsubscript{71}BM) as electron acceptor. Band alignment of inverted structure was shown in Figure 1.18. The insertion of PFN between ITO and organic layer lowers the WF of ITO from 4.7eV to 4.1eV. Similar with other groups of CPEs aforementioned, the origin of the vacuum level shift in this work was the formation of the interface dipole at the ITO surface, which was the result of the orientation of PFN with a permanent dipole.\textsuperscript{[214, 215]} In this work, conventional and inverted structured PSCs were in parallelly compared. Inverted structure devices showed PCE of 9.15\%, together with $J_{sc}$ 17.2 mA/cm\textsuperscript{2}, $V_{oc}$ 0.74V and $FF$ 72\%. While conventional structure based on ITO/PEDOT:PSS/PTB7:PC\textsubscript{71}BM/PFN/Al showed a much lower $J_{sc}$ of 15.4 mA/cm\textsuperscript{2}. The drastically increased $J_{sc}$ and thus PCE of the inverted PSCs originated from multiple reasons: ohmic contact for photogenerated charge-carrier collection (due to vacuum level shift of ITO) and the optimum photo harvest in organic activelayer (shown in the energy level alignment in Figure 1.18). The enhanced optical absorption, which was a result of redistribution of electric field intensity of the incident photons in activelayer, was verified by one-dimensional transfer matrix formalism (TMF) measurement.
Generally speaking, polymeric interface materials possess advantages of easy solution processing and good film formation, which make them attractive to academic research and industrial production. However, their drawback such as low conductivity renders a strong inverted PSCs performance on thickness of the interlayer. Thin films are regarded to be necessary for a decent performance, which, on the contrary, makes large area production of PSCs challenging. To figure out such problems, Liu et al designed a novel polymeric interlayer material based on a conjugated metallopolymer: Hg-containing derivative of amino-functionalized conjugated polymers PFEN-Hg (shown in Figure 1.17).\cite{212} This novel conjugated polymer retained all the favorable properties of its CPEs colleagues, while the introduction of Hg endows it additional advantages. The strong intermolecular, noncovalent Hg-Hg interactions increase the packing of the PFEN-Hg thin film,\cite{216} which boosts the electron transport capabilities and therefore makes relatively insensitive compared to its CPEs colleagues. In this work, PFN-ox (molecular structure shown in Figure 1.17) and PFEN-Hg were compared. As confirmed by $J$-$V$ curves shown in Figure 1.19, device performance exhibited drastic change when
the thickness of PFN-ox increase from 4 nm to 7 nm, with dramatically increased PCE from 9.03% to 1.02%. Whereas, devices with a wide range of PFEN-Hg thickness showed a small variation of PCE from 8.64% to 9.11%, even though the thickness of PFEN-Hg increased to 19 nm. The highest PCE of 9.11% was observed from 13 nm PFEN-Hg.

It is noteworthy that apart from single polymeric interlayer serving as ITO surface modifier, a quantity of metal oxide/CPE bilayer ITO surface modifiers were reported.\textsuperscript{[217-220]} Based on the same principle, polymer back bones which exhibit hydrophobic property will preferentially orient to the side of organic active layer, while negative counterions with hydrophilic property will orient to the metal oxide. This spontaneous orientation leads to the formation of a strong interfacial dipole, which will lower the conduction band of metal oxide and correspondingly facilitate the electron transport.

One of the most dramatically improvement of device performance was demonstrated by Yang et al.\textsuperscript{[217]} Based on the device structure of ITO/ZnO (PFN-Br)/PBDT-DTNT:PC_{71}BM/ MoO_{3}/ Al, PCE increased from 6.1% (control device) to 8.4% (PFN-Br modified), with simultaneously enhancement of \(V_{OC}\), \(J_{SC}\) and \(FF\). The LUMO energy levels estimated from ultraviolet photoelectron spectroscopy (UPS) were -4.46 eV for ZnO thin film and -4.08 eV for ZnO/PFB-Br, respectively.\textsuperscript{[221]} The up-shift of the LUMO energy level of ZnO/PFN-Br eliminated the previous energy barrier between the LUMO of PC_{71}BM and conduction band of ZnO, which anticipated a larger \(V_{OC}\) after CPE modification. In addition, from the dark \(J-V\) curves of inverted PSCs with/without PFN-Br, PSCs with PFN-Br exhibited nearly 10 times smaller dark current than that of
PSCs without PFN-Br. The lowered dark current densities not only indicated a larger $V_{OC}$, but also suggested the bimolecular recombination was suppressed by PFN-Br interfacial layer. In ref.220, this assumption was confirmed by photoluminescence measurement (PL) of P3HT/ (CPE)/TiO$_x$ thin films. A remarkably raised PL quenching ($\approx$25%) of P3HT can be observed after incorporating CPE layer. This result verified the diminished bimolecular recombination and enhanced photoinduced charge transfer at CPE interfacial layer, manifesting boosted $J_{sc}$ and $FF$.

Moreover, Choi et al verified that insertion a thin layer of CPE can increase the hydrophobicity of TiO$_x$, due to the measurement that contact angle increased from 33$^\circ$ to 50$^\circ$ after CPE modification.$^{[220]}$ This indicated the TiO$_x$/CPE was more favorable for the wetting of the upper active layer. In addition, the TiO$_x$ surface exhibited smoother after CPE modification. Root-mean-squared (rms) roughness for TiO$_x$ was 2.80 nm, while for TiO$_x$/CPE that value decreased to 2.05 nm. It confirmed that a much better interfacial contact was formed, which predicted a lower leakage current and reduced defects. Through the favorable modification of the metal oxide surface, $FF$ was anticipated to increase, which circumvent one of the major limitations for inverted PSCs.

In conclusion, CPEs are promising candidate to replace or modify the metal oxide or metal carbonate electron extraction layers. Significant enhancement of $V_{OC}$ is due to the dipole moment created between the cathode/BHJ composite interlayer. Moreover, CPEs are also able to increase the hydrophobicity of the ITO or metal oxide/metal carbonate layer, which are preferable for the interfacial contact and thus facilitate the electron transport. Furthermore, charge carrier recombination can be also suppressed by the introduction of CPEs.
1.6 Processing Active Layer

As the name “inverted” indicates, the electric polarity is opposite to conventional structure, which means the driving directions of holes and electrons are upside down from conventional architectures. In PSCs, the free charge carriers mainly originate from the dissociation of photo-induced excitons in active layer. To effectively and efficiently dissociate the excitons, BHJ concept was introduced,[222-224] which can not only provide sufficient D/A interfaces for charge dissociation, but also serve as efficient pathways for transportation of electrons and holes. However, due to the different surface energy of donor polymer and fullerene derivatives, inhomogeneous distribution or concentration gradient will be formed through the thin film, which causes the vertical phase separation. Isolated islands will consequently be formed and block the carrier transport to the respective electrodes. For instance, the surface energy of the donor polymer is generally lower than that of the fullerene derivatives (PCBM), which will give rise to an aggregation of the polymer at the top surface. As a consequence, the p-type polymer will hinder the transport of electrons to the upper cathode electrode in conventional PSCs. In clear contrast, in inverted PSCs, where the top electrode is anode, such vertical phase separation is favorable for the hole transport and preventing charge carrier recombination at anode electrode. This is the reason for the much improved $J_{sc}$ in inverted PSCs than that of conventional PSCs. Furthermore, this structure is still far away from the ideal comb-like structure for PSCs.[225] Therefore, achieving a better ordered vertical structure in the active layer is necessary for the further improvement of inverted PSCs performance. In this section, we’ll introduce four ways to enhance the ordering of BHJ composite.
1.6.1 Thermal annealing

Thermal annealing is a common process for improving the morphology. Xu et al.\cite{226} conducted a series of experiments to study the influence of thermal annealing on the compositions at the top and bottom surfaces of the blend films by using X-ray photoelectron spectroscopy (XPS). P3HT:PCBM blend film coated on both glass and Cs$_2$CO$_3$ were experienced fast-grown, fast-grown with anneal, slow-grown, slow-grown with anneal, respectively. The weight ratios of P3HT and PCBM were detected by using C/S atomic ratios from the XPS measurement. Both fast-grown and slow-grown film showed similar results, with higher PCBM concentration at the bottom surface. However, upon thermal annealing, PCBM concentrations at both sides of the fast-grown films decrease slightly while the slow-grown films remains invariable, predicting more thermodynamically stable for slow-grown films. Moreover, the PCBM concentration at the Cs$_2$CO$_3$/polymer interfaces is higher than those at the glass/polymer interfaces, illustrating the Cs$_2$CO$_3$ increased the vertical separation in BHJ composite. Similar to the results in glass based substrate, blend films on Cs$_2$CO$_3$ also exhibited enhanced inhomogeneous distribution after thermal annealing. PCBM to P3HT ratio at the Cs$_2$CO$_3$ side increased over one- and two-fold in the fast and slow-grown films, respectively, with only slightly decrease at the top surfaces. In this paper, the author also proposed the idea that not only surface energy contributed to the PCBM aggregation on bottom surface, but also charge transfer process plays a critical role. The idea was supported by XPS measurement, which showed a significant binding energy shift (~0.5 eV) to lower binding energy for Cs after spin-coating an ultra-thin PCBM layer and consequently resulted in a substantial charge transfer. And the results were also consistent with the
previous study from Ohno et al.\textsuperscript{[227]} The charge transfer process was originated from the dipole formed by Cs$_2$CO$_3$ on ITO substrate, which induced dipole-dipole interaction between PCBM and Cs$_2$CO$_3$. It is noteworthy that the PCBM segregation became even strong after annealing. Since the annealing process will provide driving force for the polymer film to achieve a more thermodynamically favorable morphology.

Later on, Orimo et al.\textsuperscript{[228]} demonstrated that pre-annealing of the active layer before thermal deposition of metal electrode and post-annealing after thermal deposition would cause significant difference to the morphology of the BHJ composite. From XPS measurements, it exhibited that the surface fraction of PCBM at the interface between the active blend layer and the Al electrode is as low as 31\% in the pre-annealing device but is enhanced to 72\% in the post-annealing device. The much higher PCBM concentration for post-annealing device was likely attributed to the larger diffusion constant of small molecules (PCBM) than that of polymer chains. This deduction can be further supported by the study from Ma et al.,\textsuperscript{[229]} which showed a reduced efficiency for conventional devices with pre-annealing of P3HT:PCBM film however an increased ones with post-annealing. Therefore, we may conclude that the pre-annealing for organic active layer before thermal deposition is preferable for conventional device structures, while post-annealing are advantageous for the inverted ones.

