Efficiency Enhancement in Solution Processed Organic and Organic-Inorganic Hybrid Perovskite Solar Cells

Zhengguo Xiao

University of Nebraska-Lincoln, zg.xiao1@gmail.com

Follow this and additional works at: http://digitalcommons.unl.edu/mechengdiss

Part of the Polymer and Organic Materials Commons, and the Semiconductor and Optical Materials Commons

http://digitalcommons.unl.edu/mechengdiss/89

This Article is brought to you for free and open access by the Mechanical & Materials Engineering, Department of at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Mechanical (and Materials) Engineering -- Dissertations, Theses, and Student Research by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.
UNIVERSITY OF NEBRASKA

EFFICIENCY ENHANCEMENT IN SOLUTION PROCESSED ORGANIC AND ORGANIC-INORGANIC PEROVSKITE SOLAR CELLS

by

Zhenggo Xiao

A DISSERTATION

Presented to the Faculty of

The Graduate College at the University of Nebraska

In Partial Fulfillment of Requirements

For the Degree of Doctor of Philosophy

Major: Engineering

(Materials Engineering)

Under the Supervision of Professor Jinsong Huang

Lincoln, Nebraska

July, 2015
Efficiency Enhancement in Solution Processed Organic and Organic-inorganic Hybrid Perovskite Solar Cells

By

Zhengguo Xiao

University of Nebraska, 2015

Solution processed thin film photovoltaic devices are one of the most promising renewable energy sources. Organic solar cells have been intensively studied due to their advantages of light-weight, flexibility and low-cost materials and manufacturing. Although its power conversion efficiency (PCE) has reached 11% in single junction device, there is still long way to go before they can be commercialized with a decent efficiency of 15%. The organic-inorganic hybrid perovskite materials have recently shown great potential application in solar cells. The PCE increased dramatically from 3.8% in 2009 to a certified efficiency of 20.1% in 2014. Nevertheless, both the instability and toxicity of the perovskite materials still impede its commercial mass production and application. In this dissertation, we focus on the efficiency enhancement for solution processed organic and organic-inorganic solar cells.

In Chapter 2, I demonstrated that the crystallinity of the ferroelectric polymer poly[(vinylidenefluoride-co-trifluoroethylene] (P(VDF-TrFE)) at the organic active layer/
electrode interface plays a critical role in the efficiency enhancement of organic solar cells. Only the dipoles of the ferroelectric phase can be aligned under the external applied bias and can generate extra electric field penetrating into the organic film. Then, I synthesized the ferroelectric P(VDF-TrFE) nanocrystals and successfully applied them in the low band gap polymers. A high efficiency of 6.8% was achieved in the poly[N-9′-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′benzothiadiazole)]: phenyl-C_61-butyric acid methyl ester (PCDTBT:PCBM) system compared with the efficiency of 5.3% for the optimized control device without using the P(VDF-TrFE) nanocrystals. Another small polar molecule, 2-cyano-3-(4-(diphenylamino) phenyl)acrylic acid (TPACA), was also applied to increase the efficiency of organic solar cells. The advantage of TPACA molecules over P(VDF-TrFE) is that it can be simply blended in the active layer. A high efficiency of 7.8% after poling was achieved in the poly[4,8-bis-(2-ethyl-hexyl-thiophene-5-yl)-benzo[1,2-b:4,5-b′]dithiophene-2,6-diy]-alt-[2-(2′-ethyl-hexanoyl)-thieno[3,4-b]thiophen-4,6-diy] (PBDTTT-CT):PCBM systems by blending TPACA in the active layer.

In Chapter 3, I developed a universal approach of solvent fluxing to fabricate graded bulk heterojunction (BHJ) polymer:fullerene films to increase the device efficiency. The solvent fluxing process can extract part of the fullerene inside the BHJ film to the top surface to form graded BHJ. The graded BHJ with fullerene rich at the top surface is preferred for the regular structure devices. The PCE of the devices after solvent fluxing is increased by 15%-50% compared with the control devices without solvent fluxing. Various characterizations were performed on the origin of the efficiency
enhancement, and it is concluded that the bimolecular recombination was greatly reduced in the graded BHJ devices.

In Chapter 5, a two-step spin coating approach was developed to fabricate the continuous and compact organolead trihalide perovskite (OTP) films. Benefit from the high quality pin-hole free perovskite films; the average PCE of methylammonium lead iodide (MAPbI3) perovskite devices reached 14.5% and 85% of the devices had efficiency above 14%. In Chapter 6, I discovered that the solvent annealing can be used to increase the grain size and crystallinity of the perovskite films. The carrier diffusion length of the MAPbI3 perovskite film was increased from about 250 nm of the thermal annealed film to above 1 µm after solvent annealing. The highest device efficiency reached 15.6%, and device efficiency stayed above 14.5% when the perovskite thickness increased to 1,015 nm.

In chapter 7, a novel phenomenon, giant switchable photovoltaic, was discovered in the perovskite solar cells. The switchable photocurrent reached 20.1 mA/cm² in the vertical structure OTP device under one sun illumination, and the open circuit voltage (VOC) reached 47 V in the lateral tandem devices with 125 sub-cells. I also figured out the origin of the switchable photovoltaic effect: ion motion induced switchable p-i-n structure.
To Leiyan Zhao, my wife;

To my parents and brothers;

To my parents-in-law.
ACKNOWLEDGEMENTS

First and foremost I wish to express my sincere gratitude to my advisor, Prof. Jinsong Huang, whose expertise, understanding and far-sight helped me a lot on my graduate study and research. He has been inspiring me to think deeper on the experiment. He is always giving me insightful understanding, comments and constructive criticisms on my research. I appreciate his education very much, not only for how to do research, but also for how to communicate with others on the research. I am also thankful for him to give me the freedom to explore on my own. Without his education and patient, my graduate study cannot be so fruitful.

I am grateful for having an extraordinary doctoral committee and wish to thank Professor Jeffrey E. Shield, Professor Stephen Ducharme, and Professor Yongfeng Lu for their valuable suggestions on my research and comments on my comprehensive exam, and for their precious time. Without their support, I cannot finish my graduate study and thesis.

Over the past four years of my Ph.D studies and research at University of Nebraska-Lincoln, my current and former group members helped me a lot on my experiment and they helped me grow fast. I wish to thank: Dr. Yongbo Yuan, Dr. Fawen Guo, Dr. Qingfeng Dong, Dr. Bin Yang, Dr. Yunzhang Lu, Dr. Baodong Mao, Dr. Rui Dong, Jeremy VanDerslice, Chen Bi, Yucuan Shao, Qi Wang, Yehao Deng, Miao Hu, Dr. Haotong Wei, Dr. Yanjun Fang, Dr. Liang Shen, Dr. Conghua Zhou, Dr. Qingfeng Zhang, Dr. Yang Bai et al. I appreciate their tremendous help and collaborations that made this work possible.
Most importantly, none of this would have been possible without the constant love, concern, support and patience of my family. Their support helped me overcome setbacks and stay focused on my graduate study over these difficult years. I would like to express my heart-felt gratitude to my wife, my parents and brothers, and parents-in-law.
Table of Contents

Chapter 1 Introduction to organic solar cells ................................................................. 1

1.1. Overview ....................................................................................................................... 1

1.2. Working mechanisms ................................................................................................. 1

1.3. Device characteristics ............................................................................................... 2

1.4. Challenges .................................................................................................................... 5

Chapter 2 Efficiency enhancement of OSCs using ferroelectric materials ...................... 8

2.1. Introduction to P(VDF-TrFE) ...................................................................................... 8

2.2. Efficiency enhancement of OSCs using P(VDF-TrFE) .............................................. 9

2.3. Influence of P(VDF-TrFE) crystallinity on device performance ................................. 10

2.3.1. Crystallinity of the P(VDF-TrFE) films fabricated by LB and spin coating methods 10

2.3.2. Ferroelectric properties of the LB and spun P(VDF-TrFE) films ......................... 12

2.3.3. Switch capability of the devices with LB and spun P(VDF-TrFE) interlayers ............ 14

2.3.4. Stability of the polarization in P(VDF-TrFE) ....................................................... 16

2.3.5. Can the polarization charge be screened by the photocurrent? .............................. 17

2.3.6. Direct correlation of photocurrent with polarization in P(VDF-TrFE) ...... 19

2.4. Synthesize of ferroelectric nanocrystal P(VDF-TrFE) and its application in OSCs 21
2.4.1. Motivation ........................................................................................................ 21
2.4.2. Synthesis of P(VDF-TrFE) nanoparticles and nanocrystals ....................... 22
2.4.3. Characterization of P(VDF-TrFE) nanoparticles and nanocrystals .......... 24
2.4.4. Application of nanocrystal P(VDF-TrFE) in low bandgap polymers .......... 27
2.4.5. Conclusion ....................................................................................................... 35

2.5. Efficiency enhancement in polymer solar cells with polar small molecules .... 36
2.5.1. Motivation ....................................................................................................... 36
2.5.2. TPACA as cathode interfacial layer ............................................................... 37
2.5.3. TPACA blended in the active layer ............................................................... 39
2.5.4. Origin of the efficiency enhancement ......................................................... 43
2.5.5. Universal application of the TPACA in other polymer:fullerene systems . 47
2.5.6. Conclusion ....................................................................................................... 48

Chapter 3 Universal formation of graded BHJ for efficiency enhancement ..........49
3.1. Motivation ........................................................................................................ 49
3.2. Solvent fluxing approaches ............................................................................ 51
3.3. Confirmation of the graded BHJ ................................................................. 55
3.4. Device performance ....................................................................................... 61
3.5. Origin of the efficiency enhancement ......................................................... 68
3.6. Conclusion ....................................................................................................... 75

Chapter 4 Introduction to organic-inorganic hybrid perovskite solar cells ........77
4.1. Overview .................................................................................................................. 77
4.2. A brief history ........................................................................................................... 78
4.3. Challenges ............................................................................................................... 80

Chapter 5 Inter-diffusion approach to fabricate perovskite films ......................... 81
  5.1. Inter-diffusion method .......................................................................................... 81
  5.2. Film characterization ........................................................................................... 84
  5.3. Device structure and performances ................................................................... 87

Chapter 6 Solvent annealing of the perovskite for efficiency enhancement ............ 95
  6.1. Motivation ............................................................................................................ 95
  6.2. Solvent annealing approach ............................................................................... 96
  6.3. Perovskite film characterization ........................................................................ 97
  6.4. Device structure and performance .................................................................... 101
  6.5. Origin of the efficiency enhancement ............................................................... 107

Chapter 7 Switchable perovskite solar cells .......................................................... 111
  7.1. Switchable perovskite photovoltaics with vertical structure ....................... 111
  7.2. Switchable perovskite photovoltaics with Lateral structure ...................... 115
  7.3. Origin of the switchable perovskite photovoltaic effect ............................ 118
  7.4. Conclusion ....................................................................................................... 126

Chapter 8 Summary .................................................................................................. 128

References: ................................................................................................................. 131
List of Figures

Figure 1.1 (a) The device structure of a typical BHJ-OPV; (b) Process of the conversion of incident light into electricity in OPVs. The electrons on acceptor are still bound to holes on donor right after the charge transfer, as illustrated by the ellipse in the figure. 2

Figure 1.2 Current-voltage (I-V) characteristics of a solar cell under illumination. The short circuit current ($J_{SC}$), the open circuit voltage ($V_{OC}$), and the maximum power point ($V_{max}$, $I_{max}$) are shown. 3

Figure 1.3 Equivalent circuit of a solar cell device. 5

Figure 1.4 Schematics of the influence of series and shunt resistance on the photocurrent curves. 5

Figure 2.1 Structure of P(VDF-TrFE) copolymer. 8

Figure 2.2 (a) Schematics of FE-OPV and working principle with ferroelectric polymer at the interface; (b) Photocurrent curves of Poly(4,4-dioctyldithieno(3,2-b:2',3'-d)silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl)(PSBTBT):[70]PCBM device without an FE layer (magenta line), with an FE layer before poling (black square line) and after poling (red squares). 9

Figure 2.3 (a) An illustration of the morphology of the LB and spun P(VDF-TrFE) films. (b) XRD spectra of a 50 ML P(VDF-TrFE) LB film and a spun P(VDF-TrFE) film (~150 nm) on Si substrate. 12

Figure 2.4 (a) Topography of a P(VDF-TrFE) LB film (2 μm×2 μm); (b) topography of a P(VDF-TrFE) spun film (5 μm×5 μm); (c) PFM amplitude images of a P(VDF-TrFE) LB film; (d) PFM response mapping images of the P(VDF-TrFE) spun film on
P3HT:PCBM surface. (e) Comparison of PFM amplitude of the P(VDF-TrFE) LB film and spun film on the marked positions in (c-d). ................................................................. 13

Figure 2.5 PFM amplitude (a-c) and phase images (d-f) of domain structure in the P(VDF-TrFE) nanomesa on P3HT:PCBM before and after application of a positive or negative voltage pulses. (g-h) PFM hysteresis loops (phase and amplitude) of unscreened P(VDF-TrFE) domain on P3HT:PCBM layer ............................................................................. 14

Figure 2.6 Comparison of device performance with P(VDF-TrFE) as interfacial layers by LB (a) and spin coating (b) with a device structure of ITO/ PEDOT:PSS/ P3HT:PCBM/ P(VDF-TrFE)/ Al. Comparison of switching capability of the devices with crystalline (c) and amorphous P(VDF-TrFE) (d) at both cathode and anode with a device structure of: ITO/ P(VDF-TrFE)/ P3HT:PCBM/ P(VDF-TrFE)/Au. ..................................................... 15

Figure 2.7 Variations of the open circuit voltage and short circuit current in the FE-OPV structure over two weeks of observation. ................................................................. 17

Figure 2.8 Short circuit current of LB P(VDF-TrFE) FE-OPV under 3 µW/cm² illumination. .................................................................................................................... 19

Figure 2.9 (a) In-situ monitoring of the variations in the photocurrent (under 30 mW/cm² illumination) upon annealing to induce depolarization of the ferroelectric layer. (b) Illustration of the dipole rearrangement in P(VDF-TrFE) LB and spun films as a result of annealing .................................................................................. 20

Figure 2.10 (a) Schematic of the synthesis of P(VDF-TrFE) nanoparticles (NPs). (b) Pictures of formation process of P(VDF-TrFE) NPs with different reaction time using acetone as good solvent and pure water as poor solvent. ........................................... 23
Figure 2.11 Scanning electron microscope (SEM) images of P(VDF-TrFE) as-grown NPs using water as the poor solvent (a) and water:methanol (1:10 v/v) blend solvent as the poor solvent (b). (c) P(VDF-TrFE) NP size distribution based on 71 NPs. 

Figure 2.12 (a) SEM image of the refluxed P(VDF-TrFE) NPs. Inset: enlarged image of the NPs. (b) XRD of the as-grown P(VDF-TrFE) NPs and refluxed P(VDF-TrFE) NPs.

Figure 2.13 (a) XRD of the refluxed P(VDF-TrFE) NPs under various temperatures. (b-c) Non-linear hysteresis loop (phase and amplitude) of a refluxed P(VDF-TrFE) NP on top of Au covered silicon substrate.

Figure 2.14 Schematics of FE-OPV device working mechanism. (a) After reverse bias poling, the unscreened surface charges of the P(VDF-TrFE) NPs will generate electric field and penetrate through the organic active layer, which will help the extraction of photo-generated charges; (b) three-dimensional AFM image of topology of NPs on the organic active layer surface with scale of 5×5 µm.

Figure 2.15 The photocurrent curves of PCDTBT:[70]PCBM based device with the as-grown amorphous NPs (a), and the refluxed ferroelectric P(VDF-TrFE) NPs (b) before (black square line) and after poling (red square line). (c) $J_{SC}$ variation with poling voltage for the device with the as-grown amorphous NPs (black square line), and the refluxed ferroelectric P(VDF-TrFE) NPs (red square line) after poling.

Figure 2.16 (a-e) Photocurrents of the FE-OPV devices before (black square curves) and after poling (red square curves) which have P(VDF-TrFE) NPs on top of active layer with increasing coverage. The corresponding SEM images of P(VDF-TrFE) NPs distribution are shown as insets. Scale bars in all the SEM images are 1 µm. (f) Photocurrent curves of the FE-OPV device with P(VDF-TrFE) NPs as interlayer without poling (black square),
after positive poling (red square), after negative poling (blue square) and controlled
device with Ca/Al as cathode (green square). The EQE curves of the devices with
P(VDF-TrFE) NPs after positive poling (red square) and with Ca/Al cathode (green
square) are shown in the inset................................................................. 31

Figure 2.17 (a) Molecular structure of TPACA. Energy diagram of the device before
poling (b) and after negative bias poling (c) with TPACA as the cathode interfacial layer.
(d) Photocurrent of the P3HT:PCBM device before and after negative bias poling with
TPACA as cathode interfacial layer. ................................................................. 38

Figure 2.18 Energy diagram of the device before poling (a) and after negative bias poling
(b) with TPACA blended in the active layer. (c) Photocurrent of the P3HT:PCBM device
before and after poling with TPACA blended in the active layer............................. 40

Figure 2.19 Contact angle measurement of the PHT:PCBM film without (a) and with (b)
TPACA blended in the active layer. Photocurrent (c) and dark current (d) of the device
before and after negative bias poling after methanol washing with TPACA as interfacial
layer. Photocurrent (e) and dark current (f) of the device before and after negative bias
poling after methanol washing with TPACA blended in the P3HT:PCBM active layer. 42

Figure 2.20 (a) Dark current of the device with TPACA blended in the active layer. The
inset is the dark current of the device under negative bias. (b) Built-in potential of the
P3HT:PCBM device measured by fitting the 1/C² versus voltage curve. ......................... 44

Figure 2.21 (a) Charge generation rate measured by time delayed collection field. The
charge generation efficiencies were measured under different bias from -4 V to open
circuit voltage, and were normalized by the IQE at -4V. (b) The charge extraction time of
the device before and after poling................................................................. 46
Figure 2.22 The TPACA polar molecule application in (a) PCDTBT:[70]PCBM system and (b) PBDTTT-CT:[70]PCBM system with TPACA blended in the active layer.

Figure 3.1 (a-b) Illustration of the morphology of donor (blue) and acceptor (red) distribution in regular and graded BHJ devices. Composition profile of donor and acceptor in regular (c) and graded (d) BHJ devices. A larger composition percentage is correlated with wider charge transportation path and thus larger effective conductivity.

Figure 3.2 (a), Formation of DIO:fullerene-derivatives nano-droplets after the spin coating of the polymer:fullerene-derivatives blend solution with DIO as additive; (b), Penetration of methanol into the blend film along the DIO regions; (c), Extraction of DIO as well as partial fullerene-derivatives to the surface; (d), Removing DIO with methanol from the film by spin coating; (e), Formed graded BHJ with better connectivity of donors and acceptors.

Figure 3.3 Chemical structures of donors and acceptors.

Figure 3.4 Optical images of PBDTTT-CT:[70]PCBM (a), PCDTBT:[70]PCBM(c),b,c single path absorption spectroscopy of as-prepared (black line) and methanol-fluxed (red line) and vacuum-dried (blue line) films of PBDTTT-CT:[70]PCBM (b), PCDTBT:[70]PCBM(d).

Figure 3.5 a-d, EFTEM cross-sectional images of the vacuum-dried (a), fluxed PBDTTT-CT:[70]PCBM film (c), vacuum-dried (b), and fluxed PCDTBT:[70]PCBM film (d) with energy filter set at 19±4 eV where brighter regions represent donor-rich region. The small pictures on the left of each EFTEM image are TEM images with energy filter set at 0 V which show each layer clearly, in which donors and acceptors do not have any significant contrast because they have very little differences in terms of their electron density; e,f,
Gray values, along the vertical direction, of the vacuum-dried and fluxed PBDTTT-CT:[70]PCBM films (e), and PCDTBT:[70]PCBM films (f) in the areas marked with white dashed squares on the left EFTEM images. ................................................................. 58

Figure 3.6 Quantitative determination of the composition of the vacuum-dried and fluxed PBDTTT-CT:[70]PCBM films (a) and PCDTBT:[70]PCBM films (b) along the vertical direction by ellipsometry. ........................................................................................................ 60

Figure 3.7 The composition depth profiles of PBDTTT-CT:[70]PCBM films (a) and PCDTBT:[70]PCBM (b) films measured by SIMS. All the scale bars are 50 nm. ......... 61

Figure 3.8 Photocurrent of vacuum-dried (black circle line) and fluxed (red circle line) devices of PBDTTT-CT:[70]PCBM (a), PCDTBT:[70]PCBM (b) under simulated A.M 1.5 illumination. EQE (open circle lines), reflective absorption (solid lines) and IQE (solid circle lines) of (c) PBDTTT-CT:[70]PCBM and (d) PCDTBT:[70]PCBM devices (black: vacuum-dried, red: fluxed). ........................................................................................................ 63

Figure 3.9 Device performance of PBDTTT-CT:[70]PCBM (a), PCDTBT:[70]PCBM (b), P3HT:IC_{60}BA (c), and FTQ:[70]PCBM (d) with different time interval between spin coating the blend film and solvent flux................................................................. 65

Figure 3.10 Photo current characteristics of solvent flux with different low boiling point solvent. ........................................................................................................ 66

Figure 3.11 Photocurrent curves of the vacuum-dried (black circle line) and fluxed wet film (red circle line) and fluxed pre-vacuum-dried film (blue circle line) of PBDTTT-CT:[70]PCBM (a) and PCDTBT:[70]PCBM (b). Photocurrent curves of the vacuum-dried and solvent-fluxed inverted structure devices of PBDTTT-CT:[70]PCBM (c) and PCDTBT:[70]PCBM (d). ........................................................................................................ 67
Figure 3.12 Schematics of the light to electric conversion processes in organic solar cells .............................................................................................................................................. 69

Figure 3.13 Charge generation efficiency of PBDTTT-CT:[70]PCBM (a), PCDTBT:[70]PCBM (b) devices measured by TDCF. ........................................................................................................ 70

Figure 3.14 Light intensity dependent photocurrent for PBDTTT-CT:[70]PCBM system (a:vacuum-dried, b:Fluxed) and PCDTBT:[70]PCBM system (c:vacuum-dried, d:Fluxed) ............................................................................................................................................... 71

Figure 3.15 FFs of fluxed (red square) and vacuum-dried (black square) devices under varied light intensity from 10 to 300 mW/cm² with active layer of PBDTTT-CT:[70]PCBM (a), PCDTBT:[70]PCBM (b). c,d, the exponent of $\alpha (\Delta J \propto IL^\alpha)$ under different effective applied bias $V_0-V$ on PBDTTT-CT:[70]PCBM (c), PCDTBT:[70]PCBM. .................................................................................................................................................. 72

Figure 3.16 Photo-generated carrier density at the open circuit voltage condition for PBDTTT-CT:[70]PCBM (a) and PCDTBT:[70]PCBM (c); Carrier lifetime for PBDTTT-CT:[70]PCBM (b) and PCDTBT:[70]PCBM (d); Bimolecular recombination rate $kn$ of PBDTTT-CT:[70]PCBM (e), PCDTBT:[70]PCBM (f) measured by TPV ................. 74

Figure 4.1 Organometal trihalide perovskite structure, where x=I, Cl, Br ....................... 77

Figure 4.2 (a) Mesoscopic structure perovskite solar cell with mesoporous TiO₂ layer and (b) planar structure without a mesoporous TiO₂ layer .................................................................................................................. 79

Figure 4.3 Power conversion efficiency table for thin film solar cells ......................... 80

Figure 5.1 Schematics of spin-coating of PbI₂ and MAI using orthogonal solvents and the conversion of the stacking layer into perovskite layer upon annealing ...................... 82
Figure 5.2 SEM image of the PbI₂ film (a), the annealed perovskite layer formed by interdiffusion process (b)........................................................................................................ 84

Figure 5.3 (a) Single path absorption of perovskite film after dry and various annealing durations. The inset shows the pictures, from left to right, of the spun PbI₂ film, the PbI₂/MAI film before drying, the PbI₂/MAI films after drying, and after 15 min annealing; (b) XRD pattern of MAI, PbI₂ and the perovskite films formed by interdiffusion with varied annealing time........................................................................................................ 85

Figure 5.4 (a) Photo image and device performance of the perovskite films deposited by dipping 140 nm PbI₂ film into MAI. The MAI concentration is 10 mg/ml dissolved in 2-propanol. ......................................................................................................................................................... 86

Figure 5.5 (a) Cross-section SEM image of the best-performing perovskite device. The scale bar is 500 nm. The thickness of the perovskite layer is ~270 nm; (b) Composition depth profiles of the device without the Al electrode measured by SIMS. ...................... 88

Figure 5.6 Performance of the perovskite devices. (a) Photocurrents of the device with PbI₂ thickness of 140 nm while varied MAI concentration from 40-50 mg/ml; (b) Photocurrents of the devices with perovskite films of different thickness varied from 200 to 320 nm. ......................................................................................................................................................... 89

Figure 5.7 Device performance statistics based on more than 50 devices from five batches. ......................................................................................................................................................... 92

Figure 5.8 (a) Photocurrents of a high performance perovskite device measured with different delays between measurement points (a) and different sweep directions (b). No obvious hysteresis of photocurrent was observed. (c) Measured photocurrent output at
the maximum power point of a high performance device versus time by turning on and off the illumination with a chopper. ................................................................. 93

Figure 6.1 Schematics of the interdiffusion approach and solvent-annealing-induced grain size increase. ........................................................................................................ 96

Figure 6.2 SEM images of the thermal-annealed (TA) perovskite films with thickness of 250 nm (a), 430 nm (d) and 1,015 nm, and solvent-annealed (SA) perovskite films with thickness of 250 nm (b), 430 nm (e) and 1,015 nm (h); (c,f,i) Grain size statistics of the SEM images on the left; The scale bar in the SEM pictures is 2 µm. ......................... 99

Figure 6.3 SEM pictures of the thermal-annealed and solvent-annealed 300 nm thick perovskite films after different annealing duration from 5 to 60 min. Scale bar is 2 µm. 99

Figure 6.4 (a) Average grain size versus annealing time for the 300 nm thick perovskite films; (b) XRD patterns of the thermal-annealed and solvent-annealed 300 nm thickness perovskite films; (c) Single path absorption of the perovskite films with different thicknesses. ........................................................................................................ 100

Figure 6.5 Cross-section SEM images of the thermal-annealed (a) and solvent-annealed (b) perovskite films with thickness of 1,015 nm.................................................................................. 102

Figure 6.6 Photocurrent characteristics (a-d) of the perovskite devices with film thickness of 250 nm, 300 nm, 630 nm, and 1,015 nm, respectively. (e-h) EQE of the perovskite devices with film thicknesses. Black circle line: thermal annealing; red circle line: solvent annealing; blue circle line: IQE; green line: transmittance of the glass/ITO substrate. 104

Figure 6.7 Photocurrent curves of a best performing device with (a) different scanning directions, and (b) different scanning rates measured from negative to positive bias. (c) Steady-state photocurrent output at the maximum power point (0.82 V)......................... 107
Figure 6.8 Trap density of states calculated from the thermal admittance spectroscopy measurement; (b) Photovoltage decay under 0.3 Sun illumination measured by TPV; (c) Photocurrent decay measured by TPC.

Figure 7.1 J-V characteristics of the as-prepared vertical structure devices with the structure of ITO/PEDOT:PSS)/Perovskite (300 nm)/Au. Scanning rate was 0.14 V/s and the scanning direction was labeled in the figure.

Figure 7.2 Vertical structure photovoltaic devices and their switching behavior. a, Schematics of the vertical structure device. Dark current (b) and photocurrent hysteresis (c) of the devices under continuous current sweeping at a rate of 0.14 V/s between -2.5 V and 2.5 V. The arrows in the figure show the scanning direction. d, Open circuit voltage of the device recorded after repeated poling by ±2.5 V bias for more than 750 circles. Only the first ten and last ten circles were shown.

Figure 7.3 The stability test of short circuit current for the ITO/PEDOT:PSS/Perovskite/Au vertical structure device after positive and negative poling. (The $J_{SC}$ were normalized by the value measured 24 h after the fabrication of the device (18.2 mA/cm$^2$ and -19.0 mA/cm$^2$).

Figure 7.4 Lateral structure photovoltaic devices and their switching behavior. a, Schematics of the lateral structure devices. b, A Au stripe array under microscope (reflective mode), where the electrode spacing ($d$) shown in the enlarged image (bottom) is 8 µm. The lateral photovoltaic devices connected in series were fabricated by depositing uniform perovskite films (300 nm) on preformed Au stripe electrodes with spacing between 8 and 100 µm.
Figure 7.5 a, Photocurrents of the device before and after negative and positive poling for a single cell measured at a sweeping rate of 0.05 V/s under 0.25 sun illumination; The arrows in the figure show the scanning direction. b, Photocurrents of the lateral photovoltaic devices connected in series measured at a sweeping rate of ~0.05 V/s for each cell. The poling of the lateral photovoltaic devices were conducted by either poling each cell individually or simply poling the whole area between the first and last electrodes. ................................................................. 117

Figure 7.6 Ferroelectric polarization loops measured at room temperature (a) and at 77 K (b) scanned at the same frequency of photovoltaic switch process. c, PFM topology (c), amplitude (e) and phase (f) images of the perovskite (300 nm). d, Representative PFM hysteresis loops (phase and amplitude) signal for any location on the film surface....... 120

Figure 7.7 Normalized I-V curves of lateral Au/OTP/Au solar cells with different electrode-separating distances (d) at a illumination of 0.25 sun................................. 120

Figure 7.8 Switchable photovoltaic model and mechanism study. a-b, Schematics of ion drift in perovskite during poling, and the accumulated ions in the perovskite near the electrodes induced p- and n-doping; c, Energy diagram of the p-i-n structure after poling. ........................................................................................................................................... 121

Figure 7.9 a, Schematic image of the devices with some part of the Au electrodes peeled off. The scanning area is also marked as a dashed rectangle in the image; b-c, KP FM potential image of the perovskite/Au areas after positive and negative poling of the perovskite layers (300 nm).............................................................................................................. 122

Figure 7.10 a-b, Photoluminescence from the thin perovskite layers close to either a PEDOT:PSS electrode or Au electrode. A thin gold electrode (25 nm) was used as the top
electrode so the PL emission from the perovskites close to both electrodes can be measured, and a blue light (405 nm) was used to excite only the 25 nm thick perovskite layer close to the electrodes (estimated by the extinction coefficient) of the 1,015 nm thick device. The PL measurement was conducted in-situ during the poling process to exclude other PL changing factors. The peak at 710 nm in Figure 7.10 a is from ITO. 123

Figure 7.11 In-situ monitoring of the material change in a poling process. a, Illustration of the setup used for the in-situ monitoring of the poling process using a lateral structure device. b, Snapshots of the in-situ recorded video which shows changed perovskite material close to the anode side during the poling process. The electrical field applied on the perovskite film was ~1.2 V/µm. ................................................................. 124

Figure 7.12 Dynamic poling process of the ITO/PEDOT:PSS/Perovskite (300 nm)/Au vertical structure devices at (a) varied electrical field, (b-c) temperature and (d-f) with different film morphology. The thickness of the films in d-f is 1,015 nm. (g) $J_{SC}$ versus poling time of the devices with different film annealing processes and measurement temperatures. The devices were measured under 0.1 sun when measured at 60 °C. The error bar showed the device performance variation based on the statistics of five devices of each category. And the scanning rate in Figure 7.12 was 0.14 V/s........................................ 126
List of Tables

Table 2.1 Comparison of FE-OPV performances with different ferroelectric P(VDF-TrFE) NP density before and after positive poling at -7 voltage. (The performance of the device with Ca/Al as cathode and optimized NPs spacing was averaged over 50 devices, and the performance devices with other NP spacing were averaged over 10 devices) .... 32

Table 2.2 Different polymer: fullerene-derivative blend films fabrication details (DIO (1,8-diiodooctane))............................................................................................................ 40

Table 3.1 Different polymer: fullerene-derivative blend films fabrication details ........ 55

Table 3.2 Statics of PCE of different kinds of solar cells with regular BHJ (vacuum-dried) and Graded BHJ (solvent-fluxed) structure ............................................................................. 63

Table 5.1 The thickness of perovskite layers fabricated by the interdiffusion method using precursor solutions with different PbI₂ and MAI concentrations.......................... 83

Table 5.2 Photovoltaic performance of a best-performing device under different illumination light intensities. .............................................................. 91

Table 6.1 The performances of perovskite solar cell devices with different film thickness fabricated by thermal or solvent annealing processes. (Based on ten devices of each category) ........................................................................................................ 104
Publications


2. Zhengguo Xiao, Qingfeng Dong, Hui Huang, Wenjing Tian, Jinsong Huang*, Electric-field tunable bulk and interfacial dipoles in organic solar cells. IEEE J. Photovoltaics, Accepted (2015)


7. Cheng Bi, Qi Wang, Yuchuan Shao, Yongbo Yuan, Zhengguo Xiao and Jinsong Huang*, Nonwetting Surface Driven High Aspect Ratio Crystalline Grain Growth for Efficient Hybrid Perovskite Solar Cells, Nature Communications, Accepted, 2015


14. Rui Dong, Yanjun Fang, Jungseok Chae, Jun Dai, Zhengguo Xiao, Qingfeng Dong, Yongbo Yuan, Andrea Centrone, Xiao Cheng Zeng, Jinsong Huang*. High
Gain and Low-Driving-Voltage Photodetectors Based on Organolead Triiodide Perovskites, Advanced Materials, 27, 1912-1918 (2015) (Journal Cover)


20. Yuchuan Shao, Zhengguo Xiao, Cheng Bi, Yongbo Yuan, Jinsong Huang, Origin and elimination of photocurrent hysteresis by fullerene passivation in

22. Baodong Mao, Yongbo Yuan, Yuchuan Shao, Bin Yang, Zhengguo Xiao, and Jinsong Huang*, Alkylamine assisted ultrasound exfoliation of MoS2 naosheets and organic photovoltaic application, Nanoscience and Nanotechnology Letters, 6, 685-691(2014)

23. Rui Dong, Cheng Bi, Qingfeng Dong, Fawen Guo, Yongbo Yuan, Yanjun Fang, Zhengguo Xiao, and Jinsong Huang*, An Ultraviolet to Near Infrared Broad Spectral Nanocomposite Photodetector with Gain Advanced Optical Materials, 2, 549-554 (2014)


26. Cheng Bi, Yuchuan Shao, Yongbo Yuan, Zhengguo Xiao, Chenggong Wang, Yongli Gao and Jinsong Huang*, Understanding the Formation and Evolution of


32. Y. Lu, Z. Xiao, Y. Yuan, H. Wu, Z. An, Y. Hou, C. Gao and J. Huang*, Fluorine substituted thiophene-quinoxaline copolymer to reduce HOMO level and increase


36. Yunzhang Lu, Clement Alexander, Zhengguo Xiao, Yongbo Yuan, Runyu Zhang and Jinsong Huang*, Utilizing insulating nanoparticles as spacer in the laminated flexible polymer solar cells for improved mechanical stability, Nanotechnology 23, 344007 (2012)

Book Chapter

1. Wei Chen, Feng Liu, Ondrej E. Dyck, Gerd Duscher, Huipeng Chen, Mark D. Dadmun, Wei You, Qiquan Qiao, Zhengguo Xiao, Jinsong Huang, Wei Ma, Harald Ade, Jong K. Keum, Adam J. Rondinone, Karren L. More, and Jihua Chen,
Chapter 1 Introduction to organic solar cells

1.1. Overview

In the past decades, organic solar cells (OSCs) have attracted tremendous attention due to their advantages of low-cost manufacturing and flexibility.\textsuperscript{1,2} With great efforts from the community, the power conversion efficiency (PCE) of OSCs has exceeded 11\% for a single junction cells and 12\% for tandem cells.\textsuperscript{3-6} A typical organic photovoltaic (OPV) device consists of one or more layers of organic materials located between a transparent electrode coated on substrates like glass or flexible polymer substrates, and a metal cathode of aluminum (Al), as shown in Figure 1.1a. The organic layer is generally as thin as 80-200 nm thick because of the large absorption coefficient (10\textsuperscript{5} cm\textsuperscript{-1}) and relatively low carrier mobility (10\textsuperscript{-4}-10\textsuperscript{-1} cm\textsuperscript{2}/Vs) of many organic molecules. It should be noted that, in the active layer, the polymer donors and fullerene acceptors are usually randomly mixed together, and they form so-called bulk heterojunction (BHJ). The BHJ can ensure there is enough interfaces to split the photo-generated excitons.\textsuperscript{7,8} Due to the high binding energy (0.4-1.0 eV) of Frenkel-excitons in organic semiconductors, photo-generated excitons cannot be dissociated by the weak built-in electric field provided by the electrode work function difference.

1.2. Working mechanisms

Studies of OPVs reveal that the light to electricity conversion involves four steps, which are labeled in Figure 1.1b: 1) light absorption to generate an exciton; 2) exciton diffusion; the exciton diffusion length in organic semiconductors was reported to be at the range of 10-20 nm. Therefore, the BHJ was needed. 3) charge transfer between donor
and acceptor (after this step the electrons and holes locate in different materials, but are still electrically bound together due to the low dielectric constant of organic material and proximity between them—these are referred to as charge transfer excitons (CTEs), to distinguish them from Frenkel-excitons); and 4) separation of the CTEs into free charges and extraction of the free charges to electrodes.\(^9\)

**Figure 1.1** (a) The device structure of a typical BHJ-OPV; (b) Process of the conversion of incident light into electricity in OPVs. The electrons on acceptor are still bound to holes on donor right after the charge transfer, as illustrated by the ellipse in the figure.

### 1.3. Device characteristics

**Power conversion efficiency (PCE):** The most important parameter of a solar cell is PCE, which is determined by its short circuit current \(J_{SC}\), the open circuit voltage \(V_{OC}\) and fill factor (FF) as shown in **Figure 1.2**.

\[
PCE = J_{SC} \times V_{OC} \times FF
\]
The $J_{SC}$ is defined as the current density at 0 V under illumination; the $V_{OC}$ is defined as the voltage where photocurrent output is zero. The FF is defined by the following equation:

$$\text{FF} = \frac{J_{max} V_{max}}{J_{SC} \times V_{OC}}$$

**Figure 1.2** Current-voltage ($I$-$V$) characteristics of a solar cell under illumination. The short circuit current ($J_{SC}$), the open circuit voltage ($V_{OC}$), and the maximum power point ($V_{max}$, $I_{max}$) are shown.