Nevertheless, Kang et al demonstrated a different result.\textsuperscript{[230]} Based on the device structure of ITO/WPF-oxy-F/P3HT:PCBM/PEDOT:PSS/Ag, PCE was demonstrated to increase from 2.13\% for the pristine devices to 3.86\% for the post-annealing ones under 170°C. By studying the annealing sequences for different layers, it was found that the most correlated interface is the active/PEDOT:PSS/Ag layer. $V_{oc}$ was slightly enhanced
due to increased workfunction of PEDOT:PSS/Ag with raising temperature from 110°C to 170°C, which was confirmed by Kelvin Prove measurement. Consequently, good ohmic contact can be formed between PEDOT:PSS/Ag and P3HT, resulting in an increased $V_{OC}$ and reduced $R_S$. Moreover, $R_{sh}$ was also shown to be increased by two orders of magnitude after 170°C annealing, which was originated from the smaller leakage current at negative voltage and low positive voltage. The combined reduced $R_S$ and increased $R_{sh}$ resulted in an enhanced $FF$ and thus PCE. Based on this research, we may conclude that post-annealing process will not only influence the vertical charge separation between donor and acceptor, but also change the interfacial properties. Therefore, due to the different device structure (i.e. anode/anode buffer layer and cathode/cathode buffer layer), different annealing sequences should be chosen to optimize the PSCs performance.

**1.6.2 External electric field**

It has been reported that the external bias imposed on the PSCs devices can enhance the efficiency of PSCs due to the better arrangement of conjugated polymers in organic active layer.$^{231, 232}$ However, the reason for the improved performance cannot be well elucidated, since the extra charges injected by the external field can also fill in the defects in organic layer, which can attribute to the enhanced PSCs performance as well.$^{233}$ Different from directly exerting external electric field through the electrodes, Ma et al studied the influence of external bias from two parallel metal plates on the performance of inverted PSCs.$^{234}$ The inverted device structure was as follows: ITO/ZnO/P3HT:PCBM/NiO/Ag, the external field was applied in the slow-drying process of P3HT:PCBM active layer. Devices were placed between two parallel metal
plates with bias voltage applied to them, forming an electric field perpendicular to the devices, as shown in **Figure 1.20**. The forward electric field was defined as the direction from glass to the active layer, and the opposite was defined as the backward electric field.

The controlled PSCs device without external field showed PCE of 3.16%. With the backward electric field treatment, the efficiency was improved to 3.23% and 3.51% for field strength increasing to $2.5 \times 10^5$ and $5.0 \times 10^5$ V/m, respectively. On the contrary, with the forward electric field treatment, the efficiency decreased to 3.09% and 3.04% corresponding to the same electric field strength. $J_{sc}$ and FFs increased with the raising backward electric field, which was caused by different vertical composition due to the external electric field treatment.

**Figure 1.21** shows the different vertical phase separation with different electric field treatments. Since the electric field causes the polarity of the polymer, leading to well-ordered polymer chains and PCBM side chains. This formation facilitated the charge transportation and therefore resulted in enhanced $J_{sc}$. Moreover, the polarity direction of PCBM points to its fullerene structure, so with the backward electric field, the side chains of PCBM will be aligned upward to restrain the diffusion of PCBM to the top. Also the
backward electric field decreased the tendency for self-assembled PCBM forming cluster on the top surface. Consequently, the backward electric field helps the formation of P3HT-rich domains at the top surface and PCBM-rich domains at the bottom. The P3HT-rich layer provides more channels for holes to transport and reduced the probability of electron hole recombination. Thus, the current leakage was decreased, which led to increased shunt resistance and consequently enhanced FFs. On the contrary, the forward electric treatment has the opposite influence on the vertical phase distribution. It forms the P3HT-rich surface at the bottom and PCBM-rich surface on the top which has negative effect for inverted structure.

1.6.3 Solvent additives

Inspired by the previous work of applying different solvents in the BHJ composite, which controlled the formation of thin film morphology,[235] Yao et al were the first to utilize solvent additives to better tune the nano-scaled domain size in the active layer.[236] High boiling solvent additive 1,8-octanediithiol (OT) was used with the combination of low boiling point solvent DCB. From the thin film morphology studies, a vertical phase separation was occurred during the spin-coating process, supported by the AFM images and XPS measurement. Highly ordered domains of P3HT were observed from BHJ
composites with OT addition, which was supposed to facilitate the hole transportation in inverted PSCs. It’s noteworthy that in this work, conventional structure was utilizing, therefore, we focus on the influence of solvent additives on the thin film morphology. A model was proposed in Figure 1.22 in order to explain the formation of this vertical phase separation. In Figure 1.22 (a) to (c), the P3HT and PCBM dissolved in the DCB, polymer chains extend freely in the solvent and there is not any interaction with DCB. During spin-coating, PCBM molecules are dispersed between P3HT chains, breaking the ordering of PEHT chains. However, with incorporation additive OT, the film showed much ordered phase separation (as shown in Figure 1.22d-f), which was likely due to the following reasons. Since DCB has much higher vapor pressure at room temperature than
that of OT, DCB will evaporate much faster than OT during spin-coating, causing gradually increased concentration of OT. And due to the limited solubility of PCBM in OT, PCBM will form clusters and aggregate in the OT phase. Then, the higher surface energy of PCBM than that of P3HT led to rich PCBM distribution at the bottom of the active layer, which lowered the concentration of PCBM in the upper thin film. Therefore, P3HT chains are able to self-organize to a favorable state.\textsuperscript{[237]} In summary, the PCBM aggregates formed at the bottom surface not only provide a percolation pathway for electron transport, but also caused P3HT crystallites creating percolation pathways for hole transport.

Later on, Lin et al applied this BHJ system in inverted PSCs.\textsuperscript{[238]} Poly[2,1,3-benzothiadiazole-4,7-diyli][4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4 b']dithiophene-2,6-diyli]] (PCPDTBT) was used as donor polymer and PC\textsubscript{71}BM as electron acceptor. By adding high boiling solvent additive 1,8-octanedithiol (1,8-ODT) in DCB, PCE increased from 2.09% to 3.00%. Great enhancement was observed from $J_{sc}$ (from 9.89 mA/cm$^2$ to 12.84 mA/cm$^2$), which can be explained from absorption spectra. Additional peak was induced at long wavelength upon the introduction of the processing additive. Moreover, the redshift of the absorption spectrum indicated a stronger PCPDTBT chain interaction due to the incorporation of ODT and enhanced local order within the polymer phase.\textsuperscript{[239]} Similarly, Chen et al employed mixed solvent of CB/DCB with DIO additive in inverted PSCs.\textsuperscript{[240]} Based the structure of ITO/ZnO/PBDTTT-C:PC\textsubscript{71}BM/MoO$_3$/Ag, PCE increased from 0.92% (BHJ composites from pure CB) to 4.43% (BHJ composites from wt% 1:1 DCB:CB+2% DIO). $J_{sc}$ contributed to the majority part of enhancement, raising from 3.78 mA/cm$^2$ to 11.82
mA/cm². The origins for the dramatic enhancement were demonstrated as the additional peak induced by mixed solvents and redshift of absorption spectrum as discussed before.

1.7 Top Anode Electrode

We’ve addressed charge collection at interface of cathode electrode and activelayer in the previous part. However, charge collection at the anode electrode and activelayer interface is also an important factor determining PSCs performance. For single component photovoltaic devices, $V_{OC}$ was demonstrated to scale with the difference between workfunction of cathode and anode electrode, which follows the metal-insulator-metal (MIM) model.\[^{[241]}\] However, this concept holds true only under the condition of non-ohmic contact (meaning the workfunctions of anode and cathode electrode are found in the middle of the semiconductor bandgap). Based on this principle, $V_{OC}$ for BHJ solar cells scales linearly with difference between workfunction of two electrodes under non-ohmic contact. Whereas under the case of ohmic contact, $V_{OC}$ was reported to exhibit a strong coupling with the reduction potential of the acceptor. Hau et al conducted their work to investigate the influence of different top electrodes on inverted PSCs performance.\[^{[242]}\] Based on the structure of ITO/ZnO/P3HT:PCBM/top electrode, without PEDOT:PSS as hole transporting layer, $V_{OC}$ showed a linear relationship with anode workfunction, with a slope of 0.6. However, after incorporating hole transporting layer PEDOT:PSS between anode electrode and activelayer, $V_{OC}$ remained almost invariant with different anode electrode. This was consistent with the result reported by Brabec,\[^{[243]}\] indicated the ohmic contact was formed between PEDOT:PSS and organic layer dominated the interface. Such finding demonstrated the possibility to utilize inexpensive materials as anode electrodes for large-scale fabrication of PSCs.
1.7.1 Silver nanowires

In recent years, flexible transparent conducting electrodes (TCEs) have garnered close attention due to the advances in technologies for flexible opto-electronic devices, which require highly transparent conducting material for both top and bottom electrodes.\cite{244-246} Moreover, the transparent top electrode enables the substitution of ITO with much cheaper opaque substrate, such as insulated steel or metal covered glass. Nanostructured conducting materials such as silver nanowires (Ag-NWs),\cite{247-251} carbon nanotubes (CNTs),\cite{252} graphenes\cite{253} and highly conductive polymers,\cite{254-256} which are fabricated from the latest state-of-the-art technologies, have been developed as flexible TCEs to conquer the disadvantages of the conventional electrodes, such as brittleness or low conductivity.\cite{257-259} Among them, Ag-NWs stand out as the one of the most promising candidate due to their much higher transmittances and conductivity (10-20 Ω/sq with 85% transmissivity over the wave length from 400-800 nm) over CNTs and graphenes.\cite{247} Therefore, in the following context, we’ll focus on the development of Ag-NWs as top electrode in inverted PSCs.