**External quantum efficiency (EQE):** EQE is defined as the ratio between the number of collected carriers and the number of all the incident photons on the device active area at a given wavelength. The $J_{SC}$ can be calculated by integrating EQE over the solar irradiance spectrum.

**Internal quantum efficiency (IQE):** IQE is defined as the ratio between the number of collected carriers and the number of all the absorbed photons by only the active absorber at a given wavelength. The IQE can reach 100% in some types of organic solar cells.
which indicates that all the photo-generated charge carriers can be collected by the electrode without any recombination.

**Series resistance:** The series resistance mainly originates from the resistance of the active layer and contact resistance. The main impact of series resistance is to reduce the FF, high series resistance will result in “S” shape photocurrent curves.

**Shunt resistance:** The shunt resistance may originate from defects and charge leaking paths causes power losses in solar cells. Low shunt resistance causes power loss in solar cell due to the photo-generated charge recombination and/or charge leaking.

The equivalent circuit of a solar cell device is shown in Figure 1.3 considering the presence of series and shunt resistance. The equation for a solar cell with an ideal diode condition is:

\[ I = I_L - I_0 \left( \frac{qV}{e^{qV/kT} - 1} \right) \]

Considering the presence of both series resistance and shunt resistance, the equation is modified to the following equation:

\[ I = I_L - I_0 \left( \frac{q(V + IR_S)}{e^{q(V + IR_S)/nkT} - 1} \right) - \frac{q(V + IR_S)}{R_{SH}} \]

Where \( I_0 \) is the reverse bias saturation current, \( q \) is the charge of the electron, \( n \) is the ideality factor of the diode, \( k \) is Boltzmann’s constant, and \( T \) is temperature.

Both series resistance and shunt resistance will consume power and affect the FF as shown in Figure 1.4.
Figure 1.3 Equivalent circuit of a solar cell device

Figure 1.4 Schematics of the influence of series and shunt resistance on the photocurrent curves

1.4. Challenges

The inefficient charge extraction issue remains a grand challenge for OPVs. The inefficient charge extraction is caused by the low carrier mobility ($10^{-7}$–$10^{-3}$ cm$^2$/V·s) of the existing polymer semiconductors, which yields strong recombination of both bound electron-hole pairs and free charges. The recombination of electron-hole pairs occurs in multiple paths: 1) Frenkel-exciton recombination before the photo-induced electron transfer, 2) CTE recombination (or geminate recombination) of the bound electron-hole pair after the photo-induced electron transfer, 3) Schockley-Read-Hall (SRH) recombination at the interfacial traps, dead-ends, and in the disordered band-tails, and 4)
bimolecular recombination of the free charges. The charge recombination mechanism in OPVs varies from material systems, material morphology, electric field, etc. In optimized BHJ devices, the Frenkel-exciton recombination and SRH recombination constitutes only a small portion of the total recombination loss because the photo-induced electron transfer efficiency was shown to be almost 100% efficient. The major charge recombination in most optimized OPVs falls into two categories: geminate recombination and bimolecular recombination, although the dominating charge recombination mechanism is presently under intense debate.

The significant energy loss during the charge transfer from the donor to the acceptor is also a grand challenge of OPV device efficiency enhancement. It is generally accepted that the lowest unoccupied molecular orbital (LUMO) level offset between the donor and acceptor should be larger than the exciton binding energy (0.3-0.5 eV) in order to get efficient charge transfer. However, a smaller LUMO offset of 0.12 eV was reported recently which could also result in efficient charge transfer. Up to now, most high efficiency polymer: fullerene-derivative systems have very large LUMO offset around 1 eV between donor and acceptor, which result in significant energy loss.

Another grand challenge of OPV device is its uncontrollable morphology. The organic active layer is usually fabricated by spin coating of polymer and fullerene blend solution. It is inevitable that the formed organic film have many breaks and dead ends. An ideal BHJ film morphology was suggested to have a bicontinuous donor and acceptor network with donor and acceptor nanodomains within the exciton diffusion lengths for efficient charge generation and extraction. However, the actual morphologies of
most BHJ films are generally far from ideal.\textsuperscript{10,32} Non-ideal morphologies will inevitably cause the charge recombination both in the BHJ films and at the metal/organic interface.
Chapter 2 Efficiency enhancement of OSCs using ferroelectric materials

2.1. Introduction to P(VDF-TrFE)

The polyvinylidene fluoride (PVDF) and its copolymers with TrFE, P(VDF-TrFE), are room temperature ferroelectric materials widely used for their large polarization charge density and low cost fabrication in large areas. The molecule structure is shown in Figure 2.1. There is a large dipole moment $6.4 \times 10^{-30}$ Cm pointed from fluorine to hydrogen atom, and the spontaneous polarization reaches 0.1 C/m$^2$ for some copolymers after the dipoles are aligned. The PVDF polymers usually have mixed crystalline and amorphous phases. It has been reported that pure PVDF only has degree of crystallinity of 50%, while P(VDF-TrFE) can reach almost 100% crystallinity. There are four phases for the P(VDF-TrFE) copolymer, i.e. paraelectric $\alpha$ phase, ferroelectric $\beta$, $\delta$ and $\gamma$ phases. More details for the organic ferroelectronics and P(VDF-TrFE) can be found in other references.

Figure 2.1 Structure of P(VDF-TrFE) copolymer

Ferroelectric polymers, such as P(VDF-TrFE), can be deposited by various methods including spin coating, electrospinning, nano-imprint, and Langmuir–Blodgett (LB) depositing. The spin coating from low boiling point solvent usually leads to amorphous film, which can be thermal annealed to increase its ferroelectric phase at a
temperature higher than its Curie point. LB method have been used to deposit high quality P(VDF-TrFE) monolayers.

### 2.2. Efficiency enhancement of OSCs using P(VDF-TrFE)

**Figure 2.2** (a) Schematics of FE-OPV and working principle with ferroelectric polymer at the interface; (b) Photocurrent curves of Poly(4,4-dioctyldithieno(3,2-b:2’,3’-d)silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl)(PSBTBT):[70]PCBM device without an FE layer (magenta line), with an FE layer before poling (black square line) and after poling (red squares).

Yuan et al. incorporated a thin layer of ferroelectric P(VDF-TrFE) at the organic/electrode interface to generate an extra electric field in the active layer. The ferroelectric layer was deposited on the surface of organic active layer by LB method,
followed by a thermal annealing process to convert it into ferroelectric phase. After poling under negative bias, the dipoles in the FE layer are aligned with their positive polarization charges close to the poly(3-hexylthiophene) (P3HT): phenyl-C₆₁-butyric acid methyl ester (PCBM) layer and the negative polarization charges close to the Al layer, as illustrated in Figure 2.2a. The negative polarization charges are neutralized by the electrode due to the large density of free charges in metal. The positive polarization charges can generate electric field penetrating through the organic active layer. This additional electric field can facilitate the dissociation of the bound electron-hole pairs and charge collection, leading to increased short circuit current ($J_{SC}$), fill factor (FF) and open circuit voltage ($V_{OC}$). The typical photocurrents of the devices before and after poling are shown in Figure 2.2b. The PCEs of poled OPV devices were about twice larger compared to the devices without FE layers for many types of polymer systems tested. The efficiencies of these devices are higher than the optimized with other methods.

2.3. Influence of P(VDF-TrFE) crystallinity on device performance

2.3.1. Crystallinity of the P(VDF-TrFE) films fabricated by LB and spin coating methods

The crystallinity of P(VDF-TrFE) layer plays a critical role in the efficiency enhancement of OSCs. In order to determine the effect of the crystallinity of ferroelectric polymer layer on the performance of the OPV device, it is essential to fabricate P(VDF-TrFE) of high crystallinity, and then perform thorough electrical characterization to verify its ferroelectric nature. For this reason, we fabricated two types of OPV devices, differing only in the method of deposition of the P(VDF-TrFE) copolymer film. The
P(VDF-TrFE) films were fabricated by two different methods, LB deposition from a water subphase and spin-coating from acetone solution. The films were deposited on an OPV nanocomposite layer composed of P3HT and PCBM which was deposited by spin coating on an indium tin oxide (ITO)/glass substrate. The LB-deposited 2 monolayer (ML) P(VDF-TrFE) films with an average thickness of 3.4 nm were annealed for 30 minutes at 135 °C to optimize their crystallinity.45-47 The P(VDF-TrFE) films formed by spin coating with an average thickness of 3.2 nm were annealed at a lower temperature of 90 °C for 10 min.48 Typical morphology of the P(VDF-TrFE) films fabricated by these two deposition methods is illustrated in Figure 2.3a. The samples fabricated by these two deposition methods with a thickness around 150 nm were firstly characterized by X-ray diffraction (XRD) study. LB deposition results in fabrication of highly crystalline P(VDF-TrFE) films as thin as 1 nm,48 evident by the strong and sharp combined (110)-(020) peak shown in Figure 2.3b.49 The spun P(VDF-TrFE) films show a very weak (110)-(020) diffraction peak, which indicates that these films have much poorer crystallinity. This difference is not surprising, because the boiling point of acetone (56 °C) is too low to form a crystalline copolymer due to the quick solvent evaporation in the spin coating process. In addition, the spun P(VDF-TrFE) films must be annealed above the ferroelectric-paraelectric transition temperature, which is over 100 °C for the 70% VDF copolymer, to achieve high crystallinity.50
2.3.2. Ferroelectric properties of the LB and spun P(VDF-TrFE) films

To further investigate the role of film fabrication procedure on ferroelectric properties, the P(VDF-TrFE) films have been tested by piezoresponse force microscopy (PFM).\textsuperscript{51} The results of these studies are shown in Figure 2.4a-e. The LB P(VDF-TrFE) film (2 ML) shows strong PFM contrast while the spun P(VDF-TrFE) film shows barely any PFM response, which is consistent with its low crystallinity. X-ray diffraction and PFM imaging data clearly show that the spun P(VDF-TrFE) films have very weak ferroelectricity, and therefore can function only as a regular dielectric layer.
**Figure 2.4** (a) Topography of a P(VDF-TrFE) LB film (2 μm×2 μm); (b) topography of a P(VDF-TrFE) spun film (5 μm×5 μm); (c) PFM amplitude images of a P(VDF-TrFE) LB film; (d) PFM response mapping images of the P(VDF-TrFE) spun film on P3HT:PCBM surface. (e) Comparison of PFM amplitude of the P(VDF-TrFE) LB film and spun film on the marked positions in (c-d).

The ferroelectric nature of the LB P(VDF-TrFE) films has been further confirmed by inducing polarization reversal using the electrically biased PFM tip (**Figure 2.5**). A ±10 V, 1 s voltage pulse supplied by the PFM tip can switch the polarization of the P(VDF-TrFE) crystallites up and down as is clearly observed in the PFM images. Saturated hysteresis loops measured by PFM in LB P(VDF-TrFE) on P3HT:PCBM are shown in **Figure 2.5g-h.**
2.3.3. Switch capability of the devices with LB and spun P(VDF-TrFE) interlayers

The switchable polarization of ferroelectric material results in a switchable photovoltaic and diode effects, which is a unique characteristic of ferroelectric photovoltaic device.\textsuperscript{52,53} We first compared the performance of the devices with crystalline and amorphous P(VDF-TrFE), \textit{i.e.}, prepared by LB deposition and spin coating, respectively, on the three states: as-grown, positively poled (the device is reverse biased) and negative poled (the device is forward biased). The device structure of ITO/poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (25 nm)/P3HT:PCBM (150 nm)/ P(VDF-TrFE) (2 ML)/Al (100 nm) is the same as previously reported.\textsuperscript{54} As shown in Figure 2.6a-b, the performance of the device with crystalline P(VDF-TrFE) changes dramatically with different poling states, while the
device with amorphous P(VDF-TrFE) shows little variation of photocurrent in these three states. The device with crystalline P(VDF-TrFE) has an enhanced PCE of 3.4% after positive poling and suppressed PCE of 1.4% after negative poling the P(VDF-TrFE) layer. In contrast, the PCE of device with amorphous P(VDF-TrFE) has much smaller difference between 2.5% (enhanced) and 2.0% (suppressed) after positive and negative poling, respectively. It is thus concluded that the amorphous P(VDF-TrFE) dielectric film acts primarily as a charge blocking layer, although the relatively small ferroelectric fraction may also contribute to the change. Actually, the observed small tunability of photocurrent in amorphous P(VDF-TrFE) device can be explained by the partial crystallization of P(VDF-TrFE) upon thermal annealing.

**Figure 2.6** Comparison of device performance with P(VDF-TrFE) as interfacial layers by LB (a) and spin coating (b) with a device structure of ITO/ PEDOT:PSS/ P3HT:PCBM/ P(VDF-TrFE)/ Al. Comparison of switching capability of the devices with crystalline (c)
and amorphous P(VDF-TrFE) (d) at both cathode and anode with a device structure of: ITO/ P(VDF-TrFE)/ P3HT:PCBM/ P(VDF-TrFE)/Au.

To observe more distinct current switching capability of FE-OPV devices, we inserted P(VDF-TrFE) films, prepared by both LB and spin coating methods, on both the cathode and anode sides with a device structure of ITO/ P(VDF-TrFE) (3.4 nm by LB coating, or 3.2 nm by spin coating)/ P3HT:PCBM (150 nm)/ P(VDF-TrFE)/ Au (30 nm). Since Au and ITO have very similar work functions, the dipole direction of P(VDF-TrFE) determines the diode direction of the device. Figure 2.6c-d show the dark current of the two devices under the three states. The diode conductance direction of the device with crystalline P(VDF-TrFE) was reversed by the switching pulses, while the conductance direction of the device with amorphous P(VDF-TrFE) remained unchanged. This result further confirms that crystalline P(VDF-TrFE) with robust switchable polarization is required in to enhance the efficiency of the FE-OPV devices.

2.3.4. Stability of the polarization in P(VDF-TrFE)

To be of practical use in a FE-OPV device, polarization of the ferroelectric layer needs to be stable for long periods, both in the dark and under illumination. It has been shown in our earlier work that the nanometer-thick nanocrystallites of P(VDF-TrFE) on the doped silicon substrate exhibit stable polarization over a very long period of time (> 1 month) even without any top electrode. Strong polarization retention (up to several days at least) was also reported for P(VDF-TrFE) nanoislands covered with a nanometer-thick insulating film. The photocurrent output stability of FE-OPV devices with positively poled crystalline P(VDF-TrFE) in a device structure of ITO/ PEDOT:PSS (25 nm)/
P3HT:PCBM (150 nm)/ P(VDF-TrFE) (2 ML)/ Al (100 nm) was measured over a period of more than two weeks. The measurements showed only minimal decay (10%) both for the open circuit voltage and short circuit current (Figure 2.7). This weak decay in principle may be caused by a slight depolarization of P(VDF-TrFE), but more likely to be induced by other factors such as degradation of the semiconductor polymers and oxidation of the electrodes, since the devices without the ferroelectric layer also show a similar degradation rate in our lab and those reported elsewhere. During the stability test, the devices were kept in the dark and the whole poling process was conducted in the dark.

**Figure 2.7** Variations of the open circuit voltage and short circuit current in the FE-OPV structure over two weeks of observation.

### 2.3.5. Can the polarization charge be screened by the photocurrent?

The polarization of the ferroelectric layer affects the distribution of the charges in semiconductor layer in the FE-OPV. A simple estimation shows that the photogenerated charge density in an OPV is too small to compensate the polarization charge on the P(VDF-TrFE) surface: the photogenerated charge density measured by charge extraction
in real P3HT:PCBM device under one sun illumination is about 0.5~2.8×10^{16} \text{ cm}^{-3} \text{ from zero bias to open circuit voltage,}^{56} \text{ which corresponds to a total sheet charge density in the range of } 1.2\sim6.7 \times 10^4 \text{ C/m}^2 \text{ for an active layer thickness of 150 nm, assuming a uniform charge distribution. This charge density is three orders of magnitude smaller than the polarization charge density of } 0.1 \text{ C/m}^2 \text{ at P(VDF-TrFE) surface}^{57}. \text{ Therefore, unless the photogenerated charges accumulate at the P(VDF-TrFE)/semiconductor interface over time, in which case the PCE would steadily decrease, the compensation of polarization charge of P(VDF-TrFE) by the instant photogenerated charges is negligible. In order to find out whether the photogenerated charges accumulate at P(VDF-TrFE)/semiconductor interface and gradually compensate the polarization charges, we monitored the photocurrent of the FE-OPV under a weak illumination of 3 \text{ µW/cm}^2 \text{ over a long time scale. If all the photogenerated charges were accumulated at the P(VDF-TrFE)/semiconductor interface, the device needs to be illuminated for 30 s to generate enough charges to completely screen the P(VDF-TrFE) polarization charge. The FE-OPV device was poled right before the testing. Previous results show that the retention time of P(VDF-TrFE) polarization is long enough to guarantee its polarization to be stable during this testing process. If the polarization charges are completely compensated by the photogenerated charges, a decrease in photocurrent is expected after screening. However, as shown in Figure 2.8, the device photocurrent is constant during the 90 s of observation. This result thus excludes the accumulation of significant photogenerated charge at P(VDF-TrFE)/semiconductor interface. This negligible charge accumulation is due to the efficient charge collection at the cathode interface, which is proved by the very high short-circuit current density of the FE-OPV devices}^{54}
Figure 2.8 Short circuit current of LB P(VDF-TrFE) FE-OPV under 3 μW/cm² illumination.

2.3.6. Direct correlation of photocurrent with polarization in P(VDF-TrFE)

Next experiment further highlights the essential role of the ferroelectric polarization in enhancing device efficiency. The positively poled ferroelectric layer was partially depolarized by heating it up to 135 °C into the paraelectric phase for 15 seconds and then cooling back to room temperature under zero bias. As shown in Figure 2.9, the photocurrent of the device with crystalline LB P(VDF-TrFE) dropped by 5-10% as a result of dipole misalignment after annealing. In contrast, the photocurrent of the device with amorphous P(VDF-TrFE) is found to be almost the same before and after annealing. The observed bump in the current-time curve during the heating process is probably due to the thermally assisted charge transport. The photocurrent of the device with crystalline P(VDF-TrFE) is still higher than that with amorphous P(VDF-TrFE) after thermal annealing, which might be caused by the incomplete depolarization of P(VDF-TrFE) or partial pinning of the dipoles by P3HT:PCBM and aluminum oxide. The
reduced photocurrent of the device with crystalline P(VDF-TrFE) interlayer can be explained by the loss of polarization of P(VDF-TrFE) upon thermal annealing without field cooling. The device with amorphous P(VDF-TrFE) interlayer is not affected by thermal annealing process because there is no aligned polarization in the amorphous P(VDF-TrFE). These scenarios are illustrated in Figure 2.9. This experiment is additional strong evidence that efficiency improvement in FE-OPV is caused by ferroelectricity of the inserted crystalline P(VDF-TrFE) layer.

Figure 2.9 (a) In-situ monitoring of the variations in the photocurrent (under 30 mW/cm² illumination) upon annealing to induce depolarization of the ferroelectric layer. (b) Illustration of the dipole rearrangement in P(VDF-TrFE) LB and spun films as a result of annealing.
In conclusion, it has been shown that the observed enhancement of PCE of the OPV devices with an inserted thin layer of P(VDF-TrFE) is caused by the ferroelectric polarization of the polymer. It is then critical to fabricate highly crystalline P(VDF-TrFE) films to utilize their ferroelectric behavior in FE-OPVs. Amorphous P(VDF-TrFE) films show almost no ferroelectricity and act as regular dielectric layers in the OPV devices, which generally reduces the device efficiency due to the increased contact resistance. Polarization of crystalline P(VDF-TrFE) has been shown to be very stable at the semiconducting polymer/Al interface. The instant photocurrent in FE-OPV devices is too small to screen the polarization charges of P(VDF-TrFE). The non-continuous morphology of P(VDF-TrFE) allows efficient charge extraction to the electrodes and avoids/reduces the piling up of photogenerated charges at the P(VDF-TrFE)/semiconductor interface. The switchable diode and photovoltaic enabled by the inserted ferroelectric dipoles may allow new applications of organic electronic devices.

2.4. Synthesize of ferroelectric nanocrystal P(VDF-TrFE) and its application in OSCs

2.4.1. Motivation

As discussed in section 2.3, a crystalline \( \beta \)-phase P(VDF-TrFE) film is needed to ensure its ferroelectricity.\(^{59}\) LB deposition is an excellent method for forming highly crystalline P(VDF-TrFE) film as thin as 1 nm.\(^ {40}\) However, P(VDF-TrFE) LB films generally need a thermal annealing process after the deposition to convert them into the ferroelectric phase at above the Curie temperature. In our previous studies, the P(VDF-TrFE 70:30) LB films were annealed at 135 °C for half an hour to completely convert
them to the ferroelectric phase.\textsuperscript{25,40} However, this high temperature thermal annealing process is not compatible with the fabrication process of many high performance, low bandgap polymer-based OPV devices, such as thieno[3,4-b]-thiophene/benzodithiophene (PTBs) and poly[N-9′-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′benzothiadiazole)] (PCDTBT).\textsuperscript{10,60,61} These polymers are generally heated at 70 °C or vacuumed to remove solvent in the spun films.\textsuperscript{10} A high temperature annealing at 135 °C will significantly reduce the PCEs of these polymer-based OPVs due to over annealing, causing overly large PCBM or polymer nanodomains.\textsuperscript{62} In addition, it is difficult to control the morphology of P(VDF-TrFE) LB films after thermal annealing.\textsuperscript{51} Appropriate P(VDF-TrFE) size of the nanoislands and spacing between them is critically important so that the photogenerated charges can be fully extracted rather than blocked by the large, thick insulating P(VDF-TrFE) nanoislands.\textsuperscript{40} In an optimal scenario, the size of the P(VDF-TrFE) nanoislands should not exceed the diffusion length of the electrons in donor:PCBM films.

2.4.2. Synthesis of P(VDF-TrFE) nanoparticles and nanocrystals

P(VDF-TrFE 50:50) nanoparticles (NPs) were prepared by a self-organizing process at the interface of two solvents with different polarity. P(VDF-TrFE) was dissolved in good solvent (acetone) with a concentration of 5 mg/ml. First, the 2 ml P(VDF-TrFE) acetone solution was injected into a 10 ml centrifuge tube. Then, 0.5 ml of pure acetone and 4 ml of the water:methanol blend solution were injected into the tube from the bottom. The 0.5 ml of pure acetone was used as a buffer layer, which can stabilize the reaction and avoid severe aggregation of P(VDF-TrFE) while injecting the water:methanol. Water was added to methanol to make a water:methanol blend solution
with varied volume ratio which is a poor solvent for P(VDF-TrFE). The methanol was used to tune the polarity of the poor solvent and stabilize the reaction, which would lead to more uniform and smaller size NPs. Both solvents were cooled down to 0 °C before use.

**Figure 2.10** (a) Schematic of the synthesis of P(VDF-TrFE) nanoparticles (NPs). (b) Pictures of formation process of P(VDF-TrFE) NPs with different reaction time using acetone as good solvent and pure water as poor solvent.

An interfacial layer was formed between the acetone and the water: methanol blend solution. The P(VDF-TrFE) molecules diffused to the interface of the good and poor solvents and connected with water. The strong hydrophobic interaction between water and fluorine in P(VDF-TrFE) leads to the aggregation of P(VDF-TrFE) chains and forms NPs. The hydrophobic interaction is mostly an entropic effect originating from the disruption of highly dynamic hydrogen bonds between water molecules by the nonpolar solute. Since the P(VDF-TrFE) chain cannot form hydrogen bonds with water molecules, P(VDF-TrFE) molecules tend to aggregate to NPs to reduce the surface area exposed to water and minimize the disruptive effect. The NPs were precipitated out by
the high speed centrifuge at a speed of 20,000 rpm for 10 min. The low temperature was used to lower the diffusion rate of the solvents and to stabilize the interfaces. **Figure 2.10b** shows how P(VDF-TrFE) NPs typically form at the acetone and water interface. After injection of water from the bottom, the water/acetone interface forms. P(VDF-TrFE) molecules dissolved in acetone diffuse to the interface to form NPs, and the NPs move down to the water phase by gravity. The P(VDF-TrFE) NP concentration was 2 mg/ml, which corresponds to $4.2 \times 10^{12}$ particles/ml. The dispersion of the as-grown NPs was stable and can stay transparent for several weeks.

### 2.4.3. Characterization of P(VDF-TrFE) nanoparticles and nanocrystals

**Figure 2.11** Scanning electron microscope (SEM) images of P(VDF-TrFE) as-grown NPs using water as the poor solvent (a) and water:methanol (1:10 v/v) blend solvent as the poor solvent (b). (c) P(VDF-TrFE) NP size distribution based on 71 NPs.

The tuning of the polarity (and solubility) difference changes the size of the NPs. Adding methanol into the water can reduce the polarity difference between the good and bad solvents, and the average size of NPs can be reduced from 300-500 nm using pure
water down to 60-90 nm using a water:methanol ratio of 1:10 (Figure 2.11a-b). The statistics size distribution of the P(VDF-TrFE) NPs is shown in Figure 2.11c.

Figure 2.12 (a) SEM image of the refluxed P(VDF-TrFE) NPs. Inset: enlarged image of the NPs. (b) XRD of the as-grown P(VDF-TrFE) NPs and refluxed P(VDF-TrFE) NPs.

The as-grown NPs are expected to be relatively amorphous which was shown by the XRD measurement. In order to obtain crystalline ferroelectric P(VDF-TrFE) NPs that can be used in FE-OPV devices, the P(VDF-TrFE) NPs dispersed in water:methanol were refluxed at 90 °C which is above its Curie temperature of 65 °C, for 60 minutes. The hot solution was cooled down to room temperature at the speed of 1 °C per minute. Figure 2.12a shows the SEM image of refluxed NPs which show quite different surface morphology from the as-grown smooth spherical NPs. The P(VDF-TrFE) surface is rough with a clear laminar/dendrite structure. As shown in Figure 2.12a, all the refluxed P(VDF-TrFE) NPs are expected to be converted into the ferroelectric phase to some extent because every nanoparticle shows laminar/dendrite textures.
The dramatically improved crystallinity of P(VDF-TrFE) NPs after refluxing was confirmed by XRD measurement which shows much stronger, sharp (110)-(200) peaks\textsuperscript{65,66} compared to the as-grown NPs, as shown in Figure 2.13a. The calculated lattice spacing for the d(110) peak is 0.46 nm which agrees with previous reported value of the $\beta$-phase co-polymer P(VDF-TrFE) with 50% TrFE.\textsuperscript{67} In order to further confirm the present phase is $\beta$-phase, we measured the XRD pattern of the refluxed P(VDF-TrFE) NPs film under various temperatures from room temperature to 100 °C which is above its curie temperature of 65 °C. As shown in Figure 2.13a, a second XRD peak, corresponding to the paraelectric $\alpha$-phase, starts to appear at 65° which is close to the paraelectric-ferroelectric transition temperature. The peak shifts from 19.2° at RT to 18.2° after heating the film to 80 °C, indicating the conversion of the P(VDF-TrFE) NP film
into a pure paraelectric $\alpha$-phase. As expected, the diffraction peak shifts back to $19.1^\circ$ after cooling the film back to RT.

The most straightforward method to verify the ferroelectricity of the P(VDF-TrFE) NPs is to measure the polarization hysteresis loop (P-E) loop. It is however difficult to fabricate a continuous and pin-hole free thin film with the refluxed P(VDF-TrFE) NPs without resorting to thermal annealing due to their relative large size and irregular shape. To address this issue, we used PFM to directly measure the piezoelectric hysteresis loops of individual NPs. **Figure 2.13b-c** show saturated hysteresis loops of refluxed P(VDF-TrFE) NPs measured by PFM on top of gold covered silicon substrate. It is clearly seen that the polarization of the refluxed P(VDF-TrFE) NPs is switched by the voltage bias supplied by the PFM tip, confirming the ferroelectricity of the P(VDF-TrFE) NPs.

### 2.4.4. Application of nanocrystal P(VDF-TrFE) in low bandgap polymers

![Figure 2.14](image)

**Figure 2.14** Schematics of FE-OPV device working mechanism. (a) After reverse bias poling, the unscreened surface charges of the P(VDF-TrFE) NPs will generate electric field and penetrate through the organic active layer, which will help the extraction of
photo-generated charges; (b) three-dimensional AFM image of topology of NPs on the organic active layer surface with scale of 5×5 µm.

**Figure 2.14a** shows schematics of the working mechanism of FE-OPV devices with P(VDF-TrFE) NPs as the interlayer. After positive poling under reverse bias, the unscreened polarization charges of P(VDF-TrFE) NPs on the organic active layer side will generate a large electric field pointing from the cathode to the anode. This large electric field will enhance the bound charge pair separation and increase the charge extraction efficiency. The three-dimensional AFM image of P(VDF-TrFE) NPs on top of PCDTBT:[70]PCBM film is shown in **Figure 2.14b**. In polymer:PCBM bulk heterojunction solar cells, electron diffusion lengths ranging from 40-130 nm have been reported, depending on the property of the polymer and content of PCBM. Small P(VDF-TrFE) NPs of 60-90 nm were selected as the ferroelectric interlayer so that most photogenerated carriers can go around the insulated NPs by diffusion and be collected by the electrode.
Figure 2.15 The photocurrent curves of PCDTBT:[70]PCBM based device with the as-grown amorphous NPs (a), and the refluxed ferroelectric P(VDF-TrFE) NPs (b) before (black square line) and after poling (red square line). (c) $J_{SC}$ variation with poling voltage for the device with the as-grown amorphous NPs (black square line), and the refluxed ferroelectric P(VDF-TrFE) NPs (red square line) after poling.

We first studied the influence of the crystallinity of P(VDF-TrFE) NPs on the performance of an FE-OPV by comparing the photocurrents of the devices with as-grown amorphous P(VDF-TrFE) NPs and refluxed crystalline P(VDF-TrFE) NPs as interlayers at the cathode. Figure 2.15a-b show their photocurrent curves under a 100 mW/cm$^2$ Air Mass 1.5 Global (AM1.5) illumination. There is almost no poling effect for the device with the amorphous NPs, which can be explained by their nonferroelectric nature (or switchable dipoles). In contrast, the PCE of the device with crystalline P(VDF-TrFE) NPs increased by 23% after positive poling, as shown in Figure 2.15b. This result clearly demonstrates that the crystallinity of P(VDF-TrFE) is critical for the improvement of FE-
OPV performance because only the crystal ferroelectric P(VDF-TrFE) has large density, aligned dipoles. The influence of the crystallinity of P(VDF-TrFE) nanostructures on the poling effect in FE-OPVs was highlighted by comparing the $J_{SC}$ variation under different poling voltages of the devices with as-grown amorphous P(VDF-TrFE) NPs and refluxed crystalline P(VDF-TrFE) NPs. Here, the poling voltage was increased gradually from -1 V to -8 V. As shown in Figure 2.15c, the $J_{SC}$ of the device with refluxed P(VDF-TrFE) NPs increased gradually with applied negative bias from -5 V to -7 V, and nearly saturated at -8 V, while the $J_{SC}$ of the device with as-grown NPs remained almost unchanged. The crystalline refluxed NPs were then used for the following study.
Figure 2.16 (a-e) Photocurrents of the FE-OPV devices before (black square curves) and after poling (red square curves) which have P(VDF-TrFE) NPs on top of active layer with increasing coverage. The corresponding SEM images of P(VDF-TrFE) NPs distribution are shown as insets. Scale bars in all the SEM images are 1 µm. (f) Photocurrent curves of the FE-OPV device with P(VDF-TrFE) NPs as interlayer without poling (black square), after positive poling (red square), after negative poling (blue square) and controlled device with Ca/Al as cathode (green square). The EQE curves of the devices with
P(VDF-TrFE) NPs after positive poling (red square) and with Ca/Al cathode (green square) are shown in the inset.

There should be an optimized coverage of P(VDF-TrFE) NPs for a maximized PCE because of the trade-off between the induced electric field and the increased series resistance (Rs) by the insulating P(VDF-TrFE) NPs. We continuously varied the density of P(VDF-TrFE) NPs on the PCDTBT:[70]PCBM surface by tuning the concentration of the NP solution as well as the spin speed. Figure 2.16 show the J-V curves and the corresponding SEM images with different NP coverage, and Table 2.1 summarizes the variation in the device parameters, including $J_{SC}$, $V_{OC}$, FF, PCE, $R_s$, and shunt resistance ($R_{sh}$) for the devices with different P(VDF-TrFE) NP density. For each category of devices, both the average device efficiency and best device efficiency are listed. When the NPs are very sparse, with a coverage of 2%, the positive poling of the P(VDF-TrFE) NPs caused almost no change to the photocurrent, as shown in Figure 2.16 a. However, the $R_s$ is relatively low, around 1.3 ohm/cm$^2$. The poling effect becomes obvious when the P(VDF-TrFE) NP coverage is increased to 5%. The PCE increased from 4.4% to 5.0% after poling, while the $R_s$ increased to 3.0 ohm/cm$^2$.

Table 2.1 Comparison of FE-OPV performances with different ferroelectric P(VDF-TrFE) NP density before and after positive poling at -7 voltage. (The performance of the device with Ca/Al as cathode and optimized NPs spacing was averaged over 50 devices, and the performance devices with other NP spacing were averaged over 10 devices)

<table>
<thead>
<tr>
<th>P(VDF-TrFE) NPs</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>$R_s$ (Ω.cm$^2$)</th>
<th>$R_{sh}$ (Ω.cm$^2$)</th>
<th>PCE %</th>
<th>PCE %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coverage</td>
<td>Before Poling</td>
<td>After Poling</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>---------------</td>
<td>--------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca/Al (no NPs)</td>
<td>9.8</td>
<td>5.29</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2%</td>
<td>10.6</td>
<td>5.41</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td>10.0</td>
<td>4.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18%</td>
<td>10.7</td>
<td>4.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38%</td>
<td>6.1</td>
<td>1.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50%</td>
<td>1.7</td>
<td>0.17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coverage</th>
<th>Before Poling</th>
<th>After Poling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca/Al (no NPs)</td>
<td>0.91</td>
<td>58.0</td>
</tr>
<tr>
<td>2%</td>
<td>0.91</td>
<td>53.7</td>
</tr>
<tr>
<td>5%</td>
<td>0.87</td>
<td>50.6</td>
</tr>
<tr>
<td>18%</td>
<td>0.83</td>
<td>52.0</td>
</tr>
<tr>
<td>38%</td>
<td>0.68</td>
<td>21.6</td>
</tr>
<tr>
<td>50%</td>
<td>0.57</td>
<td>12.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coverage</th>
<th>Before Poling</th>
<th>After Poling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca/Al (no NPs)</td>
<td>0.91</td>
<td>58.0</td>
</tr>
<tr>
<td>2%</td>
<td>0.91</td>
<td>53.7</td>
</tr>
<tr>
<td>5%</td>
<td>0.87</td>
<td>50.6</td>
</tr>
<tr>
<td>18%</td>
<td>0.83</td>
<td>52.0</td>
</tr>
<tr>
<td>38%</td>
<td>0.68</td>
<td>21.6</td>
</tr>
<tr>
<td>50%</td>
<td>0.57</td>
<td>12.5</td>
</tr>
</tbody>
</table>
There is a clear trend of device performance variation with the P(VDF-TrFE) NP density. With P(VDF-TrFE) NP density increasing, the series resistance before poling increases; and the poling effect becomes increasingly distinct. When the P(VDF-TrFE) NP coverage was increased to 38%, the insulating NPs greatly increased the series resistance of the device to 8.4 Ω/cm². Although the PCE increased by 144% after poling the dense P(VDF-TrFE) NPs, the total PCE was low, only 2.2%. The optimized NP coverage was found to be around 18%, which is larger than the nanomesa coverage of annealed 2 monolayer LB film (coverage: 15%). The best PCE increased from 4.74% to 6.64% after poling.

One unique characteristic of FE-OPVs is that the photocurrent of the device can be switched with a high voltage pulse. As shown in Figure 2.16, the FE-OPV device, after a reverse bias poling, has larger $J_{SC}$, $V_{OC}$, FF, and PCE than the as-obtained device. The photocurrent was switched back to the low PCE state with a relatively small forward bias of 5 V. Here, a small forward bias was used to avoid the burning of the device. We also compared the device performance of FE-OPVs with P(VDF-TrFE) NPs as the cathode interlayer and the regular devices with Ca/Al as the cathode. The efficiency of the optimized devices with Ca/Al as the cathode had a PCE of 5.19%, which is comparable to those reported elsewhere. The larger $J_{SC}$ of FE-OPV after positive poling was also confirmed by its EQE, as shown in the inset of Figure 2.16. The highest EQE reached 70% in the optimized FE-OPV device. The superior performance of FE-OPVs can be understood by the reduced charge recombination in the devices with P(VDF-TrFE) NPs which is reflected by their larger shunt resistance, higher $J_{SC}$, and FF, as shown in Table 
2.1. After positive poling, the induced electric field is expected to increase the drift length of the carriers and/or extend the charge bimolecular recombination lifetime.\textsuperscript{40} The series resistance of P(VDF-TrFE) NPs is, however, still larger than that of the device with Ca/Al as the cathode even with optimized NP spacing due to the insulating nature of the device with P(VDF-TrFE) NPs.

2.4.5. Conclusion

To the best of our knowledge, this is the first time that ferroelectric polymer NPs are synthesized by a simple solution method and applied in FE-OPVs. The size and crystallinity of P(VDF-TrFE) NPs can be easily controlled before they are inserted into the polymer solar cells. The coverage of the P(VDF-TrFE) ferroelectric interlayer can then be precisely manipulated to maximize the efficiency of FE-OPVs. In addition, it is easy to deposit the P(VDF-TrFE) NPs using a low-cost, scalable solution process, such as spray coating and spin coating.

In conclusion, we demonstrated the synthesis of ferroelectric P(VDF-TrFE) NPs and their application in enhancing the PCE of low bandgap polymer-based solar cells for the first time. A clear dependence of the device performance on the induced electric field was revealed by controlling the poling voltage as well as P(VDF-TrFE) NP coverage. Compared to the LB method, this method gives better control of P(VDF-TrFE) coverage, which is critical in optimizing the performance of FE-OPV. With the denser P(VDF-TrFE) nanoislands obtained by this method, a larger electric field, around 20±3 V/µm in PCDTBT:[70]PCBM film, can be induced by the P(VDF-TrFE) NPs which is 50-100% higher than the electric field generated by the 1-2 monolayer LB P(VDF-TrFE). After
optimization of coverage of P(VDF-TrFE) NPs, the average PCE of a PCDTBT:[70]PCBM-based solar cell reached 6.5%, 25% higher than the control devices with Ca/Al as the cathode. Our devices were highly reproducible and the PCE averaged over 50 devices. It is believed that this kind of P(VDF-TrFE) NP can be broadly applied in other low bandgap polymers to improve PCE because they do not need post-deposition thermal annealing.