In 2008, Ag-NWs was first investigated by Peumanns and his co-workers, as a substitution of ITO.\cite{247} They observed a low shunt resistance of less than 1 kΩcm², with a PCE of only 0.38%. The lower efficiency was chiefly due to the leakage current, which was the result of the extremely rough Ag-NWs electrode. They subsequently reported a fully solution processed inverted PSCs with laminated Ag-NWs as top electrode, in which the rough morphology of Ag-NWs will be less detrimental to other layers.\cite{260} Moreover, to further mitigate this harmful influence, the Ag nanowire films are pressed with a clean glass substrate to flatten the nanowire mesh prior to lamination.
Consequently, a much higher PCE of 2.5% was obtained, with *FF* of 46%. It is noteworthy that in this work, metal (Ag) substrate was used as cathode electrode, which served as an adequate barrier to moisture and oxygen in contrast to the transparent plastic.\[261,262\] Even though the efficiency was much improved, *FF* of 46% is still much lower than inverted PSCs with vacuum-deposited electrodes. It was obvious that the limited *FF* was ascribed to the inherent roughness Ag-NWs layer, which was not compatible with the thin film devices. In 2011, the same group successfully solved the significant morphology issue of Ag-NWs through embedding Ag-NWs into conductive polymer PEDOT:PSS, creating inorganic-organic composite.\[263\] Based on such design, the thick junctions between wires will be away from the active layer, avoiding it from being local thinning. Moreover, conductive PEDOT:PSS could fill the gaps between nanowires, which will not only smooth the surface of Ag-NWs, but also increase the conductivity of Ag-NWs. In this work, embedded Ag-NWs in PEDOT:PSS was employed as bottom electrode in conventional structure PSCs, which gave rise to a significant enhancement in performance. Similar efforts to improve the properties of Ag-NWs were also paid by other groups in recent years, and the applications of such technology were pervasive in conventional structure PSCs and PLEDs.\[264,265\] Later on, it was employed in visible transparent inverted PSCs by Yang’s group.\[266\] They successfully demonstrated high performance, visible transparent PSCs fabricated from all-solution process. It is noteworthy that Ag-NWs fused with TiO₂ NPs and PEDOT:PSS was used as top electrode. As introduced in their previous work, Ag-NWs was treated by TiO₂ sol-gel and PEDOT:PSS solution sequentially.\[267\] Since tighter contact between crossed Ag NWs and improved film conductivity can be achieved by TiO₂ solution
volume shrinkage and solvent evaporation, which result in capillary force. While the PEDOT:PSS coating act as a protecting layer for strong adhesion. Consequently, the treatment resulted in a highly conductive Ag-NW composite films possessing excellent optical transparency (over 80% in visible region) and mechanical properties. Finally, they achieved a decent PCE over 4% with a low band gap polymer poly(2,6’-4,8-bis(5-ethylhexylthienyl)benzo-[1,2-b;3,4-b]dithiophene-alt-5-dibutyloctyl-3,6-bis(5-bromothiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione) (PBDTT-DPP),\textsuperscript{[268]} which has a strong photosensitivity in the NIR range (650~850 nm), however owns a high transmission in the visible range. Later in 2013, Rein et al demonstrated semi-transparent solar cells as well.\textsuperscript{[251]} In their work, the author compared two anode buffer layers for solution processed Ag-NWs top electrode, and presented the high conductive PEDOT:PSS (550 S/cm) showed a much enhanced PCE compared to the lower conductive $V_2O_5$ ($<<10^{-3}$ S/cm). It indicated that higher conductive material serves as a more effective medium for the connecting of Ag-NWs. Consequently, a highest PCE of 2.37% for the semi-transparent solar cells was observed from PEDOT:PSS/Ag-NWs top electrode, which is comparable the efficiency of devices incorporating an opaque electrode.

1.7.2 PEDOT:PSS

Another efficient and attractive candidate for top electrode in inverted PSCs is the conductive material PEDOT:PSS, which has been widely utilized as top electrode in recent years. In 2008, Zhou et al\textsuperscript{[269]} first reported the high conductivity PEDOT (PH500) as anode electrode in inverted and transparent PSCs, with all-solution processing. PEO was used as ITO surface modifier to increase $V_{oc}$ by lowering the WF of ITO. An
efficiency of 0.7% was obtained by this device structure. However, the relatively low PCE was attributed to the less efficient absorption and the WF of cathode, which can be further improved to a lower value. Afterwards, Hau et al demonstrated the utilization of PEDOT:PSS as bottom and top electrode respectively and together.\cite{270} They presented that the addition of high boiling point polar compounds or solvents (diethylene glycol, ethylene glycol, dimethylsulfoxide, sorbitol, mannitol, glycerol) into the solution mixture can improve the conductivity of PEDOT:PSS by two or three orders.\cite{271} In this work, DMSO was added and increased the conductivity of PEDOT:PSS to 300~600 S/cm. When PEDOT:PSS-DMSO was used as bottom electrode to replace ITO, they found that increasing the thickness of PEDOT:PSS-DMSO resulted in the reduction of transparency and sheet resistance, which lowered the photocurrent whereas increased the FF. By tuning the thickness of PEDOT:DMSO cathode electrode, and applying Ag as anode electrode, PCE can be saturated to ~3%. Furthermore, when PEDOT:PSS-DMSO electrode applied to flexible substrate, it showed much superior mechanical properties than ITO, exhibiting improved PCE retention (92%) over that of ITO (50%) after cyclic bending test. In the architecture of using ITO as cathode electrode and PEDOT:PSS-DMSO as anode electrode, the average efficiency was demonstrated to be 2.51%, while replacement of both ITO and Ag with PEDOT:PSS showed a low efficiency of 0.47%.

Later on, similar structures and processing methods of PEDOT:PSS were reported by other groups.\cite{272-274} However, using PEDOT:PSS as transparent top electrode is severely hampered by poor wettability of this hydrophilic material dispersions on hydrophobic organic active layer surfaces. To solve this problem, Zhou et al. used a combination of a
modified PEDOT:PSS (Clevios CPP 105D) and PH1000 to increase the hydrophobicity of PEDOT:PSS and enabled it spin coating on organic activlayer surface.\textsuperscript{[274]} Alternative technique to overcome this incompatible surface potential was using stamp transfer lamination of dry PEDOT:PSS film, which was conducted by Gupta et al.\textsuperscript{[275]} They demonstrated a high conducting (900 S/cm) PEDOT:PSS (PH1000) layer, deposited by a stamp-transfer lamination technique using a poly(dimethylsiloxane) (PDMS) stamp. And to further minimize resistive losses in large area devices, PEDOT:PSS was incorporated with an Ag grid electrode, providing a proficient and versatile transparent top contact.\textsuperscript{[275, 276]} The processing procedure was shown in Figure 1.23. The resulting PCE was 2.35%, with $J_{SC}$ of 9.39 mA/cm$^2$, $V_{OC}$ of 0.54V and $FF$ of 48%. Even though a relatively lower value of $FF$ was obtained, which was originated from the leakage pathways from the non-optimized interfacial contact, it still provided a possible way to gear up the utilization of PEDOT:PSS as an more efficient and compatible electrode in inverted PSCs.

1.7.3 Dielectric/metal/dielectric structure

Since the transparent top cathode composed by thin-film of metal layer such as Ag/Al and Ag/Au has low transmittance (<60%), meaning that more than 40% of the incident light is reflected at the surface of top electrode, which contributes to the low PCE (1.1%) for PSCs.\textsuperscript{[278, 279]} Therefore, the low transmittance of the top electrode
becomes the main obstacles for achieving high performance PSCs. To circumvent this problem, a series top electrodes utilizing dielectric/metal/dielectric structure were developed.

In 2009, Tao et al first demonstrated D$_1$MD$_2$ structure with a high optical transmittance (>75%) in visible region by thermal evaporation, where Ag sandwiched between different thickness of MoO$_3$.\[280] The inner MoO$_3$ layer was utilized as hole-transporting and electron-blocking layer. The outer MoO$_3$ layer is used not only as a top-capping layer to enhance light coupling, but also lower the series resistance of photovoltaic devices. This is because the MoO$_3$/Ag anode would cause a large amount of internal reflection at the metal/air interface due to the large refractive index mismatches.\[281] However, the top MoO$_3$ layer could serve as a transparent conducting index matching layer to enhance the total transmission due to the higher refractive index of MoO$_3$ (~2.1).\[282] Therefore, by tuning the thickness of the outside MoO$_3$ layer to the optimum condition (MoO$_3$/Ag/MoO$_3$ 1/10/20nm), transmittance increased in the visible region compared to MoO$_3$/Ag anode electrode. As a consequence, device structure based on ITO/nc-TiO$_2$ (nanocrystalline titanium oxide)/P3HT:PCBM/MoO$_3$/Ag/MoO$_3$ showed superior PCE of 1.40% compared to that of MoO$_3$/Ag anode electrode (1.04%). However, $J_{sc}$ decreased from slightly from 4.04 mA/cm$^2$ to 3.85 mA/cm$^2$, which was due to the lower reflectivity of MoO$_3$/Ag/MoO$_3$ in wavelength range of 400-650 nm.

Even though the PCE from the multilayer anode electrode was not inspiring, it still provided a promising alternative for the transparent top electrode for inverted PSCs. And three critical requirements can be summarized for effective transparent top electrode: firstly, the thin dielectric layer adjacent to the organic activelayer serves to transport holes
and block electrons, which should form an Ohmic contact with the photoactive layer\textsuperscript{[283, 284]}; secondly, tuning the thickness of Ag is pretty important for balancing the sheet resistance and optical transmittance; finally, the outer dielectric layer incorporated as a light coupling layer to tune the optical properties of the anode electrode and particularly mitigate deleterious reflections caused by the large mismatch of refractive indices at the Ag/air interface.\textsuperscript{[275-287]}

Based on these principles, Jin et al successfully demonstrated the application of DMD top electrode in large area PSCs in 25.0 cm\(^2\) monolithic sub-modules.\textsuperscript{[288]} The optimized MoO\(_3\)/Ag/ MoO\(_3\) showed an optical transmission of 80\% at 520 nm, sheet resistance of \(\sim5\) \(\Omega/\text{sq.}\) PSCs devices based on the structure of Glass/Al/PCDTBT:PC\(_{71}\)BM/ MoO\(_3\)/Ag/MoO\(_3\) displayed PCE of 3.17\% in large scale, which outperformed the equivalent conventional ITO/PEDOT:PSS devices. FFs from large area devices with DMD electrode maintained almost unchanged with the laboratory-scale cells, while control ITO-PEDOT:PSS cells show a dramatic loss in FF to <30\% when fabricated on large-scale. This indicated that at large scale, the power loss in an organic solar cell is derived from the anode whose sheet resistance becomes the only area-scaling parameter. Consequently, this study opens new opportunities to create modules and sub-modules with high geometric FFs and more efficient use of substrate area.

This series of DMD structures were also utilized in inverted PSCs as bottom electrode for ITO-free cells or in conventional semi-transparent PSCs, which also exhibited promising results.\textsuperscript{[289-291]} Therefore, further studies of multilayer transparent electrode are necessary for the realization of large scale and transparent PSCs.
1.8 Device Stability

As a clean, renewable and low-cost alternative for traditional inorganic solar cells, PSCs stand out mainly because of its advantages above. However, to further commercialization, some shortcomings of PSCs should also be considered. Among them, stability is a big issue. Generally, in the conventional structure, active layer was inserted between PEDOT:PSS and low-WF metal. However, such structure meets a challenge that it may not maintain enough good stability under ambient air and moisture. Generally, the stability of PSCs can be divided into air stability and thermal stability. For air stability, the degradation of device mainly results from the diffusion of oxygen and moisture, leading to the oxidation of aluminum cathode and active layer. For thermal stability, the phase-separated morphology of the blends are not very thermodynamically stable due the fact that the materials still have a certain degree of freedom to diffuse slowly or recrystallize over time.

To solve this problem, inverted PSCs were introduced. As mentioned above, in this structure, stable ETL, HTL and high-WF metal were introduced to replace the unstable PEDOT:PSS and low-WF metals. We give some explanations on the influences of these materials to the device stability.

1.8.1 Shelf stability

The most widely used metal electrode of PSCs is low WF metal aluminum and calcium, which is highly reactive to oxygen and moisture to form insulated oxide. Among them, the dominant degradation is the diffusion of water through pores in the metal and reaction to form metal oxide, such as Al₂O₃. This oxide is insulated and created a
transport barrier for charge carriers. In the inverted devices, silver is the ideal electrode because it is less reactive than Al and not prone to be degraded by oxygen and water. Also, oxygen is another factor to cause the reaction of Al₂O₃. Frederik C. Krebs and Kion Norrman\textsuperscript{[292-294]} did a systematic work on the oxygen induced degradation by using TOF-SIMS (Time of flying-secondary ion mass spectrometry) methodologies for over 13,000 hours. They demonstrated that there are two main passages for oxygen diffusion into the devices: a. through pinpoles or between grains in the Al cathode; b. through the edge between aluminum and active layer. On the other hand, Al is believed to gradually dissolve in the constituents of the active layer and form kinds of organoaluminum species and react with oxygen forming Al₂O₃, especially at the Al/C₆₀ interface, which was confirmed by using isotope \textsuperscript{18}O marking method. While by replacing Al with Silver in inverted PSCs, the inert metal electrode may solve all this problems.