2.5. Efficiency enhancement in polymer solar cells with polar small molecules

2.5.1. Motivation

Interfacial layers play important but different functions in improving OSC performance. Dielectric materials such as lithium fluoride (LiF) and Cesium carbonate (Cs₂CO₃), metal oxides such as Zinc oxide (ZnO) and titanium oxide (TiO₂) and n-type organic/polymer conjugated materials are employed as electron transporting and/or hole blocking layers. Polar materials is a very promising interfacial layers and have been broadly applied in OSCs to increase its efficiency. Organic molecules with strong dipole moments have been employed to increase the internal electric field of the OSCs to achieve a high $V_{OC}$. In section 2.3 and 2.4, we reported a new category of air stable material, ferroelectric polymer P(VDF-TrFE), as interfacial layer which has large density of field switchable dipoles. This ferroelectric material can be inserted at the polymer/electrode interface to tune the work function of the metal electrode which results in higher $J_{SC}$ and FF due to the increased internal electric field after poling. P(VDF-TrFE) can also be inserted at the donor/acceptor interface to tune their energy offset which result in higher $V_{OC}$. However, the P(VDF-TrFE) itself is insulating so that
it will increase the series resistance of the device. On the other hand, it is hard to be blended in the active layer since it cannot be dissolved in 1,2-Dichlorobenzene (DCB) solvent.

We found that a polar small molecule 2-cyano-3-(4-(diphenylamino)phenyl)acrylic acid (TPACA) can be inserted into the device to improve the $V_{OC}$ and PCE of OSCs by tuning the internal electric field. TPACA can be inserted at the polymer/electrode interface or easily blended in the active layer to increase the device efficiency. The efficiency of the OSC device has been increased by 30%-90% for all the systems tested, including P3HT, PCDTBT and poly[4,8-bis-(2-ethyl-hexyl-thiophene-5-yl)-benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]-alt-[2-(2'-ethyl-hexanoyl)-thieno[3,4-b]thiophen-4,6-diyl] (PBDTTT-CT), with the highest efficiency reached 7.83% for the PBDTTT-CT: [6,6]-phenyl-C$_{71}$-butyric acid methyl ester ([70]PCBM) system.

2.5.2. TPACA as cathode interfacial layer

In our experiments, P3HT and PCBM based bulk heterojunction solar cells were initially used as the standard cell to evaluate the function of the dipole molecules since it is a well-established material system.$^{40,77}$ A regular device structure of ITO/PEDOT:PSS/polymer:fullerene/Al was employed. One advantage of this structure is the absence of low work function metals like Ca which can increase the stability of the devices. TPACA, dissolved in ethanol, was spun on top of the dry P3HT:PCBM layer to form a cathode interfacial layer. Figure 2.17b-c shows the energy diagram of the pristine device and after poling with TPACA at the cathode interface. After negative bias poling, the dipoles of the TPACA are aligned, which can increase the work function of the Al cathode. The
current density-voltage (J-V) curves are shown in **Figure 2.17d**. Without poling, the $J_{SC}$, $V_{OC}$, FF, and PCE of the solar cell device were 7.90 mA/cm$^2$, 0.43 V, 56.4%, and 1.91%, respectively. After poling under -13 V for around 10 s, the $V_{OC}$ increased from 0.43 to 0.59 V. Also, an increase in $J_{SC}$ of 0.60 mA/cm$^2$ and an enhancement of FF from 56.4% to 70.4% were also observed after poling the TPACA film by a negative bias. Thus, the PCE was increased from 1.91% to 3.53%. This indicates that, after negative bias poling, TPACA molecules will be aligned to form a dipole pointing from Al to active layer, same as the direction of the built-in electric field pointing from Al to ITO, resulting in an increase of the built-in electric field.

**Figure 2.17** (a) Molecular structure of TPACA. Energy diagram of the device before poling (b) and after negative bias poling (c) with TPACA as the cathode interfacial layer.
(d) Photocurrent of the P3HT:PCBM device before and after negative bias poling with TPACA as cathode interfacial layer.

2.5.3. TPACA blended in the active layer.

One unique property of small polar molecule TPACA over ferroelectric materials is that it can be dissolved in processing solvent like DCB, so that it can be simply blended in DCB with polymers and fullerenes. Here, the TPACA was added in the P3HT:PCBM blend solution before spin coating. It is noted that the weight ratio of the TPACA in the P3HT:PCBM bulk heterojunction film is only 0.25% (Table 2.2). More TPACA would ruin the film morphology and decrease the device performance.
Figure 2.18  Energy diagram of the device before poling (a) and after negative bias poling (b) with TPACA blended in the active layer. (c) Photocurrent of the P3HT:PCBM device before and after poling with TPACA blended in the active layer.

Table 2.2 Different polymer: fullerene-derivative blend films fabrication details (DIO (1,8-diiodooctane))

<table>
<thead>
<tr>
<th>Materials</th>
<th>PBDTTT-CT:[70]PCBM</th>
<th>PCDTBT:[70]PCBM</th>
<th>P3HT:PCBM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer:fullerene weight ratio (polymer concentration)</td>
<td>1:1.5</td>
<td>1:4 (4 mg/ml)</td>
<td>1:1 (17.5 mg/ml)</td>
</tr>
<tr>
<td>Working solvent</td>
<td>DCB</td>
<td>DCB:CB (3:1 V/V)</td>
<td>DCB</td>
</tr>
<tr>
<td>TPACA weight ratio</td>
<td>100:150:1</td>
<td>40:160:1</td>
<td>200:200:1</td>
</tr>
<tr>
<td>Spin coating parameter</td>
<td>900 rpm for 60 sec.</td>
<td>2400 rpm for 14 sec.</td>
<td>800 rpm for 20 sec.</td>
</tr>
<tr>
<td>Annealing condition</td>
<td>No annealing</td>
<td>No annealing</td>
<td>150 °C for 10 min</td>
</tr>
<tr>
<td>Film thickness</td>
<td>~105 nm</td>
<td>~80 nm</td>
<td>~150 nm</td>
</tr>
</tbody>
</table>

In this case, the TPACA is expected to be in the bulk active layer rather than at the interface between active layer and electrode. After negative bias poling, the dipoles of TPACA in the bulk can also be aligned which result in increasing of the work function of the cathode. As shown in Figure 2.18c, before poling, the $J_{SC}$, $V_{OC}$, FF, and PCE of the device are 9.34 mA/cm$^2$, 0.43 V, 55.8%, and 2.22%, respectively, which are comparable to the device without TPACA blended in the active layer. After poling at -13 V for
around 10 s, the efficiency increased to 4.32% with a $J_{SC}$ of 10.2 mA/cm$^2$, a $V_{OC}$ of 0.60 V, and a FF of 70.6%. To verify the orientation of the dipole moment of the polar molecules is critical for the device performance, the P3HT:PCBM based solar cell with TPACA in the bulk was poled at +3 V to switch the dipole direction. As shown in Figure 2.18c, after forward bias poling, the efficiency dramatically decreased to 0.04% with a $J_{SC}$ of 1.31 mA/cm$^2$, a $V_{OC}$ of 0.13 V, and a FF of 21.0%. Here a lower poling voltage was used to avoid the burning of the device by the large injection current. This indicates that the forward bias poling led to unfavourable dipole moment pointing from ITO toward Al, which dramatically reduced the built-in electric field in the active layer.
**Figure 2.19** Contact angle measurement of the PHT:PCBM film without (a) and with (b) TPACA blended in the active layer. Photocurrent (c) and dark current (d) of the device before and after negative bias poling after methanol washing with TPACA as interfacial layer. Photocurrent (e) and dark current (f) of the device before and after negative bias poling after methanol washing with TPACA blended in the P3HT:PCBM active layer.

Blending the P3HT:PCBM and TPACA in one-step spin coating can be simpler comparing to fabricating double layer of P3HT:PCBM and TPACA films in two steps. One may argue that TPACA may self-assemble to form a thin layer on top of P3HT:PCBM during the slow dry process after spin-coating the blending film of P3HT:PCBM:TPACA. For clarification, we measured the contact angle of the P3HT:PCBM films with and without TPACA blended in the active layer. TPACA is more hydrophilic than the P3HT:PCBM film so that the contact angle of the film is expected to be smaller if the TPACA molecules are self-assembled at the top surface after thermal annealing. However, as shown in **Figure 2.19a-b**, the contact angles of both films with and without TPACA are the same at 91° which indicate that the TPACA molecules are blended in the active layer. In addition, two control experiments were carried out. First, after spin coating of TPACA film on top of P3HT:PCBM film where TPACA worked as interfacial layer, methanol was used to wash the film. Second, methanol was employed to wash the bulk film where TPACA was blended in the bulk. As shown in **Figure 2.19c-d**, there is no poling effect for the devices with TPACA interfacial layer after methanol wash, which indicates that methanol can wash off the TPACA on top of the blend film. However, the performance of solar cell devices with TPACA blended in the bulk P3HT:PCBM films still has an obvious enhancement after
the poling. This indicates that after spin coating the P3HT:PCBM:TPACA mixed solution, the TPACA stays inside of the bulk film P3HT:PCBM after the film preparation.

2.5.4. Origin of the efficiency enhancement

It is noted that the performance enhancement using small polar molecules is different from the reported system where doping P3HT:PCBM with ferroelectric dipoles resulted in increase of $J_{SC}$ and FF and no change of $V_{OC}$ after negative bias poling. In our case, the main increase of the PCE is due to the larger $V_{OC}$ after poling. The increased $V_{OC}$ can be reflected by the reduced saturated dark current of the devices and the built-in potential measured by the capacitance. As shown in Figure 2.20a, the negative bias poling reduces the reverse saturated dark current by two orders of magnitude. This can be understood from the general expression for $V_{OC}$ in OPV devices:

$$V_{OC} = \frac{n k T}{q} \ln \left( \frac{J_{SC}}{J_0} + 1 \right)$$

where $k$ is the Boltzmann constant, $T$ is temperature, $q$ is the elemental electron charge, $J_{SC}$ is the photocurrent density due to exciton dissociation, $J_0$ is the saturated dark current density, and $n$ is the diode ideal factor.

The built-in potential of the device was found out by the capacitance vs voltage measurement. Figure 2.20 shows built-in potential of the P3HT:PCBM:TPACA device before and after negative bias poling, measured by fitting the $1/C^2$ versus voltage. The device was measured at 100 KHz in the dark using LCR meter. The built-in potential was increased from 0.47 V before poling to 0.66 V after negative bias poling, which is correlated $V_{OC}$ of the devices under different poling conditions. The slightly increased $J_{SC}$
and FF after negative bias poling the device can be explained by the reduced charge recombination due to the increased built-in electric field.

**Figure 2.20** (a) Dark current of the device with TPACA blended in the active layer. The inset is the dark current of the device under negative bias. (b) Built-in potential of the P3HT:PCBM device measured by fitting the $1/C^2$ versus voltage curve.

In order to examine the influence of increased built-in electric field on the charge generation and transporting property of the device, both charge generation efficiency and charge extraction time were measured on the P3HT:PCBM based device with TPACA blended in the active layer. It is believed that the primary photoexcitations in organic semiconductors are strongly bound Frenkel excitons while only free charges contribute to
photocurrent. Two models have been proposed to explain the fundamental processes resulting in the formation of extractable free charge carriers.\textsuperscript{80,81} In the first model, the separation of the excitons forms Coulombically bound electron-hole pairs (polaron pairs, PPs) at the donor-acceptor heterojunction. In this case, the carrier generation yield can be enhanced in the presence of an electric field, while a small fraction of PPs can separate into free carriers by diffusion. In the second model, exciton dissociation directly yields free carriers, indicating that the electric field should not influence the formation of extractable carriers.\textsuperscript{81} To probe the photo-generation of the P3HT:PCBM:TPACA blended film based solar cells, time-delayed collection field (TDCF) experiments\textsuperscript{82,83} were employed to study the relationship between free charge generation yield and the bias applied on the device. In our system, different bias (from -4 to +0.6 V) was applied at the devices during the excitation and prior to the application of charge collection bias of -4 V. The rising time of the trigger pulse and the electrical bias pulse was 10 ns. After a delay time of 500 ns which is much less than the charge carrier lifetime in P3HT:PCBM system,\textsuperscript{84} a collection bias of -4 V was employed to sweep the carriers through the organic layer and extract them at the electrodes.

As shown in Figure 2.21a, the charge generation yield is bias independent in P3HT:PCBM system which agrees with previous study,\textsuperscript{85} and the charge generation yield is the same for the device under different poling conditions. This means that the increased internal electric field after negative bias poling did not increase the charge generation. On the other side, the charge extraction time shown in Figure 2.21b was decreased at the same voltage after negative bias poling, which indicates the internal electrical field can facilitate the charge extraction after negative bias poling. For the charge extraction time
measurement, the bias applied on the device was kept the same after the laser pulse illumination.

**Figure 2.21** (a) Charge generation rate measured by time delayed collection field. The charge generation efficiencies were measured under different bias from -4 V to open circuit voltage, and were normalized by the IQE at -4V. (b) The charge extraction time of the device before and after poling.
2.5.5. Universal application of the TPACA in other polymer:fullerene systems

It is exciting that blending TPACA in the bulk active layer is a general method to increase the OSC device efficiency. Here, two low-bandgap polymers PCDTBT and PBDTTT-CT were employed to fabricate the devices with regular structure of ITO/PEDOT:PSS/polymer:[70]PCBM:TPACA/Al. The device fabrication details including the TPACA weight ratio in the bulk active layer is described in the experiment details section. The $J$-$V$ curves are shown in Figure 2.22. For PCDTBT polymer, the efficiency of the solar cells increased from 4.45% to 5.79% with enhanced $V_{OC}$ and FF, but a same $J_{SC}$ after negative bias poling. The efficiency is higher than the reported efficiency (5.4%) of the PCDTBT based solar cells with a regular structure of ITO/PEDOT:PSS/PCDTBT:[70]PCBM/Ca/Al in our system with higher $V_{OC}$ and FF. For PBDTTT-CT:[70]PCBM system, after negative bias poling, the $V_{OC}$ and FF were enhanced and $J_{SC}$ was improved slightly, resulting in a significantly improved efficiency of 7.83%, which is also much higher than our previously reported efficiency (7.0%) for this polymer with the device structure of ITO/PEDOT:PSS/ PBDTTT-CT:[70]PCBM/Ca/Al.86

(a) ITO/PEDOT/PCDTBT:PC$_{70}$BM:TPACA/Al

(b) ITO/PEDOT/PBDTTT-CT:PC$_{70}$BM:TPACA/Al
In conclusion, a polar molecule, TPACA, was employed to tune the built-in electric field of the organic solar cells to improve their device performances. TPACA can either be inserted at the cathode interface as interfacial layer, or blended in the bulk active layer. After poling, the PCE was significantly increased with enhancements in $J_{SC}$, $V_{OC}$ and FF. Also, negative bias poling of the solar cells based on TPACA blended in P3HT:PCBM active layer can increase the efficiency, which is consistent with the dark current and capacitance studies. TPACA showed universal applications in enhancing the performance of other low-bandgap polymers. For example, an efficiency of 7.83% was achieved for PBDTTT-CT based solar cells after poling. This contribution offers a general method to tune the internal electric field to enhance the performance of OSCs and sheds light on understanding the mechanism of the charge generation and extraction in OSCs.
Chapter 3 Universal formation of graded BHJ for efficiency enhancement

3.1. Motivation

The discovery of BHJ structures paved the road for high efficiency energy conversion by OPVs in the last decade.\textsuperscript{1,10,87-93} The morphology of BHJ films plays a critical role in charge generation, collection, or recombination in BHJ OPV devices.\textsuperscript{29-32,94-96} An ideal BHJ film morphology was suggested to have a bicontinuous interdigitated donor and acceptor network with donor and acceptor nanodomains within the exciton diffusion lengths or the uncertain length of light\textsuperscript{27,28} for efficient charge generation and extraction.\textsuperscript{29-33} However, the actual morphologies of most BHJ films are generally far from ideal due to the random mixing of donor and acceptor in solution. Regular BHJ films fabricated from the blended solution inevitably have many breaks and dead ends.\textsuperscript{10,32} Strategies such as thermal annealing,\textsuperscript{57,94,97,98} solvent annealing,\textsuperscript{99} and mixing additives\textsuperscript{88,100,101} have been shown to successfully improve the morphologies of some BHJ films by increasing crystallinity of the donors and acceptors and/or forming nanodomains of donors and acceptors with suitable domain size to facilitate exciton dissociation and charge generation. However, these methods did not address the connectivity of the donor and acceptor network and are only applicable to specific material systems. On the other hand, attempts to form the ideal BHJ structures using pre-formed n-type nanorod/nanowire arrays followed by infiltration of semiconducting polymers have not resulted in PCEs comparable to those made of blended films, which might be limited by interface issues.\textsuperscript{102} Another issue with regular BHJ films is the mismatch between the photocurrent distribution and charge transport channel width in the vertical direction: electron current is higher toward the cathode side, and hole current is
higher toward anode side due to nonsymmetrical charge collection in OPVs,\textsuperscript{103,104} while the distribution of donors and acceptors in regular BHJ films is generally uniform due to the uniform mixing of them in solution. This mismatch could cause the photogenerated charges piling up which end up with recombination. It can severely reduce device PCE when the photogenerated charge density is high, in cases such as low bandgap active layers and under strong illumination, or when photogenerated charges cannot be efficiently extracted out of the active layer due to low carrier mobility or a thick active layer.\textsuperscript{105,106} All of these nonideal morphologies inevitably cause the charge recombination both in the BHJ films and at the metal/organic interface, in forms of geminate recombination,\textsuperscript{107,108} or bimolecular recombination.\textsuperscript{109,110}

Figure 3.1 (a-b) Illustration of the morphology of donor (blue) and acceptor (red) distribution in regular and graded BHJ devices. Composition profile of donor and acceptor in regular (c) and graded (d) BHJ devices. A larger composition percentage is correlated with wider charge transportation path and thus larger effective conductivity.
Compositionally graded BHJ films, donor enriched at the anode and acceptor enriched at the cathode side, were proposed to facilitate the charge extraction and to reduce charge recombination in several highly efficient OPVs, such as P3HT:PCBM and poly[(4,4′-bis(2-ethylhexyl)dithieno[3,2-b;2′,3′-d]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5′-diyl] (PSBTBT):PCBM. The higher donor content at the top surface also explains the higher PCEs in their inverted structure device rather than in the regular structure device. As illustrated in Figure 3.1, the composition profile of the graded BHJ films with a donor rich anode side and an acceptor rich cathode side better matches the distribution of current, which should reduce the piling up of electrons close to the cathode side and holes close to the anode side and reduce the leakage of photogenerated charges to the wrong electrodes, thus reducing bimolecular charge recombination. However, the graded BHJs with preferred composition profiles were only observed in a few high efficiency material systems which require special substrate surfaces and suitable surface energy differences between donors and acceptors for its formation. In addition, these graded BHJs do not necessarily provide better bicontinuous connectivity of donors and acceptors.

3.2. Solvent fluxing approaches

We developed a method to effectively form the graded BHJ by a very simple solvent-fluxing process which is applicable to all solution-processed BHJ films which involves additives. The fluxing process also improved the morphologies of the BHJ films by forming more uniform [70]PCBM domain distribution in the plane direction of the films and resulted in higher charge collection efficiency. As a result, PCE enhancements
by 15-50% are achieved for all graded BHJ systems tested compared with the optimized regular BHJ OPVs.

**Figure 3.2** (a), Formation of DIO:fullerene-derivatives nano-droplets after the spin coating of the polymer:fullerene-derivatives blend solution with DIO as additive; (b), Penetration of methanol into the blend film along the DIO regions; (c), Extraction of DIO as well as partial fullerene-derivatives to the surface; (d), Removing DIO with methanol
from the film by spin coating; (e), Formed graded BHJ with better connectivity of donors and acceptors.

The schematics of the method using solvent-fluxing to form graded BHJ are shown in Figure 3.2. Firstly, a high boiling point additive 1,8-diiodooctane (DIO) was added to the polymer donors: fullerene-derivative solutions. After spin coating the blended solution on top of ITO/PEDOT:PSS substrate, the working solvent, such as DCB, evaporated while DIO stayed in the blend film for a long time due to its high boiling temperature of 333 °C. It was found that the blended films were still wet and sticky after one day of storage at room temperature, indicating the extremely slow evaporation of DIO. Previous study shows that DIO is a better solvent for fullerene-derivatives (>120 mg/ml for PCBM) than traditional solvents, such as chlorobenzene, because of their strong interactions caused by the partial negative charge of iodine in DIO and electrophilic-deficient property of fullerene-derivatives.\textsuperscript{116} DIO then grasped fullerene-derivatives into nanodroplets during evaporation of DCB.\textsuperscript{116,117} Secondly, the wet blended films were fluxed with low boiling point solvents, such as methanol (Figure 3.2b). Methanol does not dissolve fullerene-derivatives or semiconducting polymers but mixes very well with DIO. Therefore, after dripping methanol on the top of the blended films, methanol quickly penetrated into the wet films, dissolved the DIO, and connected the DIO:fullerene-derivative nanodroplets, as illustrated in Figure 3.2b. DIO dissolved in methanol diffused to the surface of the films, indicated by the quick darkening of the film after dripping methanol onto the film because solid-state fullerene has much stronger absorption in visible range than fullerene solution. The fast extraction of DIO from inside of the BHJ film brings some fullerene-derivatives dissolved in DIO toward the film
surface and thus forms the graded composition in the vertical direction, as illustrated in *Figure 3.2c*. Thirdly, while methanol was spun off of the surface of the film, DIO was fluxed away by methanol (*Figure 3.2d*), leaving the deeper colored graded BHJ films after methanol dried (*Figure 3.2e*). The graded BHJ structure, with an increasing fullerene-derivative percentage from bottom to top, formed after methanol dried.

**Figure 3.2** In situ characterization of the BHJ films

---

**Figure 3.3** Chemical structures of donors and acceptors

The chemical structures of the chemicals used in this study are shown in *Figure 3.3*: PBDTTT-CT, PCDTBT), Poly[6-fluoro-2,3-bis-(3-octyloxyphenyl) quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (FTQ), P3HT, [70]PCBM, and indene-C60 bisadduct ([60]ICBA). The PBDTTT-CT:[70]PCBM and PCDTBT:[70]PCBM solution were kept at 50 °C to 60 °C and 40 °C to 50 °C respectively. All other solutions were spin-coated at room
temperature. PBDTTT-CT:[70]PCBM, PCDTBT:[70]PCBM and FTQ:[70]PCBM were fast-dried, and P3HT:[60]ICBA was slowly-dried with the films covered by a glass petri dish. The fabrication details of the films are shown in Table 3.1

**Table 3.1 Different polymer: fullerene-derivative blend films fabrication details**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Polymer and fullerene-derivative weight ratio (polymer concentration)</th>
<th>Working solvent</th>
<th>DIO volume ratio</th>
<th>Spin coating parameter</th>
<th>Annealing condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDTTT-CT:</td>
<td>1:1.5 (10 mg/ml)</td>
<td>DCB</td>
<td>3%</td>
<td>900 rpm for 60 sec.</td>
<td>No annealing</td>
</tr>
<tr>
<td>[70]PCBM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCDTBT:</td>
<td>1:4 (4 mg/ml)</td>
<td>DCB:CB (3:1 V/V)</td>
<td>0.4%</td>
<td>2400 rpm for 14 sec.</td>
<td>No annealing</td>
</tr>
<tr>
<td>[70]PCBM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P3HT:</td>
<td>1:1 (17.5 mg/ml)</td>
<td>DCB</td>
<td>3%</td>
<td>800 rpm for 20 sec.</td>
<td>150 °C for 10 min</td>
</tr>
<tr>
<td>[60]ICBA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FTQ:</td>
<td>1:1 (15 mg/ml)</td>
<td>DCB</td>
<td>0.4%</td>
<td>1000 rpm for 50 sec.</td>
<td>110 °C for 1 min</td>
</tr>
<tr>
<td>[70]PCBM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3. Confirmation of the graded BHJ

The extraction of DIO by methanol-fluxing can be observed by the naked eyes because of the color change of the BHJ films. The dried BHJ films have deeper color than the wet film due to the stronger Pi-Pi conjugation between the solid semiconducting molecules, which were observed in all of the BHJ films tested. Figure 3.4 shows pictures
of PBDTTT-CT:[70]PCBM and PCDTBT:[70]PCBM films with partial areas fluxed and the corresponding absorption spectra measured at both fluxed and pristine areas. The methanol-fluxed areas are darker than the rest for both PBDTTT-CT:[70]PCBM and PCDTBT:[70]PCBM films. The absorption spectra in the fluxed areas are almost identical to the overnight, vacuum-dried BHJ films. This gives a direct correlation between the color changes and the extraction of DIO by solvent-fluxing. The difference between methanol-fluxing and vacuum-drying of DIO is that the quick extraction of DIO nanodroplets by methanol will also pull some fullerene-derivatives toward the BHJ film surfaces and thus form the graded BHJs.

**Figure 3.4** Optical images of PBDTTT-CT:[70]PCBM (a), PCDTBT:[70]PCBM (c), b,c single path absorption spectroscopy of as-prepared (black line) and methanol-fluxed (red line) and vacuum-dried (blue line) films of PBDTTT-CT:[70]PCBM (b), PCDTBT:[70]PCBM (d).
The formation of graded BHJs by methanol-fluxing was verified by multiple characterization methods. First, the formation of the graded BHJs was revealed by measuring the vertical composition profile of PBDTTT-CT:[70]PCBM and PCDTBT:[70]PCBM films using Energy-Filtered Transmission Electron Microscopy (EFTEM). The low energy plasmon peak (19±4eV) of polymer donors\textsuperscript{118-120} was used to highlight the donor so that brighter regions (higher gray value) represent donor-rich region in the EFTEM images. The following conclusions can be drawn from the FETEM images (Figure 3.5a-d) as well as the gray value distribution of the vacuum-dried and fluxed films (Figure 3.5e-f): 1) The PBDTTT-CT content along the vertical direction in the vacuum-dried PBDTTT-CT:[70]PCBM film is almost constant, while there is a spontaneous un-favored composition gradient in the vacuum-dried PCDTBT:[70]PCBM with PCDTBT rich at the top surface (cathode side). 2) There is a clear graded distribution of the PBDTTT-CT and [70]PCBM in the fluxed film with linearly increasing PBDTTT-CT content toward the PEDOT:PSS (anode side), as shown by the gray value in Figure 3.5e; The composition gradient of the PCDTBT:[70]PCBM film was completely reversed after solvent-fluxing, leaving a PCDTBT-rich region close to the PEDOT:PSS which is favored for higher efficiency in the regular structure device. 3) The distribution of polymers and [70]PCBM in the vacuum-dried PBDTTT-CT:[70]PCBM and PCDTBT:[70]PCBM films is nonuniform in the film plane. There are some randomly distributed, large [70]PCBM-rich regions with size ranging from 50-200 nm. Both fluxed BHJ films have more uniform polymer and [70]PCBM domain distribution in the film plane.
Figure 3.5 a-d, EFTEM cross-sectional images of the vacuum-dried (a), fluxed PBDTTT-CT:[70]PCBM film (c), vacuum-dried (b), and fluxed PCDTBT:[70]PCBM film (d) with energy filter set at 19±4 eV where brighter regions represent donor-rich region. The small pictures on the left of each EFTEM image are TEM images with energy filter set at 0 V which show each layer clearly, in which donors and acceptors do not have any significant contrast because they have very little differences in terms of their electron density; e,f, Gray values, along the vertical direction, of the vacuum-dried and fluxed PBDTTT-CT:[70]PCBM films (e), and PCDTBT:[70]PCBM films (f) in the areas marked with white dashed squares on the left EFTEM images.

Second, spectroscopic ellipsometry measurements were performed to quantitatively verify the vertical composition profile. The PBDTTT-CT:[70]PCBM and PCDTBT:[70]PCBM blends were spun on silicon wafers coated with PEDOT:PSS to maintain the same surface condition as the working device while reducing the complexity of the model required to analyze the ellipsometric data. The optical properties of PEDOT:PSS, PBDTTT-CT, PCDTBT, and [70]PCBM were determined individually and
were held fixed when calculating the vertical phase separation. The blended films were
discretized into eleven equal segments in the vertical direction, and the percentage of
PBDTTT-CT in each segment was allowed to vary in accordance with the Bruggeman
effective medium approximation. \(^\text{121}\) A linear variation in the PBDTTT-CT and PCDTBT
percentage provided the best fit to the experimental data while maintaining a unique
solution for the vertical compositional profile. The ellipsometric measurement utilized a
300 µm diameter beam so the measurement reflects the average condition of the sample
and does not resolve the fine spatial variations in the compositional profile. The analysis
procedure used to model the ellipsometric data is stated in the supporting materials. As
shown in Figure 3.6a-b, the vacuum-dried PBDTTT-CT:[70]PCBM film has nearly
uniform composition distribution in the vertical direction. Whereas, the fluxed PBDTTT-
CT:[70]PCBM film has a clear composition gradient with more PBDTTT-CT on the
bottom surface. The vacuum-dried film of PCDTBT:[70]PCBM blended film has a
spontaneous graded composition with PCDTBT rich at the top surface. After methanol-
fluxing, the [70] PCBM was extracted toward the top surface which is favored for the
regular BHJ device. Both results agree well with the EFTEM result. The blended film
structure was modeled using a graded effective median approximation where the weight
percentage of PBDTTT-CT in PBDTTT-CT: [70]PCBM blended films at the bottom
(anode) and top (cathode) interfaces was determined to be 60% and 27%, respectively.
The weight percentage of PCDTBT in PCDTBT:[70]PCBM blended films at the bottom
and top interfaces was determined to be 25% and 17% respectively, which is in good
accordance with the weight ratio of polymer in the blended film (40% for PBDTTT-
CT:[70]PCBM and 20% for PCDTBT:[70]PCBM system).
Figure 3.6 Quantitative determination of the composition of the vacuum-dried and fluxed PBDTTT-CT:[70]PCBM films (a) and PCDTBT:[70]PCBM films (b) along the vertical direction by ellipsometry.

Third, secondary ion mass spectrometry (SIMS) was conducted to directly measure the composition profile of the BHJ films. The content of the polymer was derived from the sulfur atom ratio in the BHJ films, and the results were shown in Figure 3.7a-b. The weight percentage of PBDTTT-CT of the vacuum-dried film is relatively uniform across the whole film, while it increases linearly with position in the fluxed film. After methanol-fluxing, the PBDTTT-CT content on the top of the film reduced to 30 wt%, while that at the bottom of the film increased to 51 wt%. The same variation trend of composition profile was observed for vacuum-dried and methanol-fluxed PCDTBT:[70]PCBM films. The composition profile of PCDTBT of the vacuum-dried PCDTBT:[70]PCBM showed a negative slope, while the slope was changed to positive in methanol-fluxed PCDTBT:[70]PCBM film. These results are in excellent agreement with
the EFTEM and ellipsometric results above and the weight ratio of polymers in the BHJ films, which further confirms the formation of gradient BHJ films by the solvent-fluxing method.

![Figure 3.7](image)

**Figure 3.7** The composition depth profiles of PBDTTT-CT:[70]PCBM films (a) and PCDTBT:[70]PCBM (b) films measured by SIMS. All the scale bars are 50 nm.

### 3.4. Device performance

The photocurrent density-voltage ($J_{ph}$-$V$) characteristics of vacuum-dried and solvent-fluxed devices as well as the reflective absorption (RA), EQE and IQE of PBDTTT-CT:[70]PCBM, PCDTBT:[70]PCBM are shown in **Figure 3.8**. The device’s performance of PBDTTT-CT:[70]PCBM, PCDTBT:[70]PCBM, P3HT:[60]ICBA, FTQ:[70]PCBM is summarized in **Table 3.2** with statistics based on more than 20 devices for each category. The PCEs of PBDTTT-CT:[70]PCBM, PCDTBT:[70]PCBM,
P3HT:[60]IcBA, FTQ:[70]PCBM after solvent-fluxing were increased from 6.9% to 8.6%, 5.4% to 7.2%, 4.9% to 6.0%, and 4.4% to 6.0%, respectively. The fabrication parameters and the optimized DIO percentages for each material system are shown in Table 3.1. The FF of 62.5%, IQE of 90% and efficiency of 8.6% for PBDTTT-CT:[70]PCBM based devices, and FF of 67.3%, IQE of >90% and efficiency of 7.2% for PCDTBT:[70]PCBM based devices are the highest reported values for these material systems. The slight $V_{OC}$ variation might be caused by the interplay of various effects of solvent fluxing: passivation effect increases $V_{OC}$ while increased crystallinity reduces $V_{OC}$. The solvent-fluxing method reported here is a new paradigm to optimize the efficiency of some material systems, such as PBDTTT-CT:[70]PCBM and FTQ:[70]PCBM, that cannot be further improved by other established approaches, including thermal annealing, solvent annealing, or additives.
Figure 3.8 Photocurrent of vacuum-dried (black circle line) and fluxed (red circle line) devices of PBDTTT-CT:[70]PCBM (a), PCDTBT:[70]PCBM (b) under simulated A.M 1.5 illumination. EQE (open circle lines), reflective absorption (solid lines) and IQE (solid circle lines) of (c) PBDTTT-CT:[70]PCBM and (d) PCDTBT:[70]PCBM devices (black: vacuum-dried, red: fluxed).

Table 3.2 Statics of PCE of different kinds of solar cells with regular BHJ (vacuum-dried) and Graded BHJ (solvent-fluxed) structure

<table>
<thead>
<tr>
<th>Materials</th>
<th>Blend film drying methods</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>PCE Average</th>
<th>PCE Best</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCDTBT: [70]PCBM</td>
<td>Vacuum-dried</td>
<td>10.5±0.4</td>
<td>0.89±0.01</td>
<td>55.0±0.5</td>
<td>5.20%±0.20</td>
<td>5.4%</td>
</tr>
<tr>
<td></td>
<td>Methanol-fluxing</td>
<td>11.5±0.4</td>
<td>0.92±0.01</td>
<td>65.7±0.7</td>
<td>6.95%±0.15</td>
<td>7.2%</td>
</tr>
<tr>
<td>PBDTTT-CT: [70]PCBM</td>
<td>Vacuum-dried</td>
<td>16.4±0.4</td>
<td>0.76±0.01</td>
<td>53.5±0.5</td>
<td>6.90%±0.10</td>
<td>7.0%</td>
</tr>
<tr>
<td></td>
<td>Methanol-fluxing</td>
<td>17.2±0.3</td>
<td>0.78±0.01</td>
<td>63.3±0.7</td>
<td>8.40% ±0.20</td>
<td>8.6%</td>
</tr>
<tr>
<td>P3HT: [60]ICBA</td>
<td>Vacuum-dried</td>
<td>9.8±0.2</td>
<td>0.82±0.01</td>
<td>60.9±0.5</td>
<td>4.90%±0.10</td>
<td>5.0%</td>
</tr>
<tr>
<td></td>
<td>Methanol-fluxing</td>
<td>10.3±0.2</td>
<td>0.80±0.01</td>
<td>72.1±0.3</td>
<td>5.90% ±0.10</td>
<td>6.0%</td>
</tr>
</tbody>
</table>
A general guideline is prescribed for the formation of graded BHJ by the solvent-fluxing method: 1) The boiling point of the solution additive must be higher than the working solvent so that only the additive remains in the blended films before the fluxing process; 2) The additive should selectively dissolve fullerene-derivatives so that it brings fullerene-derivatives to the surface during the solvent-fluxing process; 3) The fluxing solvent should mix well with additive but not dissolve polymers or fullerene-derivatives, so that it can pull the additive as well as fullerene-derivatives to the surface and only wash off the additive; and 4) There is an optimal time interval between the deposition of the active layer and the solvent-fluxing so that the fullerene-derivative extraction process does not interrupt or damage the polymer crystallization. Previous studies show that the working solvent drying process plays an important role in determining the morphology of BHJs because the self-organization of polymer predominately occurs in wet films.99 It is expected that performing the solvent-fluxing process too early interrupts the polymer crystallization, while performing the solvent-fluxing process too late is not effective in extracting fullerene-derivatives because the framework of the polymer will be too rigid.
Figure 3.9 Device performance of PBDTTT-CT:[70]PCBM (a), PCDTBT:[70]PCBM (b), P3HT:IC_{60}BA (c), and FTQ:[70]PCBM (d) with different time interval between spin coating the blend film and solvent flux.

The photocurrent curves of the devices with different time intervals are shown in Figure 3.9. It was found that a time interval of 10 minutes was optimal for the PBDTTT-CT:[70]PCBM, PCDTBT:[70]PCBM, and FTQ:[70]PCBM-based devices, and 30 min for a P3HT:IC_{60}BA-based device. 4) The thickness of the active layer should match the penetration depth of the methanol solvent so that DIO near the PEDOT:PSS side can also be extracted out. From the various characterizations on the PBDTTT-CT:[70]PCBM (100 nm) and PCDTBT:[70]PCBM (80 nm) films shown in Figure 3.5-3.7, the depth composition profile of the films can be modified at the PEDOT:PSS side, which indicates the penetration depth of the methanol is larger than 100 nm.
To test the versatile and universal application of this approach, several other low boiling point solvents, including methanol, ethanol, and isopropanol, were tested for the fluxing process. All of these low boiling point solvents mix well with DIO and do not dissolve fullerene-derivatives or the donor polymers. The device performance using these solvents is shown in Figure 3.10. All of them resulted in almost the same device performance enhancement compared to the vacuum-dried devices.