Steven K. Hau, Hin-Lap Yip et al.\textsuperscript{[295]} has compared the stability between the forward structure using Al as the ETL and inverted structure using ZnO as ETL. They used the high temperature sol-gel processed ZnO inverted device using a P3HT: PCBM weight ratio of 1:0.6 (~200 nm) giving an average power conversion efficiency (PCE) of ~3.5%. Several plots are shown below including PCE, \textit{Jsc} (short circuit current density), \textit{VOC} (open circuit voltage) and fill factor. All of the four parameters of conventional PSCs have a dramatic decline showing the degradation in the first 5 days, while the inverted PSCs still maintain over 90% performance.

Generally, the PEDOT:PSS is the most popular material as the hole transport layer in the world. The solution of PEDOT: PSS is acidic and usually with a pH of 1-3, which is very corrosive to the low work function electrode metal such as Al and Ca, as well as the
ITO electrode. Kawano et al. studied the effect of the PEDOT:PSS layer on the degradation of MDMO-PPV solar cells and they find a large difference in stability between the condition of humid and dry. The humid condition leads to a rapid degradation either in air or in nitrogen. For device of PEDOT:PSS free, the degradation becomes slower. The author concludes that the hygroscopic PEDOT:PSS layer takes up water from the atmosphere increasing the sheet resistance. Another research on the role of PEDOT:PSS in cathode oxidation by Voroshazi et al. concludes that it will enhance the oxidation due to its hygroscopic nature. In the inverted structure, TMOs such as MoO$_3$ is deposited as the hole transport layer instead of the acid layer improve the stability. Hancox et al. have find the life time increase of small molecule solar cells with a MoO$_x$ hole-transport layer.

1.8.2 Operation stability

Our group has investigated the operation stability for the general inverted PSCs with architecture of: ITO/ ZnO/ Active Layer/ MoO$_x$/ Ag/ Al. As shown in Figure 1.25,$^{[296]}$ inverted PSCs with ZnO buffer layer did not show obviously degradations in $J_{sc}$ , $V_{oc}$ and $FF$ after continuously illuminating the devices for 4 h. However, for the inverted PSCs without ZnO buffer layer, significant degradations in $V_{oc}$, $FF$ and $J_{sc}$ were observed after continuously illuminating the devices only for 1 h. All these results indicate that inverted PSCs by using ZnO as the buffer layer have a good operational stability, and the inverted PSCs without ZnO buffer layer are unstable under the illumination condition. By studying the absorption of ZnO, we conclude that a good operational stability of inverted PSCs with ZnO buffer layer is probably originated from the ZnO block the UV light resulting in a negligible UV light induced photodegradation.
of organic materials. A significant degradation observed from inverted PSCs without ZnO buffer layer is attributed to the UV light induced photodegradation because UV light directly shining the organic layer through ITO electrode.

1.9 Figure of merit

The performance of a solar cell is characterized by measuring the current density to voltage (J-V) characteristics under illumination with the AM1.5G solar spectrum (1000 W/m²) at a temperature of 25 °C (Figure 1.26a), where AM1.5G is short for air mass 1.5 global, referring to the mass of air that solar light has to travel through being 1.5 times larger than for light incident at zenith (i.e. on a surface facing the sun with a solar zenith angle of 48.2°). Figure 1.26b display the general J-V curve of a solar cell.

The power conversion efficiency (PCE) is defined as a measure of the degree of incident sunlight being converted into electricity and is calculated from the equation:

\[ PCE = \frac{V_{OC} \cdot J_{SC} \cdot FF}{P_{in}} = \frac{P_{MPP}}{P_{in}} \]

Where the open circuit voltage \((V_{OC})\) is the potential when the current is zero and the
short circuit current ($J_{SC}$) is the maximum current that can run through the device. The fill factor ($FF$) is determined by the resistances present in the cell indicating the ease of charge collection and the amount of leakage current in the device. FF can be calculated as the ratio between maximum power point ($P_{MPP}$) and the theoretically maximum obtainable power density ($P_{max}$):

$$FF = \frac{P_{MPP}}{P_{in}} = \frac{V_{MPP} \cdot J_{MPP}}{V_{OC} \cdot J_{SC}}$$

The incident light power density ($P_{in}$) used for determining the $J$-$V$ curve is standardized according to the Air Mass (AM) 1.5 standard resembling the sunlight from a solar zenith angle of 48.19° at sea level. This is similar to the sun light in northern Europe and northern America.

1.10 Conclusion

In conclusion, to further improve the device stability for PSCs, inverted PSCs was invented by introducing more air-stable TMOs and high-WF metals, and change the electrical polarity of the devices, benifitting the vertical phase separation in active layer. In order to further increase the PCE, modification materials were inserted between organic/inorganic interfaces to decrease the series resistance and optimize the electrical coherence. Moreover, on the angle of fabrication cost, the high WF electrodes also allow for the potential for coating the top metal electrode by a printing and coating processes that will help to further minimize fabrication costs. Above all, an integrated engineering approach to develop materials, devices and improve the interfaces and processing to improve the device performance of the inverted PSCs is described. Consequently, lower-cost, more stable and higher performance inverted PSCs show a dramatic prospecting future in energy market.
CHAPTER II

SOLUTION-PROCESSED IRON (II,III) OXIDE MAGNETIC NANOPARTICLE THIN FILM ALIGNED BY AN EXTERNAL MAGNETOSTATIC FIELD AS A HOLE EXTRACTION LAYER FOR POLYMER SOLAR CELLS

2.1 Introduction

In the past two decades, bulk heterojunction (BHJ) polymer solar cells (PSCs) have been attracting intense attention because of their advantages over traditional inorganic solar cells such as flexibility, low cost, light weight, large area, cleanliness, quietness, and processing simplicity.[1-4] Recent progresses in BHJ PSCs have shown a power conversion efficiency (PCE) of 12%,[5] which indicates that PSCs are strongly competitive with their inorganic counterparts. In PSCs, the BHJ composite is sandwiched between a poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS)-coated indium–tin oxide (ITO) anode and a low-work-function cathode, e.g., calcium (Ca) or aluminum (Al); however, the acidic PEDOT:PSS etches ITO and causes device degradation during the operation of PSCs. One solution to circumvent the problem is to use p-type metal oxides such as MoO$_3$,[6-8] NiO,[9] and V$_2$O$_5$[10, 11] as a hole extraction layer (HEL) to replace the PEDOT:PSS anode buffer layer. The PCEs of PSCs incorporating with a vacuum-deposited metal oxide as a HEL were comparable to those
using a PEDOT:PSS anode buffer layer,\(^{[6-11]}\) whereas the PCEs of PSCs incorporating a solution-processed metal oxide as a HEL were lower than those using a PEDOT:PSS anode buffer layer.\(^{[12-13]}\) Therefore, looking for a suitable material as a HEL is one ongoing research direction to enhance the performance of PSCs.\(^{[14]}\) Many materials have been utilized as a HEL in PSCs,\(^{[6-11]}\) but the improvements in the PCEs are still not satisfying. Therefore, new approaches need to be investigated. Here, we report a facile method to enhance the efficiency and improve the stability of PSCs. Two types of Fe\(_3\)O\(_4\) magnetic nanoparticle (MNP) thin films, pristine Fe\(_3\)O\(_4\) and Fe\(_3\)O\(_4\) MNPs aligned by an external magnetostatic field, were introduced as a HEL in PSCs. Significant enhancements in the efficiency and stability were observed from PSCs incorporated with Fe\(_3\)O\(_4\) MNP thin films. To our best of knowledge, this is the first reported study on the effect of both a MNP thin film and MNP thin films aligned by an external magnetostatic field on the performance of PSCs.

2.2 Experiment

We firstly started our experiment by using different materials, which is specifically described below.

2.2.1 Materials

Poly(3-hexylthiophene-2,5-diyl) (P3HT) was purchased from Rieke Metals Inc. and used as received. \([6,6]\)Phenyl-C61-butyric acid methyl ester (PC\(_{61}\)BM) was purchased from 1-Material Inc. and used as received.

The oleic acid capped Fe\(_3\)O\(_4\) MNP (5 mg mL\(^{-1}\) in toluene) was purchased from Sigma-Aldrich and used as received. The mean size of the oleic acid capped Fe\(_3\)O\(_4\) MNP is about 5 nm.
A square magnet (C750, 3/4 in. cube, Licensed NdFeB) was purchased from Amazing Magnets Co.

2.2.2 Fe₃O₄ thin film preparation.

The ITO-coated glass substrates were first cleaned by the following procedures: wiping with detergent, rinsing with deionized water, and ultrasonicating in acetone and isopropanol sequentially for 30 min. Finally, the substrates were dried overnight in an oven. After ITO substrates were treated with UV ozone for 20 min under an ambient atmosphere, a thin film of a Fe₃O₄ MNP was cast from an oleic acid capped Fe₃O₄ MNP toluene solution on top of them. Subsequently, a thin film of a Fe₃O₄ MNP was thermally annealed at 300 °C for 45 min. As described in Figure 2.1a, in order to fabricate a thin film of a Fe₃O₄ MNP aligned by an external magnetostatic field (represented by Fe₃O₄ MNP W/H), the Fe₃O₄ MNP thin film was aligned by an external vertical magnetostatic field with a magnetostatic field intensity of ca. 600 gauss with the film under thermal annealing. Such a magnetostatic field was generated by a magnet placed right above the ITO substrates (schematically shown in Figure 2.1a). The thickness of the Fe₃O₄ MNP thin film is about 30 nm.
2.2.3 Thin film characterization

Tapping-mode atomic force microscopy (AFM) images were obtained by using a NanoScope NS3A system (Digital Instrument) to observe the surface morphologies and thicknesses of various thin films. The transmission spectra of thin films of a Fe$_3$O$_4$ MNP (~30 nm thickness) and PEDOT:PSS (~30 nm) were measured using a HP 8453 spectrophotometer.

X-ray photoelectron spectroscopy (XPS) images were measured by a PHI 5000 Versa Probe II scanning XPS microprobe to identify the components of a solution-processed Fe$_3$O$_4$ MNP thin film after low-temperature annealing and/or external magnetostatic field alignment.

The surface electrical conductivities of Fe$_3$O$_4$ MNP thin films with and without external magnetostatic field alignment were conducted on a Bruker Dimension Icon system with a Peak Force Tapping Tunneling AFM (PFTUNA) module. The probe was a PFTUNA with a spring constant of ~0.5 Nm$^{-1}$ and 20 nm platinum/iridium coating on both the front and rear. The spring currents were measured with a bias voltage applied to the sample. The ramp rate of 0.4 Hz and the force set point of ~60 nN were used for both thin films.