It is noted that methanol treatment was used recently to improve the efficiency of thieno[3,4-b]-thiophene/benzodithiophene (PTB7):[70]PCBM devices, which is ascribed to the passivation of surface traps and a corresponding increase of surface charge density. In that study, the PTB7:[70]PCBM films were first vacuum-dried to remove DIO; therefore, the methanol-fluxing can only cause surface passivation rather than change the morphology or vertical composition distribution inside the BHJ films. To manifest their difference, the performances of the PBDTTT-CT:[70]PCBM and
PCDTBT:[70]PCBM devices were compared using these two different solvent treatments, and the photocurrents were shown in Figure 6. Efficiency enhancements were observed rising from 6.9% to 7.4% for PBDTTT-CT:[70]PCBM devices and from 5.0% to 6.0% for PCDTBT:[70]PCBM devices after methanol-fluxing of the vacuum-dried films, which can be ascribed to the reported surface passivation effect. In contrast, methanol-fluxing of the wet films gave much higher efficiencies of 8.6% for PBDTTT-CT:[70]PCBM and 7.2% for PCDTBT:[70]PCBM devices, demonstrating the importance of the graded BHJs in efficiency enhancement.

**Figure 3.11** Photocurrent curves of the vacuum-dried (black circle line) and fluxed wet film (red circle line) and fluxed pre-vacuum-dried film (blue circle line) of PBDTTT-CT:[70]PCBM (a) and PCDTBT:[70]PCBM (b). Photocurrent curves of the vacuum-dried and solvent-fluxed inverted structure devices of PBDTTT-CT:[70]PCBM (c) and PCDTBT:[70]PCBM (d).
In order to further examine the contribution of the graded structure on the performance enhancement of the solvent-fluxed BHJ devices, inverted structure devices were fabricated with a device structure of: ITO/ Cs$_2$CO$_3$ (0.3 nm)/PBDTTT-CT(or PCDTBT):[70]PCBM (80-100 nm)/Molybdenum trioxide (MoO$_3$) (8 nm)/Ag. Such inverted structure devices give comparable device performances with regular structure BHJ devices if the BHJ films were vacuum-dried as shown in Figure 3.11c-d. After a methanol-fluxing process which brings [70]PCBM to the top surface, both $J_{SC}$ and FF reduced in the inverted graded BHJ devices, and the PCE of the devices decreased from 6.8% to 6.2% for PBDTTT-CT:[70]PCBM devices, and from 5.0% to 4.1% for PCDTBT:[70]PCBM devices, respectively. This result excludes the other factors, including enhanced carrier mobility, molecular crystallinity and/or orientation variation (if there is) by the solvent-fluxing process, and confirmed graded BHJ junctions as dominating mechanism for the observed efficiency enhancement.

### 3.5. Origin of the efficiency enhancement

It is acknowledged that the graded BHJ film with fullerene acceptor rich at the cathode interface and polymer donor rich at the anode interface can result in better device performance. However, the origin of the efficiency enhancement has not been identified. The main reason is that the graded BHJ can only be formed in few specific polymer systems and different polymer:fullerene system usually has different dominate recombination, which makes it difficult to draw a conclusion between the regular BHJ device and graded BHJ device. Here in this part, we studied the origin of the efficiency enhancement by both steady state measurement and transient measurement. It is found
that the biomolecular recombination in graded BHJ device was dramatically reduced compared with the regular BHJ device.

![Diagram of light to electric conversion processes in organic solar cells]

**Figure 3.12** Schematics of the light to electric conversion processes in organic solar cells

The efficiency of BHJ OPVs is determined by the efficiencies of light absorption, free charge generation, and free charge transportation and extraction. We examined the four processes step by step. Firstly, the absorption spectra of the regular BHJ device (vacuum-dried) and graded BHJs are almost identical; the change of light absorption efficiency is thus excluded.

The influence of the solvent-fluxing process on charge generation efficiencies was first examined by comparing the vacuum-dried, solvent-fluxed BHJ devices with DIO as additive and devices without DIO as additive using an established TDCF method. The charge generation efficiencies were measured under different bias from -4 V to open circuit voltage, and were normalized by the IQE at -4V. The laser intensity of the N₂ laser, with a shot-to-shot energy deviation of < 3%, was attenuated by neutral density filters so that the photocurrent pulse height generated was comparable to the $J_{SC}$. An upgraded Keithley semiconductor parameter analyzer (4200-SCS) with two synchronized voltage
output channels was used to trigger the nitrogen laser and provide charge collection bias, respectively. The rising time of the trigger pulse and the electrical bias pulse was 10 ns. The nitrogen laser provides a simultaneous TTL pulse output with a full width at half maximum (FWHM) of 1 ns during the laser pulse output, enabling an accurate identification of the delay time between the laser pulse and charge extraction pulse. A digital oscilloscope with a bandwidth of 500 MHz was used to record the voltage pulse over a 50 Ω resistance which was connected in series with the device.

![Figure 3.13](image-url) Charge generation efficiency of PBDTTT-CT:[70]PCBM (a), PCDTBT:[70]PCBM (b) devices measured by TDCF.

The following conclusion can be made from the data in Figure 3.13: 1) The field-dependent charge generation efficiency in the PBDTTT-CT:[70]PCBM devices without DIO additive is strong, while it is still obvious but weaker in the PCDTBT:[70]PCBM without DIO additive. 2) Both types of devices show weak field-dependent charge generation efficiency as long as DIO was added; 3) Solvent-fluxing of the BHJs did not change the charge generation efficiency compared to the vacuum-dried BHJ films for either PBDTTT-CT:[70]PCBM or PCDTBT:[70]PCBM films with DIO additive. This
result agrees with the morphology studies that the DIO additive resulted in smaller and/or purer PCBM domains and increased charge generation efficiency.\textsuperscript{95,124,125} Therefore, although it is unknown yet whether the solvent-fluxing process could induce molecule orientation or crystallinity change, it can be determined that the solvent-fluxing process does not change the charge generation efficiencies in the PBDTTT-CT:[70]PCBM and PCDTBT:[70]PCBM BHJ films.

**Figure 3.14** Light intensity dependent photocurrent for PBDTTT-CT:[70]PCBM system (a:vacuum-dried, b:Fluxed) and PCDTBT:[70]PCBM system (c:vacuum-dried, d:Fluxed)

After excluding other possible mechanisms, a conclusion can be made that the enhanced PCEs in solvent-fluxed BHJ devices mainly originate from reduced charge recombination. The degree of charge recombination suppression by this method is expected to vary with active materials’ chemical structure, purity, dominating
recombination types, carrier mobility, incident light intensity, bias, et al. Nevertheless, it was found that the major contribution for the PCEs enhancement in all the graded BHJ devices comes from the increased FF (Table 3.2), which should be ascribed to the reduced bimolecular recombination in the graded BHJ films. The small variation of series resistance, from 0.84 ohm·cm² to 1.26 ohm·cm² in PBDTTT-CT:[70]PCBM devices after methanol fluxing, cannot explain the observed large FF enhancement. This agrees with the expectation that graded BHJ can reduce the bimolecular recombination as it gives better matched charge collection pathways for electrons and holes toward their respective electrodes,¹¹³ which is confirmed by the 2-8 times increased hole and electron mobilities in both PBDTTT-CT:[70]PCBM and PCDTBT:[70]PCBM BHJ films after methanol-fluxing, measured by the single carrier devices.

Figure 3.15 FFs of fluxed (red square) and vacuum-dried (black square) devices under varied light intensity from 10 to 300 mW/cm² with active layer of PBDTTT-
CT:[70]PCBM (a), PCDTBT:[70]PCBM (b). c,d, the exponent of $\alpha$ ($\Delta J \propto I_L^\alpha$) under different effective applied bias $V_0-V$ on PBDTTT-CT:[70]PCBM (c), PCDTBT:[70]PCBM.

The reduced bimolecular recombination in graded BHJ devices was confirmed by comparing the FF of the methanol-fluxed and vacuum-dried PBDTTT-CT:[70]PCBM and PCDTBT:[70]PCBM devices at varied light intensity. The photocurrent curves of the devices are shown in Figure 3.14. As shown in Figure 3.15a-b, when the light intensity is below 10 mW/cm$^2$, both vacuum-dried and solvent-fluxed BHJ devices give the largest FF because the charge generation rate is low. Both BHJ devices have declining FF with the increased light intensity from 10 to 300 mW/cm$^2$, while the graded BHJ devices shows a much slower or negligible declining rate, proving the effective reduction of bimolecular recombination by the graded BHJ. The reduced bimolecular recombination was also confirmed by the measuring the dependence of effective photocurrent density ($\Delta J = J_{ph} - J_d$, where $J_d$ is the dark current density) with light intensity ($I_L$) which generally have a relationship of $\Delta J \propto I_L^\alpha$. Although the numerical correlation between the fitting parameter $\alpha$ and percentage of bimolecular recombination among total recombination is still under debate, a smaller $\alpha$ unequivocally indicates more bimolecular recombination.\textsuperscript{110,126} Figure 3.15c-d show $\alpha$ under different effective applied bias ($V_0-V$, where $V_0$ is the voltage where effective photocurrent is zero, and $V$ is the applied external bias). Both methanol-fluxed devices give larger $\alpha$ than the vacuum-dried devices under low effective applied bias, proving the bimolecular recombination was reduced in the graded BHJ devices.
Figure 3.16 Photo-generated carrier density at the open circuit voltage condition for PBDTTT-CT:[70]PCBM (a) and PCDTBT:[70]PCBM (c); Carrier lifetime for PBDTTT-CT:[70]PCBM (b) and PCDTBT:[70]PCBM (d); Bimolecular recombination rate $k(n)$ of PBDTTT-CT:[70]PCBM (e), PCDTBT:[70]PCBM (f) measured by TPV.

To directly evaluate the influence of fluxing process on the charge recombination process, transit photovoltage (TPV) measurement of the vacuum-dried and solvent-fluxed devices was conducted to determine the bimolecular recombination rate and free charge lifetime at $V_{OC}$.127-129 For the TPV and differential capacitance experiment, we closely
followed the reported method. The device was serially connected to a digital oscilloscope (LeCroy LT 342, with sampling rate of 500 Ms/s, bandwidth of 500 MHz), and the input impedance of the oscilloscope was 1 MΩ to form the open circuit condition for monitoring the charge decay dynamics. In order to change $V_{OC}$ and charge density in the device, a Newport Xe lamp was used as the background light illumination with broad range tunable light intensity. A strongly attenuated UV laser pulse (SRS NL 100 Nitrogen Laser) was used as a small perturbation to the background illumination on the device. The laser-pulse-induced photovoltage variation ($\Delta V$) was smaller than 5% of the $V_{OC}$ produced by the background illumination. The wavelength of the N$_2$ laser is 337 nm, the repeating frequency was $\sim$10 HZ, and the pulse width was less than 3.5 ns. The $\Delta Q$ was obtained by the integration of $J_{SC}$ over time according to the equation of $\Delta Q = \int J(t)dt$. The electrode capacitance charge density was subtracted from all the measured charge densities.

The total free charge density was calculated from a TPV test using a differential capacitance technique. The lifetimes of the free charge at $V_{OC}$, obtained by fitting the TPV transient ($\frac{d\Delta n}{dt} = -\alpha \Delta n/\tau$), are increased by around ten times after solvent-fluxing, as shown in Figure 3.16. The bimolecular recombination rate, $k(n) = [\tau(n)n]^{-1}$, of the solvent-fluxed devices is one to two orders of magnitude lower than the vacuum-dried devices, which further confirms that the solvent-fluxed BHJ devices have lower bimolecular recombination.

3.6. Conclusion
In summary, we report a method to boost the efficiency of BHJ OPVs by forming compositionally graded BHJ structure with better donor/acceptor bicontinuous connection using a simple solvent-fluxing process. The formation of graded BHJ was confirmed by multiple independent characterization methods. The PCE of the graded BHJ devices were enhanced by 15%-50% compared with the uniform distributed BHJ devices. Various characterizations demonstrated that the bimolecular recombination was greatly reduced in the graded BHJ device.
Chapter 4 Introduction to organic-inorganic hybrid perovskite solar cells

4.1. Overview

Organometal trihalide perovskites (OTP) are emerging as a new generation of solution processable photovoltaic materials which are low cost and nature-abundant. The structure is shown in Figure 4.1. It is a typical three dimensional perovskite structure materials with chemical formula of ABX$_3$, where A is the organic cation, B is lead (Pb) or tin (Sn), and X is the halide ions.

![Organometal trihalide perovskite structure](image)

**Figure 4.1** Organometal trihalide perovskite structure, where x=I, Cl, Br

The OTP perovskite materials have many attractive optoelectronic properties for photovoltaic applications:\textsuperscript{131,136,141,143,144,146} (1) Strong absorption coefficient; The absorption coefficient of methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) perovskite was estimated to be around 1.5×10$^4$ at 550 nm, which indicates that it needs only 650 nm to absorb most the visible light. (2) Appropriate bandgap; the bandgap of the perovskite materials can be tuned from 1100 nm for CH$_3$NH$_3$SnI$_3$, to 800 nm for CH$_3$NH$_3$PbI$_3$, to 400 nm for CH$_3$NH$_3$PbCl$_3$. (3) High electron and hole mobilities and diffusion lengths. The carrier mobility measured by Hall Effect was estimated to be at the order of 45
cm²/Vs. The carrier diffusion length is longer than 1 µm in the CH₃NH₃PbI₃ film. (4)
Unique defect property and shallow point defects. In addition, The OTP materials are soluble in some polar solvents like H₂O, N,N-Dimethylformamide (DMF), Dimethyl sulfoxide (DMSO), and gamma-Butyrolactone (GBL) etc, so that they can be processed using solution process.

4.2. A brief history

The OTP materials were first used for thin film transistors at the early 1990s. In 2009, Miyasaka et al. tried to use CH₃NH₃PbBr₃ and CH₃NH₃PbI₃ as dye in the dye sensitized solar cells where the mesoporous TiO₂ and a liquid electrolyte were used. An efficiency of 3.8% was achieved. Two years later, N. G. Park et al. increase the efficiency of CH₃NH₃PbI₃ up to 6.5%. The first breakthrough happened in 2012 when the solid hole transporting layers was used. Snaith’s group reported an efficiency of 10% in the mesoporous structure device by replacing TiO₂ with aluminum oxide (Al₂O₃). The second breakthrough happened in 2013, Snaith’s group demonstrated a 15% efficiency in planar structure solar cells where a compact TiO₂ layer was used. This was a very exciting result which indicates that the perovskite are bipolar conducting materials. The schematics of the mesoporous structure and planner structure devices are shown in Figure 4.2. Later, it was demonstrated that the carrier diffusion length in the CH₃NH₃PbI₃Cl₃₋ₓ reached around 1 µm.
Figure 4.2 (a) Mesoscopic structure perovskite solar cell with mesoporous TiO$_2$ layer and (b) planar structure without a mesoporous TiO$_2$ layer.

High PCE of higher than 19% has been achieved in both mesoporous structure devices as well as planar heterojunction (PHJ) devices. The highest certified efficiency has reached 20.1%. It takes about three years to increase the efficiency from 10% to 20%, while it takes tens of years for other kinds of inorganic solar cells, as shown in Figure 4.3.
**Figure 4.3** Power conversion efficiency table for thin film solar cells.

### 4.3. Challenges

Although the PCE of perovskite solar cells have been increased dramatically to 20.1%, there are still many challenges for this type of solar cell before they can be commercialized. One challenge is the toxic property of the material due to the lead. Another grand challenge is its instability. The water solubility of the perovskite materials make them instable under atmosphere. Although some capsulations using polymer matrix can prolong the lifetime of the devices, no long-term stability over years have been demonstrated yet.
Chapter 5 Inter-diffusion approach to fabricate perovskite films

Depositing a continuous, leakage-free perovskite film with thickness comparable to the charge diffusion length has shown to be very difficult using solution processes.\textsuperscript{131,136,146,148,149} Non-continuous perovskite films were frequently observed using lead iodide (PbI\textsubscript{2}) and methylammonium halide (CH\textsubscript{3}NH\textsubscript{3}X, or MAX) blend, which might be related to the interaction of perovskite with substrate surface.\textsuperscript{146,148} It maybe also due to the low viscosity perovskite solution and quick crystallization of the mixed precursor upon drying the spun films.\textsuperscript{150} The PCE of low-temperature solution processed perovskites devices in the range of 4~12\% were far below those devices with mesoporous structure or fabricated by thermal evaporation.\textsuperscript{131,133,146}

In this chapter, we report a method to form continuous and compact iodine perovskite (MAPbI\textsubscript{3}) films by the inter-diffusion of spin-coated stacking layers of PbI\textsubscript{2} and MAI. The high quality film achieved allows the fabrication of leakage-free photovoltaic devices and high PCE of 15.4\% under one sun, and 17.1\% under 0.03 sun illumination.

5.1. Inter-diffusion method

Methylammonium iodide (CH\textsubscript{3}NH\textsubscript{3}I, MAI) was synthesized using the method described by Michael M. Lee, \textit{et. al.} A concentrated aqueous solution of hydroiodic acid (HI) (15.0 mL, 57 wt\% in water, Alfa Aesar) was reacted with methylamine (CH\textsubscript{3}NH\textsubscript{2}) (13.5 mL, 40 wt\% in aqueous solution, Alfa Aesar) at 0 °C for 2 h with constant stirring under nitrogen atmosphere. Methylammonium was crystalized through removing the
solvent by a rotary evaporator. The generated white powder was washed with diethyl ether (Alfa Aesar) three times and dried in vacuum overnight.

Figure 5.1 Schematics of spin-coating of PbI$_2$ and MAI using orthogonal solvents and the conversion of the stacking layer into perovskite layer upon annealing.

The deposition and thermal annealing processes of the PbI$_2$/MAI stacking layers films is illustrated in Figure 5.1. For the film fabrication, PbI$_2$ and MAI were first dissolved in DMF and 2-propanol, respectively, as precursor solutions at varied concentration. The precursors were then spun onto PEDOT:PSS covered ITO glass with PbI$_2$ layer underneath MAI layer at 6,000 rpm for 35 s. A supersaturated hot solution of PbI$_2$ was used for a quick drying to obtain a pin-hole free and conformal PbI$_2$ layer on PEDOT:PSS surface. Since PbI$_2$ has relatively low solubility in 2-propanol, the spin-coating of MAI did not wash off PbI$_2$. It is surprise that the MAI layer thickness depends on not only the precursor solution concentration but also the thickness of the underneath PbI$_2$ layer, which might be caused by the immediate reaction of the precursor upon their contacting. A thicker MAI layer is generally found on thicker PbI$_2$ layer even using MAI solutions of the same concentration. The detail of the film thickness is shown in Table 5.1. The bilayer films were then annealed at temperature of 100 °C for varied durations.
Then, the PCBM (dissolved in DCB, 2% wt) was spin coated on top of the perovskite layer at 6000 rpm for 35 s. then the films was annealed at 100 °C for 60 min. The device was finished by thermal evaporating C\(_{60}\) (20 nm), 2,9-dimethyl-4,7- diphenyl-1,10-phenanthroline (BCP, 8 nm) and Al (100 nm). The device area is defined to be the overlap of the ITO and Al electrodes to be 9.6 mm\(^2\)

**Table 5.1** The thickness of perovskite layers fabricated by the interdiffusion method using precursor solutions with different PbI\(_2\) and MAI concentrations.