2.2.4 PSCs fabrication and characterization

In PSC devices, the BHJ composite is P3HT mixed with PC$_{61}$BM (P3HT: PC$_{61}$BM = 1:0.8 by weight). Approximately a 80-nm-thick P3HT:PC$_{61}$BM thin film was cast from a P3HT: PC$_{61}$BM /dichlorobenzene (o-DCB) solution onto an ITO/ Fe$_3$O$_4$ MNP substrate inside a glovebox within a nitrogen atmosphere. After that, 6-nm-thick Ca and then 100-nm-thick Al were sequentially vacuum-deposited on top of the BHJ composite with a
base pressure of $6 \times 10^{-6}$ mbar through a shadow mask. The device area was 0.045 cm$^2$. The current density-voltage ($J$-$V$) characteristics were obtained by using a Keithley model 2400 source measure unit. A Newport Air Mass 1.5 Global (AM1.5G) full-spectrum solar simulator was applied as the light source. The light intensity was 100 mW cm$^{-2}$, which was calibrated by utilizing a monosilicon detector (with a KG-5 visible color filter) of National Renewable Energy Laboratory to reduce the spectral mismatch. The incident photon-to-electron conversion efficiency (IPCE) spectra of PSCs were measured by a solar cell quantum efficiency measurement system (QEX10) from PV Measurements. The impedance spectra (IS) were obtained using a HP 4194A impedance/gain-phase analyzer, with an oscillating voltage of 10 mV and a frequency of 1 Hz to 1 MHz. PSCs were held at their respective open-circuit potentials, while the IS spectrum was being recorded.

2.3 Results and Discussion

A Fe$_3$O$_4$ MNP was selected to serve as a HEL because these MNPs possess unique electrical, chemical, magnetic, optical, and anticorrosive properties.$^{[15-16]}$ Although

![Figure 2. 2 XPS Fe 2p core-level spectrum of the Fe$_3$O$_4$ MNP thin film.](image-url)
various methods were used to fabricate a Fe$_3$O$_4$ MNP thin film, we present a simple approach for depositing a Fe$_3$O$_4$ MNP thin film from an oleic acid capped Fe$_3$O$_4$ MNP solution and then aligning the Fe$_3$O$_4$ MNP thin film by an external magnetostatic field. This approach allows us to use low-cost solution processing to fabricate a Fe$_3$O$_4$ MNP thin film as a HEL for BHJ PSCs. XPS was employed to investigate the major component of a solution-processed Fe$_3$O$_4$ MNP thin film. Figure 2.2 shows the XPS spectrum of a Fe$_3$O$_4$ MNP thin film. The Fe$_3$O$_4$ MNP thin film exhibited typical Fe 2p peaks of Fe$_3$O$_4$ at 723.4 and 710.3 eV, respectively. Also, typical Fe 2p$_{1/2}$ and 2p$_{3/2}$ lines are at 723.6 and 710.4 eV, respectively. Thus, the major component of a Fe$_3$O$_4$ MNP thin film deposited from an oleic acid capped Fe$_3$O$_4$ MNP solution, whether followed by thermal annealing or external magnetostatic field alignment, is stoichiometrically confirmed to be Fe$_3$O$_4$. 

Figure 2.3 Transmission spectra of PEDOT:PSS and Fe$_3$O$_4$. 

![Normalized Transmittance vs Wavelength](image)

Figure 2.3 Transmission spectra of PEDOT:PSS and Fe$_3$O$_4$. 

and 710.4 eV, respectively.$^{[17]}$ Thus, the major component of a Fe$_3$O$_4$ MNP thin film deposited from an oleic acid capped Fe$_3$O$_4$ MNP solution, whether followed by thermal annealing or external magnetostatic field alignment, is stoichiometrically confirmed to be Fe$_3$O$_4$. 

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The transmission spectra of thin films of Fe₃O₄ MNP and PEDOT:PSS coated on an ITO substrate are shown in **Figure 2.3**. Compared to that of a PEDOT:PSS thin film, better transmittance from 500 to 1100 nm are observed from a thin film of a Fe₃O₄ MNP, which indicates that a Fe₃O₄ MNP thin film is qualified to be a anode buffer layer, through which more visible light is able to transmit from the ITO/ Fe₃O₄ MNP into a BHJ active layer without significant absorption losses.

**AFM** is used to study the thin-film morphology of Fe₃O₄ MNP and Fe₃O₄ MNP W/H. **Figure 2.4** presents thin-film phase images and height images of Fe₃O₄ MNPs with and without external magnetostatic field alignment. The nanoscale of Fe₃O₄ MNP W/H is larger than that of Fe₃O₄ MNP, indicating that the domain of a Fe₃O₄ MNP is enlarged after magnetic alignment. The root-mean-squared roughnesses of Fe₃O₄ MNP thin films with and without external magnetostatic field alignment are in the same scale region, but Fe₃O₄ MNP W/ H is a little smoother than a Fe₃O₄ MNP from the 3D image. The smooth surface implies that a BHJ composite layer can be easily deposited on top of a Fe₃O₄
MNP W/H thin film and form a better contact with the BHJ active layer, thus leading to enhanced PCE. In addition, no sharp peak of ITO is observed from ITO/ Fe₃O₄ MNP or ITO/ Fe₃O₄ MNP W/H, indicating that the rough surface of the ITO substrate has been planarized well by the Fe₃O₄ layer.

The $J$-$V$ curves of BHJ PSCs under illumination are shown in Figure 2.5a. We calculated the series resistance ($R_S$) and shunt resistance ($R_{SH}$) from the slope of $J$-$V$ curves at 0 mA cm$^{-2}$ and 0 V, respectively. The $R_S$ and $R_{SH}$ values from these three PSCs are summarized in Table 2.1. A low series resistance from PSCs with Fe₃O₄ MNP W/H is due to the small contact resistance and bulk resistance of the photoactive material, indicating that high currents will flow through the cell at low applied voltages. The large shunt resistance indicates that shorts or leakages of the photocurrent are minimal in the device. Under AM1.5G illumination with a light intensity of 100 mW cm$^{-2}$, an open-circuit voltage ($V_{OC}$) of 0.60 V, a short-circuit current density ($J_{SC}$) of 7.81 mA cm$^{-2}$, a fill factor (FF) of 54.5%, and a corresponding PCE of 2.55% were obtained from PSCs by using a Fe₃O₄ MNP as a HEL. At the same conditions, a $V_{OC}$ of 0.61 V, a $J_{SC}$ of 7.81 mA cm$^{-2}$, a FF of 53.7%, and a corresponding PCE of 2.70% were observed from PSCs by using Fe₃O₄ MNP W/H as a HEL. For PSCs with PEDOT:PSS as an anode buffer layer, a $V_{OC}$ of 0.60 V, a $J_{SC}$ of 7.22 mA cm$^{-2}$, a FF of 55.0%, and a corresponding PCE of 2.38% were observed. More than 80 devices were fabricated and characterized.

<table>
<thead>
<tr>
<th>anode buffer layer</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$R_{SH}$ (Ω cm$^{-2}$)</th>
<th>$R_S$ (Ω cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>0.60</td>
<td>7.22</td>
<td>1870</td>
<td>17.3</td>
<td>55.0</td>
<td>2.38</td>
</tr>
<tr>
<td>Fe₃O₄ MNP</td>
<td>0.60</td>
<td>7.81</td>
<td>965</td>
<td>16.0</td>
<td>54.5</td>
<td>2.55</td>
</tr>
<tr>
<td>Fe₃O₄ MNP W/H</td>
<td>0.61</td>
<td>8.25</td>
<td>1713</td>
<td>9.23</td>
<td>53.7</td>
<td>2.70</td>
</tr>
</tbody>
</table>
under the same conditions. The device performance parameters are summarized in Table 2.1. The deviation in the efficiencies of these devices is less than 5%. These results demonstrated that a Fe₃O₄ MNP thin film can be used as a HEL in PSCs, and PSCs using Fe₃O₄ MNP and Fe₃O₄ MNP W/H as a HEL, respectively, possessed higher performance compared with those using PEDOT:PSS as an anode buffer layer.

The PSCs were further characterized by IPCE spectroscopy. As shown in Figure 2.5b, the integrated $J_{SC}$ from IPCE are 7.20, 7.77, and 8.23 mA cm$^{-2}$ for PSCs incorporated with PEDOT:PSS, Fe₃O₄ MNP, and Fe₃O₄ MNP W/H thin films, respectively. All calculated $J_{SC}$ values are consistent with those obtained from the $J-V$ characteristics.

In order to analyze enhanced PCEs of PSCs, the internal series resistance ($R_S$) of PSCs incorporated with Fe₃O₄ MNP by IS was investigated and compared with those from PSCs using PEDOT:PSS as a buffer layer. $R_S$ of PSCs consists of sheet resistance ($R_{SH}$; contact resistance between the BHJ composite and adjacent electrodes, resistance associated with probe lines and interconnections, etc.) and charge-transport resistance ($R_{CT}$, bulk resistivity of semiconducting materials). The IS analysis enabled us to monitor the specific electrical properties of the interfaces that cannot be determined by direct-current measurements. The only difference of PSCs with various HELs in our investigation is in $R_{SH}$. The Nyquist plots of PSCs were measured at an applied voltage of 0.6 V under AM1.5G illumination with a light intensity of 100 mW cm$^{-2}$ and are shown in Figure 2.6a. From the plots, the resistance of PSCs using PEDOT:PSS as an anode buffer layer is ca. 19.9 Ω cm$^2$ and ca. 16.8 Ω cm$^2$ for PSCs using Fe₃O₄ MNP as a HEL. A resistance of 16.8 Ω cm$^2$ is observed from PSCs using Fe₃O₄ MNP W/H as a HEL. These
results demonstrated that the charge-transfer resistances of PSCs using Fe$_3$O$_4$ MNP as a HEL are reduced compared with that using PEDOT:PSS as an anode buffer layer. Thus, a high performance is anticipated from PSCs incorporating a Fe$_3$O$_4$ MNP.

We further investigated the electrical conductivity of Fe$_3$O$_4$ MNP thin films by evaluating the $J$-$V$ curves observed from a sandwiched device with a structure of ITO/thin film/Al.$^{[20, 21]}$ Figure 2.6b displays the $J$-$V$ curves of ITO/thin film/Al devices, where thin films are a PEDOT:PSS layer, a Fe$_3$O$_4$ MNP layer, and a Fe$_3$O$_4$ MNP W/H layer, respectively. The thicknesses of these layers were controlled to be identical with the value of 30 ± 1.4 nm. At the same applied voltages, both Fe$_3$O$_4$ MNP and Fe$_3$O$_4$ MNP W/H possess similar current densities, while the PEDOT:PSS thin film possesses the lowest current densities among these three thin films. For example, at 2 V, the current density of Fe$_3$O$_4$ MNP thin films with and without external magnetostatic field alignment is ca. 200 mA cm$^{-2}$, which is larger than ca.122 mA cm$^{-2}$ observed from that of the PEDOT:PSS thin film. Moreover, $J$-$V$ curves of Fe$_3$O$_4$ MNP and Fe$_3$O$_4$ MNP W/H are linear and symmetric, which is similar to that of the PEDOT:PSS thin film, indicating that an ohmic contact between the ITO anode and Fe$_3$O$_4$ MNP thin film is formed.$^{[22]}$
This observation is consistent with the band alignment shown in Figure 2.1b&c (the Fermi level of Fe₃O₄ is cited from ref 34). The ohmic contact formed between the ITO anode and Fe₃O₄ MNP HEL implies that there is no barrier for Fe₃O₄ MNP HEL to extract and transport separated holes from the BHJ composite.

In order to further understand the underlying of enhanced PCE, the surface electrical conductivities of Fe₃O₄ MNP and Fe₃O₄ MNP W/H were conducted by PFTUNA measurement. The peak currents are shown in Figure 2.7. At the same condition (zoom size), Fe₃O₄ MNP W/H shows a surface electrical conductivity of 1.15 pA, which is nearly twice as high as that of Fe₃O₄ MNP (0.67 pA). These results indicated that external magnetostatic fields probably change the molecular alignment within Fe₃O₄ MNP and alter the surface electrical conductivity of Fe₃O₄ MNP.

Studies have shown that dipoles would be generated when MNP was aligned by an external magnetostatic field. In particular, an external magnetostatic field exerts a torque
on MNP, thus producing magnetic dipole moments, which drives MNP to polarize within an external magnetostatic field.\textsuperscript{[23-25]} In a Fe\textsubscript{3}O\textsubscript{4} MNP thin film, the “head-to-tail” structure of a Fe\textsubscript{3}O\textsubscript{4} MNP is formed to minimize the systematic energy,\textsuperscript{[23]} while if an external magnetostatic field is vertically positioned to Fe\textsubscript{3}O\textsubscript{4} MNP, Fe\textsubscript{3}O\textsubscript{4} MNP will form a separated isotropic structure because of parallel moment repulsion, which leads to changes of the film morphology and enhances the surface electrical conductivity of a Fe\textsubscript{3}O\textsubscript{4} MNP thin film.\textsuperscript{[26-29]} In addition, an extra dipole will enhance charge separation and transportation within a HEL.\textsuperscript{[30]} The dipoles of a Fe\textsubscript{3}O\textsubscript{4} MNP are random in all directions without an external magnetostatic field alignment. After external magnetostatic field alignment, a Fe\textsubscript{3}O\textsubscript{4} MNP is rearranged in a certain order by the mechanism of magnetic dipolar interaction. Spontaneously, the dipoles of a Fe\textsubscript{3}O\textsubscript{4} MNP were parallel in the presence of a vertically applied magnetostatic field. This will drive a Fe\textsubscript{3}O\textsubscript{4} MNP thin film to generate an electric field. This electric field, with the electric field generated by two electrodes because of different work functions, would drive more separated charge carriers to transport to the corresponding electrodes compared with those using a Fe\textsubscript{3}O\textsubscript{4} MNP HEL without magnetostatic field alignment.\textsuperscript{[31-33]} Therefore, PSCs using Fe\textsubscript{3}O\textsubscript{4} MNP W/H as a HEL possess higher performance compared with those using a Fe\textsubscript{3}O\textsubscript{4} MNP as a HEL.

We also studied the stability of PSCs. We tested the devices every 12 h. The results of self-stability of PSCs are shown in Figure 2.8. By using a Fe\textsubscript{3}O\textsubscript{4} MNP to replace PEDOT:PSS, the stabilities of PSCs are significantly enhanced. For PSCs with a Fe\textsubscript{3}O\textsubscript{4} MNP as a HEL, PCEs remained at approximately 95% of the original value for 72 h, while PCEs of PSCs with PEDOT:PSS as an anode buffer layer degraded evidently by
10%. The half-life of PSCs with a Fe₃O₄ MNP as a HEL is nearly 600 h, but that of PSCs using PEDOT:PSS is only about 300 h. Therefore, utilization of a Fe₃O₄ MNP as a HEL in BHJ PSCs can significantly improve the air stability of PSCs.

2.4 Conclusion

Efficient and stable BHJ PSCs by using a thin layer of a Fe₃O₄ MNP as a HEL were fabricated. Efficiencies observed from PSCs using Fe₃O₄ MNP as a HEL show higher PCEs than those using PEDOT:PSS as an anode buffer layer and the stability of PSCs is significantly enhanced. We further found that PSCs using a thin layer of Fe₃O₄ MNP, followed with external magnetostatic field alignment exhibiting both enhanced efficiency and dramatically enhanced stability compared with those using PEDOT:PSS as an anode buffer layer. Our finding demonstrated that utilization of Fe₃O₄ MNP as a HEL in PSCs blazes a trail to achieve highly efficient and long-time-stable PSCs.
CHAPTER III

ENHANCED PERFORMANCE OF POLYMER SOLAR CELLS USING PEDOT:PSS DOPED WITH IRON(II,III) OXIDE MAGNETIC NANOPARTICLES ALIGNED BY AN EXTERNAL MAGNETOSTATIC FIELD AS AN ANODE BUFFER LAYER

3.1 Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs) have shown great potential as one of the renewable and cost-effective energy sources.\textsuperscript{[1-3]} BHJ PSCs are generally consisting of an active layer of conjugated polymer blended with fullerene derivative sandwiched by an indium tin oxide (ITO) anode and a metal cathode. Typically, poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) is used as an anode buffer layer to smooth the surface of ITO and reduce the contact resistance between BHJ composite active layer and the ITO anode.\textsuperscript{[4]} However, the acidic PEDOT:PSS etches ITO substrate and thus degrades the performance of BHJ PSCs.\textsuperscript{[5-7]} Moreover, the thin film of PEDOT:PSS is plague and possesses low conductivity (ca. 1 S cm\textsuperscript{-1}),\textsuperscript{[8, 9]} which limits the development of PSCs with high efficiency. In order to circumvent these problems, p-type metal oxides such as MoO\textsubscript{3}, NiO, V\textsubscript{2}O\textsubscript{5} were used to substitute PEDOT:PSS buffer layer.\textsuperscript{[8,10-12]} The power conversion efficiency (PCE) of
PSCs incorporating with vacuum-deposited metal oxide as a hole extraction layer were comparable to those using PEDOT:PSS anode buffer layer,$^{[13]}$ whereas the PCEs of PSCs incorporating with solution-processed metal oxides were lower than those using PEDOT:PSS.$^{[14]}$ Therefore, reducing the acidity of and enhancing the electrical conductivity of PEDOT:PSS is probably a proper approach to realize low-cost manufacturing PSCs with high efficiency and good stability.

Several methods have been reported for enhancement of the electrical conductivity of PEDOT:PSS, for example, PEDOT:PSS doped with an organic compound, or an ionic liquid, or an anionic surfactant was used for minimizing its acidity.$^{[15]}$ Recently, Xie et al. observed a 50% enhanced PCE from PSCs by using PEDOT:PSS doped with a cationic surfactant as an anode buffer layer.$^{[16]}$ Huang et al. reported high performance PSCs by using one dimensional n-PEDOT as an anode buffer layer.$^{[17]}$ However, the improvements in PCEs through these methods were still not sufficient and new approaches need to be explored.

Here, we report a facile method to enhance efficiency and improve stability of PSCs. By using thin film made from the solution of PEDOT:PSS doped with Fe$_3$O$_4$ magnetic nanoparticles (MNP) (represent by (PEDOT:PSS): Fe$_3$O$_4$) as an anode buffer layer, and above (PEDOT:PSS): Fe$_3$O$_4$ MNP thin film aligned by an external magnetostatic field (represent by [(PEDOT:PSS): Fe$_3$O$_4$] W/H), as an anode buffer, respectively, significantly enhanced efficiency and improved stability of PSCs were observed.

### 3.2 Experiment

In this section, we mainly focus on the study on different thin films and use several characterizations to detect the differences in our three types of anode buffer layers.
3.2.1 Film characterization

Tapping-mode AFM images were obtained by using a NanoScope NS3A system (Digital Instrument).

Bright-field TEM experiments were carried out with a JEOL transmission electron microscope using an accelerating voltage of 120 kV.

XPS images were measured by a PHI 5000 Versa Probe II scanning XPS microprobe to identify the components on the surface of all the films.

3.2.2 PSCs fabrication

PSCs structure is ITO/anode buffer layer/polymer:fullerene BHJ composite/Ca/Al, where anode buffer layer is PEDOT:PSS, (PEDOT:PSS):Fe₃O₄ and [(PEDOT:PSS):Fe₃O₄] W/H, respectively. Firstly, ITO coated glass slides were cleaned by detergent, followed by ultrasonic washing in deionized water, acetone and isopropanol, and subsequently dried in an oven overnight. After that, the anode buffer layer, PEDOT:PSS or PEDOT:PSS doped with Fe₃O₄ magnetic nanoparticles (5 % by volume), was spin-coated from corresponding solutions, respectively. The anode buffer layer, PEDOT:PSS and (PEDOT:PSS):Fe₃O₄ layer coated ITO substrates were annealed at 150 °C for 10 minutes in air. For the anode buffer layer with an external magnetostatic field alignment, a magnet is directly put on the top of the thin film during thermal annealing process. The thickness of buffer layer is ~ 40 nm. After that, all the anode buffer layer coated ITO substrates were transferred into glove box with N₂ atmosphere. BHJ composite of PBDTTT-C-T:PC₇₁BM (1:1.5, weight ratio) was spin-coated onto top of buffer layer from ortho-dichlorobenzene (o-DCB) solution. The thickness of BHJ active layer was ~ 140 nm. Finally, metal top electrode, Ca and Al were sequentially deposited onto BHJ active
layer in vacuum onto with a pressure of ca. $4 \times 10^{-6}$ mbar. The active area of PSCs was measured to be 0.045 cm$^2$.

**3.2.3 PSCs characterization**

The current-density–voltage ($J$-$V$) curves characteristics were measured using a Keithley 2400 Source Measure Unit. The solar cells were characterized using a Newport Air Mass 1.5 Global (Am 1.5G) full spectrum solar simulator with an intensity of 100mWcm$^{-2}$. The light intensity was determined by a monosilicon detector (with KG-5 visible color filter) calibrated by National Renewable Energy Laboratory (NREL) to reduce spectral mismatch.

The incident photon-to-electron conversion efficiency (IPCE) spectra of PSCs were measured by solar cell quantum efficiency measurement system (QEX10) from PV Measurements.

The impedance spectra (IS) were obtained using a HP 4194A impedance/gain-phase analyzer, all under illumination, with an oscillating voltage of 10 mV and frequency of 1 Hz to 1 MHz. PSCs were held at their respective open circuit potentials obtained from the $J$-$V$ measurements, while the IS spectrum was recorded.

**3.3 Results and Discussion**

Several results and discussions are made below. We firstly studied the samples and gives demonstrations on our results.

**3.3.1 Samples**

$\text{Fe}_3\text{O}_4$ MNP was selected to modify the electrical properties of PEDOT:PSS because it possesses special electrical, chemical, magnetic, optical, and anticorrosive properties.$^{[18]}$ Moreover, it is expected that the reaction between basic $\text{Fe}_3\text{O}_4$ MNP and acidic
PEDOT:PSS would reduce the acidity of PEDOT:PSS and simultaneously generate Fe$^{3+}$ ions, thus resulting in high electrical conductivity.

In order to verify whether the Fe$_3$O$_4$ MNP was doped into PEDOT:PSS, pH value of the solution of PEDOT:PSS doped with Fe$_3$O$_4$ MNP was checked and compared with that of pristine PEDOT:PSS. The pH value of the solution of PEDOT:PSS became 5 ~ 6 from 1 ~ 2$^{[19, 20]}$ after doping 5% Fe$_3$O$_4$ MNP into the solution of PEDOT:PSS. The change of pH value indicated that the sulfonic acid in PSS was reacted with Fe$_3$O$_4$ MNP and generated the counter ions, Fe$^{3+}$, at the same time. In order to confirm that Fe$^{3+}$ was generated by above reaction, the solution was further checked by a coordination reaction between the Fe$^{3+}$ ions and the thiocyanate ions (SCN$^-$). It was found that the color of potassium thiocyanate solution quickly changed from colorless to red upon addition of a few drops of the solution of PEDOT:PSS doped with Fe$_3$O$_4$ MNP. The red color was originated from the iron thiocyanate complex ([Fe(SCN)$_n$]$^{3-n}$($n=1$-6))$^{[21]}$ which was formed by the Fe$^{3+}$ ions coordinated with SCN$^-$. These results indeed demonstrated that

![Figure. 3.1 Transmittance spectra of thin films of PEDOT:PSS, Fe$_3$O$_4$ magnetic nanoparticles, and (PEDOT:PSS): Fe$_3$O$_4$ magnetic nanoparticles.](image-url)
Fe₃O₄ MNP was reacted with PEDOT:PSS. As a result, extra Fe³⁺ ions were generated and the acidity of PEDOT:PSS was reduced. With the introduction of extra Fe³⁺ ions, the morphology of PEDOT:PSS film is also expected to be changed.[22]

3.3.2 Transmittance

Figure 3.1 presents the transmittance spectra of pristine PEDOT:PSS, pristine Fe₃O₄ MNP, and (PEDOT:PSS):Fe₃O₄ thin films. The spectra of pristine Fe₃O₄ MNP thin film show 97% transmittance from 400 to 1100 nm. The transmittance spectrum of (PEDOT:PSS):Fe₃O₄ thin film is a superposition of pristine PEDOT:PSS and Fe₃O₄ MNP. The transmittance of (PEDOT:PSS):Fe₃O₄ thin film is greater than that of pristine PEDOT:PSS. Good transmittance from 400 to 1100 nm indicated more visible light is able to pass through (PEDOT:PSS):Fe₃O₄ thin film into BHJ active layer.

3.3.3 Morphology

As expected, the morphology of PEDOT:PSS film would change with introduction of extra Fe₃O₄ MNP into PEDOT:PSS.[22] The film morphologies of these thin films were investigated by transmission electron microscopy (TEM). A comparison of bright field TEM images of pristine PEDOT:PSS, pristine Fe₃O₄ MNP and (PEDOT:PSS):Fe₃O₄ thin
films is shown in Figure 3.2. The thin film of pristine PEDOT:PSS is uniform and homogenous. The thin films of pristine Fe$_3$O$_4$ MNP and (PEDOT:PSS):Fe$_3$O$_4$ are uniform as well. However, the Fe$_3$O$_4$ MNP is clearly observed from the latter two samples. Interestingly, the mean sizes of Fe$_3$O$_4$ MNP presents in PEDOT:PSS thin film were evidently smaller than those of pristine Fe$_3$O$_4$ MNP and the shape of Fe$_3$O$_4$ MNP became irregular. The spherical particles look like to have been “bitten” by PEDOT:PSS, as shown in Figure 3.2c. This is attributed to partially etched Fe$_3$O$_4$ MNP by sulfonic acid groups. All these results provide further evidence suggesting that Fe$_3$O$_4$ MNP was reacted with PEDOT:PSS, generating extra counter Fe$^{3+}$ ions and reducing acidity of PEDOT:PSS. Thus, we expect high electrical conductivity from thin film of (PEDOT:PSS) : Fe$_3$O$_4$.

Due to the generation of Fe$^{3+}$ ions, the space between PEDOT and PSS chains could be changed by the screen effect.$^{[22,23]}$ To confirm this hypothesis, the film morphologies of PEDOT:PSS, (PEDOT:PSS):Fe$_3$O$_4$ and [(PEDOT:PSS):Fe$_3$O$_4$] W/H were further investigated by Atomic Force Microscopy (AFM). AFM images of PEDOT:PSS, (PEDOT:PSS):Fe$_3$O$_4$ and [(PEDOT:PSS):Fe$_3$O$_4$] W/H are shown in Figure 3.3. As compared with pristine PEDOT:PSS (Figure 3.3a), aggregated PEDOT and voids in the images of (PEDOT:PSS):Fe$_3$O$_4$ (Figure 3.3b) and [(PEDOT:PSS):Fe$_3$O$_4$] W/H (Figure 3.3c) suggested that the morphology of PEDOT:PSS was changed after the doping of PEDOT:PSS with Fe$_3$O$_4$ MNP. Moreover, due to the screen effect from the generated Fe$^{3+}$ions, larger PEDOT domains were formed, which would facilitate hole transport through the thin film.$^{[22,23]}$
3.3.4. Thin film electrical conductivity

Figure 3.4 shows the current-density-voltage \((J-V)\) characterization of the diodes with a structure of ITO/anode buffer layer/Al, where ITO is indium tin oxide, anode buffer layer is PEDOT:PSS, (PEDOT:PSS):Fe\(_3\)O\(_4\) and [(PEDOT:PSS):Fe\(_3\)O\(_4\)] W/H, respectively. The different slope of \(J-V\) curves indicated that these thin films possess different electrical conductivities. Greater slope indicates better conductivity. Thus, at the same biased voltage, the electrical conductivity of [(PEDOT:PSS):Fe\(_3\)O\(_4\)] W/H is the largest, followed by (PEDOT:PSS):Fe\(_3\)O\(_4\), while PEDOT:PSS is the least conductive. In order to further confirm such conductivity difference, the surface electrical conductivity of PEDOT:PSS, (PEDOT:PSS):Fe\(_3\)O\(_4\) and [(PEDOT:PSS):Fe\(_3\)O\(_4\)] W/H were measured by peak force tunneling AFM (PFTUNA).\(^{[24]}\) The peak current images of these thin films are presented in Figure 3.5. The peak current for each measurement is set to 2.0 pA. It was found that the number of highly conductive domains for PEDOT:PSS (Figure 3.5a) is the smallest, while for (PEDOT:PSS):Fe\(_3\)O\(_4\) (Figure 3.5b) is moderate. Thus, surface
conductivity of (PEDOT:PSS):Fe$_3$O$_4$ is larger than that of PEDOT:PSS. Remarkably, a significant enhancement in surface conductivity was observed from [(PEDOT:PSS):Fe$_3$O$_4$] W/H thin film. Highly conductive domains, which are largest in size among these three samples and well distributed throughout the whole thin film, were observed from [(PEDOT:PSS):Fe$_3$O$_4$] W/H as shown in Figure 3.5c. Therefore, the surface electrical conductivity of [(PEDOT:PSS):Fe$_3$O$_4$] W/H is larger than that of (PEDOT:PSS):Fe$_3$O$_4$ which is larger than that of PEDOT:PSS. These results are in good agreement with the observation from Figure 3.4. This high surface electrical conductivity would facilitate charge transport through the thin film towards the ITO anode, resulting in large $J_{SC}$ in PSCs.$^{[2]}$ Consequently, enhanced device performance is expected from PSCs with [(PEDOT:PSS):Fe$_3$O$_4$] W/H as an anode buffer layer.$^{[22,23]}$

3.3.5. Solar cells performance

Figure 3.6 shows a schematic illustration of fabrication procedure of anode buffer layers, (PEDOT:PSS):Fe$_3$O$_4$ and [(PEDOT:PSS):Fe$_3$O$_4$] W/H, device structure of PSCs, and molecular structures of the electron donor, PBDTTT-C-T (a low bandgap polymer derived from the thienothiophene (TT) and benzo[1,2-b:4,5-b’]dithiophene (BDT) alternating units),$^{[25]}$ and the electron acceptor, PC$_{71}$BM ([6,6]-phenyl-C$_{71}$-butyric acid

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methyl ester). The thin film of (PEDOT:PSS):Fe$_3$O$_4$ was casted from the solution of (PEDOT:PSS):Fe$_3$O$_4$ (Fe$_3$O$_4$: 5% by volume) followed with thermal annealing at 150 °C for 10 minutes. The thin film of [(PEDOT:PSS):Fe$_3$O$_4$] W/H was casted from the solution of (PEDOT:PSS):Fe$_3$O$_4$ (Fe$_3$O$_4$: 5% by volume) followed with an external magnetostatic field alignment during the thermal annealing treatment. After that, BHJ composite of PBDTTT-C-T:PC$_{71}$BM (1:1.5 by weight) was spin-coated on the top of either (PEDOT:PSS):Fe$_3$O$_4$ or [(PEDOT:PSS):Fe$_3$O$_4$] W/H thin films. Finally, the top electrode (Ca coated with Al) was sequentially thermally deposited onto BHJ layer in vacuum. PSCs with pristine PEDOT:PSS anode buffer was also fabricated as a control device.

The $J$-$V$ characteristics of PSCs with PEDOT:PSS as an anode buffer layer (represented by PSCs-PEDOT:PSS), PSCs with (PEDOT:PSS):Fe$_3$O$_4$ as an anode buffer layer (represented by PSCs-(PEDOT:PSS):Fe$_3$O$_4$) and PSCs with [(PEDOT:PSS):Fe$_3$O$_4$] W/H as an anode buffer layer (represented by PSCs-[(PEDOT:PSS):Fe$_3$O$_4$] W/H), measured under a simulated sun light with air mass 1.5 global (AM 1.5 G) at light intensity of 100 mW cm$^{-2}$, are shown in Figure 3.7. PSCs-PEDOT:PSS exhibited an $V_{OC}$ of 0.79 V, a short-circuit current density ($J_{SC}$) of 10.79 mA cm$^{-2}$ and fill factor (FF) of 58.0%, yielding a corresponding PCE of 4.94%. Where PSCs-(PEDOT:PSS):Fe$_3$O$_4$ exhibited $V_{OC}$ of 0.78 V, $J_{SC}$ of 12.99 mA cm$^{-2}$, and FF of 58.0%, yielding a corresponding PCE of 5.85%. This value is about 18% larger than that from PSCs-PEDOT:PSS. PSCs-[(PEDOT:PSS):Fe$_3$O$_4$] W/H exhibited $V_{OC}$ of 0.78 V, $J_{SC}$ of 14.78 mA cm$^{-2}$, and FF of 59.3%, yielding a corresponding PCE of 6.84% which is about 38% higher than those from PSCs-PEDOT:PSS. More than 100 devices were fabricated and the average values of PCEs shown a deviation of less than 5%.
The PSCs were further characterized by the incident photon to charge carrier efficiency (IPCE) spectroscopy. The IPCE spectra of PSCs are shown in Figure 3.7b. Apparently, the IPCE values, ranged from 400 to 800 nm for PSCs-[PEDOT:PSS]:Fe$_3$O$_4$ W/H are higher than those of PSCs-(PEDOT:PSS):Fe$_3$O$_4$ and PSCs-PEDOT:PSS. The calculated $J_{SC}$ based on IPCE spectra are 10.36 mA cm$^{-2}$, 12.47 mA cm$^{-2}$ and 14.10 mA cm$^{-2}$ for PSCs-PEDOT:PSS, PSCs-(PEDOT:PSS):Fe$_3$O$_4$, and PSCs-[PEDOT:PSS]:Fe$_3$O$_4$ W/H, respectively. All these calculated $J_{SC}$ are consistent with the $J_{SC}$ values obtained from $J$-$V$ characteristics of PSCs.

From Figure 3.7a, we observed that all PSCs possessed a similar $V_{OC}$, but significantly difference in photocurrents ($J_{SC}$). In these PSCs, however, the only difference is in the anode buffer layer. Therefore, it is reasonable to conclude that both Fe$_3$O$_4$ MNP and an external magnetostatic field have significant influence on $J_{SC}$.

In order to investigate enhanced $J_{SC}$ from PSCs-(PEDOT:PSS):Fe$_3$O$_4$ and PSCs-[PEDOT:PSS]:Fe$_3$O$_4$ W/H, X-ray photoelectron spectroscopy (XPS) was carried
out to characterize the surface properties of PEDOT:PSS, (PEDOT:PSS):Fe$_3$O$_4$ and [(PEDOT:PSS):Fe$_3$O$_4$] W/H thin films. As shown in Figure 3.8a, the major components of the surface of all the three-type-films are the same. The partial enlarged Figure 3.8b shows that all these three thin films exhibit no typical peaks of Fe$_3$O$_4$ (Fe 2p$_{1/2}$ and 2p$_{3/2}$ peaked at 723.6 and 710.4 eV, respectively). These results indicate the doped Fe$_3$O$_4$ MNP are frozen inside the PEDOT:PSS thin film. Therefore, the possibility that the migration of Fe$_3$O$_4$ MNP into BHJ composite layer to enhance $J_{SC}$ can be ruled out.

In PSCs, separated charge carriers have to be transported through the buffer layer to the corresponding electrodes. Thus, anode buffer layer with high electrical conductivity is favorable to offer direct pathways for separated holes to be transported to the ITO anode. As described above, the electrical conductivity of (PEDOT:PSS):Fe$_3$O$_4$ thin film is higher than that of PEDOT:PSS. Therefore, $J_{SC}$ observed from PSCs-(PEDOT:PSS):Fe$_3$O$_4$ is higher than that of PSCs-(PEDOT:PSS). For PSCs-[(PEDOT:PSS):Fe$_3$O$_4$] W/H, in addition to the high electrical conductivity of (PEDOT:PSS):Fe$_3$O$_4$, the external magnetostatic filed probably also plays an important role in enhancing $J_{SC}$. In the presence of an external magnetostatic field, Fe$_3$O$_4$ MNP exhibits superparamagnetism at
The randomly distributed Fe$_3$O$_4$ MNP within PEDOT:PSS thin film could be self-assembled, which was driven by the dipole-dipole interaction among Fe$_3$O$_4$ MNP.$^{[26-28]}$ This self-assembled Fe$_3$O$_4$ MNP certainly will enhance the electrical conductivity of (PEDOT:PSS):Fe$_3$O$_4$ thin film. Moreover, it has been reported that weak magnetic field can increase the dissociation ratio of triplet excitons, yielding a positive magnetoconductance and increasing the current through PSCs due to the long lifetime of the triplet excitons compared to that of the singlet excitons in conjugated polymers.$^{[29,30]}$ All these effects arise from the addition of Fe$_3$O$_4$ MNP into PEDOT:PSS, followed with an external magnetostatic filed alignment, result in $\sim$ 38% enhancement in $J_{SC}$.

In order to further verify the electrical conductivities of these three thin films, the internal series resistances ($R_S$) of these three PSCs were investigated by impedance spectroscopy (IS). The IS analysis enables us to monitor the detailed electrical properties of the interface that cannot be determined by direct current measurements. The $R_S$ is
composed of the sheet resistance ($R_{\text{SH}}$) of the electrodes, the charge-transfer resistance ($R_{\text{CT}}$) at the interfaces between the ITO anode and buffer layer, and the anode buffer and BHJ active layer, inside of BHJ active layer. For these three PSCs, the only difference is the $R_{\text{CT}}$ at the interfaces between the ITO anode and buffer layer, between the anode buffer and BHJ active layer. Figure 3.9 shows the Nyquist plots of PSCs measured under the light intensity of 100 mW cm$^{-2}$ and at the applied voltage of 0.78 V. From the plots, $R_{\text{CT}}$ of 13 kΩ, 19 kΩ and 25 kΩ are observed from PSCs-[(PEDOT:PSS):Fe$_3$O$_4$] W/H, PSCs-(PEDOT:PSS):Fe$_3$O$_4$ and PSCs-PEDOT:PSS, respectively. These results indicated that electrical conductivity of [(PEDOT:PSS):Fe$_3$O$_4$] W/H thin film is indeed higher than that of (PEDOT:PSS):Fe$_3$O$_4$ thin film, which is higher than that of PEDOT:PSS thin film. Therefore, the magnetostatic field can induce rearrangement of film morphology of (PEDOT:PSS):Fe$_3$O$_4$ at nanoscale, resulting in not only enhanced charge transport inside the buffer layer, but also reduced interfacial series resistance. As a result, enlarged $J_{\text{SC}}$ is observed from PSCs-[(PEDOT:PSS):Fe$_3$O$_4$] W/H.

The stabilities of all three PSCs were also studied. Figure 3.10 compared the self-stabilities of PSCs-PEDOT:PSS, PSCs-(PEDOT:PSS):Fe$_3$O$_4$ and PSCs-[(PEDOT:PSS):Fe$_3$O$_4$] W/H, respectively. Since PSCs are with a conventional architecture of ITO/buffer layer/BHJ active layer/Ca/Al, the degradation are caused by hygroscopic and acidic erosion caused by PEDOT:PSS, and oxidation of top metals (Ca coated by Al). In order to compare the stability influenced by the anode buffer layer, all PSCs were encapsulated to minimize contribution of oxidation of the top metal electrode. PSCs-[(PEDOT:PSS):Fe$_3$O$_4$] W/H remains approximately 55% of the original value after 90 days; PSCs-(PEDOT:PSS):Fe$_3$O$_4$ remains approximately 55% of the
original value after 85 days, while PSCs-PEDOT:PSS degrades evidently after only 12 hours and remains 50% of the original value after 5 days. These results demonstrated that the stability of PSCs by using the thin films of \((\text{PEDOT:PSS}):\text{Fe}_3\text{O}_4\) and \([(\text{PEDOT:PSS}):\text{Fe}_3\text{O}_4]\) W/H, respectively, are significantly improved as compared with those by using PEDOT:PSS thin film as an anode buffer layer.

3.4 Conclusion

In conclusion, we have successfully demonstrated that enhanced efficiency and improved stability of PSCs can be realized by using thin film fabricated from the solution of PEDOT:PSS doped Fe$_3$O$_4$ magnetic nanoparticles, and above thin film aligned by an external magnetostatic field as an anode buffer layer, respectively. The enhanced efficiency and improved stability are resulted from a combination of reduced acidity of PEDOT:PSS and enhanced electrical conductivity originated from generated counter ions and the paramagnetism of Fe$_3$O$_4$ magnetic nanoparticles by an external magnetostatic field. Our results certainly inspire a new approach towards the low-cost manufacturing polymer (organic) solar cells with both high efficiency and good stability.
4.1 Conclusions

For PSCs, stability and efficiency are two issues that limit the commercialization in energy market. And for conventional structures of PSCs, PEDOT:PSS are widely used as the anode buffer layer to smooth the ITO surface and modify the interfacial properties. However, the acidic nature of PEDOT:PSS is the dominant reason for the degradation of PSCs devices. Therefore, we used the Fe$_3$O$_4$ MNPs as the anode buffer layer to replace the PEDOT:PSS layer in PSCs. Compatible device performance and dramatic enhanced stability were firstly improved compared with the control devices. Furthermore, by using an external MF to align the MNPs, smoother surface of MNPs layers and higher surface conductivity were obtained, indicating enhanced device performance compared to the devices using MNPs as the HEL but without MF treatment.

However, the PCE in such devices are still inferior and the price for using MNPs is still high. On this concern, we introduce MNPs into PEDOT:PSS layer, hoping stability and electrical properties of PEDOT:PSS layer can be improved by using smaller amount of MNPs. Moreover, external MF was further applied to tune the morphological changes inside of the PEDOT:PSS. As a consequence, the electric conductivity of the MNPs
doped PEDOT:PSS layer with external MF treatment is enhanced, which was systematically confirmed by using diode, IS, surface conducting AFM. And device performance and stability are further improved simultaneously.

4.2 Out look

As mentioned before, in PSCs, photons can be absorbed in the active layer, creating the photon-induced excitons followed by the diffusion of excitons to form Charge Transfer (CT) states at the Bulk Heterojunction (BHJ) interfaces. Such CT states may either recombine again or dissociate into free charge carriers, which can be collected at the electrodes to form the current source of the solar cell. However, the recombined CT states is a dramatic part of energy loss in the photovoltaic process in PSCs. Moreover, the PSCs is a vertical two terminal device with an active layer (BHJ composite) sandwiched between different electrodes. The series resistance between different layers inside the devices is another concern for the energy loss. Therefore to further improve the PCE, such energy losses must be considered in the first time. On the other hand, electric energy conversion is generally accompanied by the magnetic phenomena, and the mechanism understanding in PSCs is still unintelligible.

Here we only address the energy loss in the series resistance due to the contact between anode buffer layer and the active layer by using Fe$_3$O$_4$ MNPs and MNPs doped PEDOT:PSS as the anode buffer layer and using external MF to tune the surface morphology of such ABLs. Consequently, the contact between such organic/inorganic layers has been improved, mainly due to the MF induced formation of a smoother surface and higher electric conductive surface of these ABLs. However, the complicated mechanism in the active layer is still unintelligible and the energy loss in recombination
inside photovoltaic processing in the active layer still remains large. On this concern, our next step is to focus on the study to further compress the recombination in PSCs by using MNPs as the dopant in the BHJ composite.
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