<table>
<thead>
<tr>
<th>MAI PbI(_2)</th>
<th>1.75%</th>
<th>2.25%</th>
<th>2.5%</th>
<th>3.0%</th>
<th>3.5%</th>
<th>4.0%</th>
<th>4.5%</th>
<th>5.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>13%</td>
<td>60-70 nm</td>
<td>80-90 nm</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>20%</td>
<td>-----</td>
<td>130-140 nm</td>
<td>135-145 nm</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>25%</td>
<td>-----</td>
<td>-----</td>
<td>160-180 nm</td>
<td>180-190 nm</td>
<td>190-200 nm</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>30%</td>
<td>-----</td>
<td>-----</td>
<td>180-190 nm</td>
<td>190-200 nm</td>
<td>200-215 nm</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>35%</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>205-215 nm</td>
<td>225-240 nm</td>
<td>250-270 nm</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>40%</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>250-260 nm</td>
<td>270-300 nm</td>
<td>280-300 nm</td>
<td>-----</td>
</tr>
<tr>
<td>45%</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>280-300 nm</td>
<td>300-320 nm</td>
<td>320-340 nm</td>
</tr>
</tbody>
</table>
5.2. Film characterization

SEM picture in Figure 5.2a reveals a very continuous PbI$_2$ film which is uncommon for an inorganic salt. The dried PbI$_2$/MAI bilayer films are rougher than PbI$_2$ layer due to formation of MAPbI$_3$ microcrystals upon drying and thermal annealing. Nevertheless, they are still continuous and pinhole-free across the whole device area, as shown by the large area SEM in Figure 5.2b. In contrast, the MAPbI$_3$ films spun from premixed PbI$_2$ and MAI blend solutions generally are non-uniform with many microstructures on the surface.

![SEM image of the PbI$_2$ film (a), the annealed perovskite layer formed by interdiffusion process (b)](image)

**Figure 5.2** SEM image of the PbI$_2$ film (a), the annealed perovskite layer formed by interdiffusion process (b)

We studied the interdiffusion process of PbI$_2$ and MAI stacking layers. A thickness ratio of 1.4 for MAI:PbI$_2$ layer, calculated from the density and molecular weight, is needed to form stoichiometry iodine perovskite by assuming a complete interdiffusion
and reaction of the precursors. The thickness of the PbI$_2$ layer was varied from 40 nm to 200 nm and the thickness of MAI varied from 60 nm to 250 nm by controlling the concentration of the precursor solutions and the spin-rate, which were summarized in Table 5.1. There is quick reaction of MAI and PbI$_2$ upon their contact, evidenced by the observed immediate color change of the bilayer films right after the spin-coating of MAI layer, which is consistent with previous observations in mesoporous structure devices.

The pictures of the films at different stages are shown in Figure 5.3a, showing the evolution of color change of the films. There is still unreacted MAI and PbI$_2$ right after its deposition, shown by the SEM image of as prepared PbI$_2$ and MAI stacking layers. The devices made of such films show low PCE below 1% with typical S-shape photocurrent, a signature of large series resistance caused by the insulating MAI and/or PbI$_2$. A thermal annealing is thus still needed to drive the interdiffusion of MAI and PbI$_2$, which can be visually observed by the increased darkness of the MAPbI$_3$ films.

Figure 5.3 (a) Single path absorption of perovskite film after dry and various annealing durations. The inset shows the pictures, from left to right, of the spun PbI$_2$ film, the
PbI₂/MAI film before drying, the PbI₂/MAI films after drying, and after 15 min annealing; (b) XRD pattern of MAI, PbI₂ and the perovskite films formed by interdiffusion with varied annealing time.

The interdiffusion of the PbI₂/MAI films and formation of perovskite after varied annealing time was studied by absorption spectra and XRD. Figure 5.3a shows typical absorption spectra of a PbI₂/MAI stacking film after different annealing durations from 0 min to 2 hours at temperature of 100 °C. The absorption at wavelength around 740 nm from perovskite quickly increased during the first 15 mins of thermal annealing, and then saturated after 1 hour annealing. The XRD patterns versus time of these films have the same variation trend with absorption spectra. As shown in Figure 5.3b, both MAI and PbI₂ peaks disappear after 15 min annealing and remains almost unchanged afterwards. No impurity peaks were identified from XRD patterns. This indicates the long-range interdiffusion of MAI and PbI₂ occurs primarily during the first 15 min annealing.

Figure 5.4 (a) Photo image and device performance of the perovskite films deposited by dipping 140 nm PbI₂ film into MAI. The MAI concentration is 10 mg/ml dissolved in 2-propanol.
It should be noted that the interdiffusion approach reported here is very different from the sequential deposition method reported by Burschka et al.\textsuperscript{1} which makes good mesoporous structure perovskite solar cells but not PHJ ones. We dipped 140 nm PbI$_2$ film into MAI solution; however, we obtained very non-uniform, rough perovskite films, as shown in Figure 5.4. The efficiency of the devices based on these films only reached 3.2\%. Another difference is that the thermal annealing process is required in the interdiffusion method reported here to make sure that the compact PbI$_2$ can be fully reacted with MAI. In the mesoporous perovskite photovoltaic devices with porous TiO$_2$ structures,\textsuperscript{151} PbI$_2$ absorbed on TiO$_2$ can be much thinner because of the very large surface area of mesoporous structure needed to absorb enough PbI$_2$. Due to the very thin PbI$_2$ in a mesoporous structure, the reaction of PbI$_2$ and MAI can be very quick and complete without resorting to thermal annealing. However, for the spun compact PbI$_2$ and MAI stacking layers, there is still unreacted MAI and PbI$_2$ right after deposition, shown by the SEM image of as-prepared PbI$_2$ and MAI stacking layers. The devices made of such films show low PCE, below 1\%, with typical S-shaped photocurrent, a signature of large series resistance caused by the insulating MAI and/or PbI$_2$. A thermal annealing is thus still needed to drive the interdiffusion of MAI and PbI$_2$, which can be visually observed by the increased darkness of the MAPbI$_3$ films.

5.3. Device structure and performances
Figure 5.5 (a) Cross-section SEM image of the best-performing perovskite device. The scale bar is 500 nm. The thickness of the perovskite layer is ~270 nm; (b) Composition depth profiles of the device without the Al electrode measured by SIMS.

The devices have a structure of ITO/PEDOT:PSS/MAPbI$_3$/PCBM (20 nm)/C$_{60}$/ (20 nm)/ BCP (8 nm) /Al (100 nm). The device area is 9.6 mm$^2$, determined by the overlap of the cathode and anode electrodes. In order to avoid the overestimation of the photocurrent density by the piping effect, an aperture size of 8 mm$^2$ was used to define the light absorption area. A Schott KG5 color-filtered Si diode (Hamamatsu S1133) was used to calibrate the light intensity of the solar simulator before photocurrent measurement to avoid optical mismatch.

The cross-section SEM of the whole device is shown in Figure 5.5 which shows a continuous, pin-hole free perovskite formed on PEDOT:PSS with film thickness variation less than 20 nm. SIMS measurement on the real device without Al electrode, as shown in Figure 5.5b, reveals a layered structure and the penetration of Pb$^{2+}$ and I$^-$ across the whole perovskite layer. The depth composition profile of Pb$^{2+}$ and I$^-$ shows a graded composition with increased Pb$^{2+}$ and I$^-$ toward the PEDOT:PSS side, which might be
caused by the incomplete diffusion of traceable PbI\textsubscript{2} to the surface but most likely by non-uniform sputtering of the perovskite layer. Nevertheless the deficiency of Pb\textsuperscript{2+} on top surface of these perovskite films was also observed by X-ray photoelectron spectroscopy measurement. Hall effect measurement reveal a $p$-type provskite and low extrinsic hole concentration around $4\sim 10\times 10^{13}$ cm\textsuperscript{-3}, which might due to the Pb deficient in the perovskite films formed by the interdiffusion approach.

**Figure 5.6** Performance of the perovskite devices. (a) Photocurrents of the device with PbI\textsubscript{2} thickness of 140 nm while varied MAI concentration from 40-50 mg/ml; (b) Photocurrents of the devices will perovskite films of different thickness varied from 200 to 320 nm.

In our devices, a PCBM layer spun onto the perovskite layer followed by thermal annealing is used to passivate the perovskite surface and grain boundaries. Hall effect measurement has shown that PCBM passivation can reduce extrinsic hole concentration caused by the unintentional doping in solution processed perovskite by three times and improve the carrier mobility by three times. The additional C\textsubscript{60} layer further passivates perovskite films and reduce the trap state density.\textsuperscript{21} The device performance is very sensitive to the precursor thickness ratio, thermal annealing time, as well as perovskite
thickness. Unmatched PbI$_2$ or MAI thickness always results in reduced $J_{SC}$ and $FF$, which might be caused by the traceable insulating precursors or nonstoichiometric compounds.

**Figure 5.6a** shows typical photocurrents of the devices with a fixed PbI$_2$ thickness (140 nm) and varied MAI thickness, demonstrating how the device performance was optimized. **Figure 5.6b** shows the photocurrents of the devices with varied perovskite thicknesses varied from 200 nm to 320 nm. It is clear that a thicker perovskite film absorbs more light and thus yields a larger photocurrent, while a too-large thickness causes loss of photovoltage, most likely due to the increased charge recombinations. The optimized MAPbI$_3$ devices have a perovskite thickness of 270-300 nm which is twofold longer than that of the previously measured low end of the electron and hole diffusion length of around 100-130 nm.$^{141,143}$ The long carrier extraction length should be ascribed to the excellent crystallinity, passivation by fullerenes, and/or low extrinsic doping of perovskite films formed by interdiffusion. It demonstrates the advantages of the interdiffusion approach in the formation of high quality perovskite films. The highest PCE devices were obtained by annealing of the PbI$_2$/MAI with a thickness of 140/190 nm at 100 °C for 2 hours. The device was measured under AM 1.5 simulated one sun illumination.

The best performing device has a $J_{SC}$ of 19.6 mA/cm$^2$, FF of 79.3%, $V_{OC}$ of 0.99 V, and PCE of 15.4%. **Figure 5.6c** shows the EQE of the device. The calculated $J_{SC}$ from the EQE spectra is 18.9 mA/cm$^2$, which is close to the measured $J_{SC}$ of 19.6 mA/cm$^2$. It is noted that there are two troughs in the EQE spectrum at around 400 nm and 600 nm, which is caused by the stronger reflection of the glass/ITO substrates at these wavelength
regions. Another best performing device with larger photocurrent but smaller $V_{OC}$ shows even higher efficiency of 16-17% at a lower light intensity of 3.2-30 mW/cm$^2$, as summarized in Table 5.2. The light intensity was tuned by applying neutral density filters of different optical densities. The higher efficiency under lower light intensity is ascribed to the reduced charge recombination evidenced by the larger FF, up to 82%. There is still room to further increase the carrier diffusion length for efficiency enhancement. Although a larger $J_{SC}$ of 22 mA/cm$^2$ could be reached in our devices with thicker perovskite thickness, the $V_{OC}$ and FF generally reduce, pulling down the PCE, which still needs a thorough understanding on the charge recombination process in perovskite materials and electrode interfaces to recover the $V_{OC}$ and FF.

**Table 5.2** Photovoltaic performance of a best-performing device under different illumination light intensities.

<table>
<thead>
<tr>
<th>Light intensity (mW/cm$^2$)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.20</td>
<td>0.78</td>
<td>0.85</td>
<td>82.2</td>
<td>17.0</td>
</tr>
<tr>
<td>31</td>
<td>7.09</td>
<td>0.92</td>
<td>77.0</td>
<td>16.2</td>
</tr>
<tr>
<td>100</td>
<td>20.59</td>
<td>0.94</td>
<td>78.8</td>
<td>15.3</td>
</tr>
</tbody>
</table>
Figure 5.7 Device performance statistics based on more than 50 devices from five batches.

One significant improvement of the device performance reported in this work is from the large FF of around 80% for most of our devices. The statistics of FF, $J_{SC}$, and $V_{OC}$ are shown in Figure 5.7a-d. In addition to the reduced charge recombination in perovskite layers due to their good crystallinity and passivation by PCBM, both at the top surface and at the grain boundaries inside the perovskite films, the compact and leakage-free perovskite films formed by the interdiffusion process should also contribute to the large FF. Most of the devices have a low saturated dark current density in the order of $10^{-4}$-$10^{-3}$ mA/cm$^2$ at -2 V. The 15.4% device has a large shunt resistance of 4.67 kΩ·cm$^2$ and a small series resistance of 1.06 Ω·cm$^2$ calculated from the photocurrent curve which is among the best values reported. Another merit of the interdiffusion method for fabricating perovskite devices is that it gives an excellent yield of high PCE devices.
which is attractive for large-scale production of perovskite devices. The statistics of the PCE based on more than 50 devices from five batches are shown in Figure 5.7d. The average PCE is 14.5% and 85% of the devices have efficiency above 14%.

**Figure 5.8** (a) Photocurrents of a high performance perovskite device measured with different delays between measurement points (a) and different sweep directions (b). No obvious hysteresis of photocurrent was observed. (c) Measured photocurrent output at the maximum power point of a high performance device versus time by turning on and off the illumination with a chopper.

It has been reported that photocurrent hysteresis appears in some perovskite devices, which is strongly dependent on the device fabrication process as well as the measurement scanning rate and directions.\(^{154}\) The origin of photocurrent hysteresis was ascribed to either the traps, ferroelectric properties of the perovskite material and/or the electromigration of ion in the perovskites. Here we changed the scanning rate from very fast to very slow, with a delay between measurement voltage points increased from 0 to 500 ms, which corresponds to the scan rate of 10.4 V/s to 0.033 V/s. The slowest scanning rate is comparable to what Snaith *et al.* reported.\(^ {154}\) As shown in Figure 5.8a-b, no obvious hysteresis of photocurrent was observed by changing the sweep rates or
direction in our devices or the sweep rates. This indicates that the origin of hysteresis in photocurrent is more likely due to the traps formation in some non-optimized film and device fabrication process. The ultimate way to examine the efficiency of a solar cell device is to measure its power output at the load point. If there is large density of traps in the devices or photocurrent hysteresis for other reasons, the photocurrent would rise slowly upon turning on illumination. Figure 5.8c shows that the photocurrent rose quickly to maximum in the timescale limited by the spin rate of the chopper, proving the presence of a negligible amount of charge traps in our optimized devices.

The interdiffusion method can be simply applied to other types of perovskite materials for incorporating Cl, Br, F, or other elements from precursor solutions and can also start with thermally evaporated precursor stacking layers to relieve the strict requirements for composition controlling in the co-evaporation process. The low temperature used is compatible with plastic flexible substrates. The interdiffusion approach can be potentially scaled up for large area device fabrication with established solution-process techniques, such as die-slot coating, gravure coating, and doctor blade coating.
Chapter 6 Solvent annealing of the perovskite for efficiency enhancement

6.1. Motivation

Material crystallinity is paramount in determining the electronic properties in both organic and inorganic electronic materials and performance of electronic devices.\textsuperscript{99,155-157} Thermal annealing is the most broadly applied technique to increase the crystallinity of materials, especially thin films, because of its simplicity. Complementary to thermal-annealing, solvent-annealing, where solvent vapor is introduced during the crystallization of the bulk or thin film materials,\textsuperscript{155,156} was found to be an effective method to increase the crystallinity of some very specific organic semiconductors but was never demonstrated in inorganic semiconductors.

High PCE of 18\% has been achieved in both mesoporous structures and PHJ structure perovskite devices, using either spin-casting or thermal-evaporation deposition methods.\textsuperscript{131-138,140-144,151,158} One issue with solution-processed perovskite thin films is that the polycrystalline films have a relatively small grain size of a couple of hundred nanometers due to the quick reaction of lead iodide (PbI\textsubscript{2}) and methylammonium iodide (MAI) and the quick crystallization of these perovskite materials.\textsuperscript{159} Most of the best performing devices have a perovskite thickness of around 300 nm.\textsuperscript{131,157} Perovskite film that is thicker, up to 1 \(\mu\)m, is desired so that sunlight can be absorbed more completely, especially in the red to infrared range. Another merit of having a thicker perovskite film is that the device’s manufacturing yield can be increased, which is especially important in larger scale manufacturing using high throughput methods such as printing, blade coating, or gravure coating. This is because a thicker film reduces the chance of leakage spot
formation, the importance of which has already been broadly recognized by the organic photovoltaic field.\textsuperscript{160} Thermal annealing could be used to increase the grain size and crystallinity of these perovskites to some extent; but the margin is very small, as shown in this work. Moreover, high temperature thermal annealing, or even low temperature thermal annealing for long periods, decomposes the perovskite films; and the device efficiency decreases.\textsuperscript{161,162}

6.2. Solvent annealing approach

In this chapter, we report that solvent annealing effectively increases the crystallinity and grain size of CH$_3$NH$_3$PbI$_3$ film. The average grain size of the solvent-annealed trihalide CH$_3$NH$_3$PbI$_3$ films increased to 1 µm, which is comparable to the film thickness, while maximum grain size in thermal-annealed films was only around 260 nm. Solvent annealing dramatically improved the electronic properties of the perovskite films. The best performing device with planar structure had an efficiency of 15.6% under air mass global (AM 1.5G) spectrum illumination with a perovskite thickness of 630 nm, and efficiency dropped only slightly to 14.5% when the pervoskite thickness increased to 1 µm.

\textbf{Figure 6.1} Schematics of the interdiffusion approach and solvent-annealing-induced grain size increase.
The perovskite films were fabricated by the interdiffusion of spun stacking of double layers of PbI$_2$ and MAI, as illustrated in Figure 6.1. PbI$_2$ and MAI were first dissolved in DMF and 2-propanol, respectively, as precursor solutions at varied concentration. The precursors were then spun onto PEDOT:PSS covered ITO glass in the sequence of PbI$_2$ and MAI. Since PbI$_2$ has relatively low solubility in 2-propanol, the spin coating of MAI did not wash off the PbI$_2$. Our previous studies showed that the interdiffusion method can form continuous, compact perovskite films. The thickness of the perovskite films was controlled from 160 nm to 1,015 nm by changing the concentration of precursors. The stacking films were then annealed at a temperature of 100 °C with or without DMF vapor for one hour. The films without solvent annealing only went through thermal annealing and were used as control samples. Since both PbI$_2$ and MAI have high solubility in DMF, the DMF vapor provided a wet environment so that the precursor ions and molecules could diffuse a longer distance than in all solid-state thermal annealing, which promotes the grain growth and yields a larger grain size, as illustrated in Figure 6.1b-c.

6.3. Perovskite film characterization

Figure 6.2 shows the SEM top surface images of perovskite films with thicknesses of 250 nm, 430 nm, and 1,015 nm, respectively, with and without solvent annealing. Their in-plane grain size distributions are shown on the right side of the SEM images. The filmthicknesses are also marked as black vertical dashed lines in the grain size histograms. The following conclusions can be drawn from the SEM study. First, all of the films with and without solvent annealing follow a normal grain growth mode where the average grain size increases uniformly in all directions; Second, the grain size of the
solvent-annealed films increases almost linearly with the film thickness up to 1,015 nm, while the maximum grain size in the thermal-annealed films remains around 260 nm irrespective of film thickness. Third, the average grain sizes of the solvent-annealed films are always slightly larger or comparable to the film thicknesses, which should greatly enhance the charge extraction process. This is because the photogenerated charges do not need to go through any grain boundaries during their transport in the out-of-plane direction before being collected by the electrodes.
Figure 6.2 SEM images of the thermal-annealed (TA) perovskite films with thickness of 250 nm (a), 430 nm (d) and 1,015 nm, and solvent-annealed (SA) perovskite films with thickness of 250 nm (b), 430 nm (e) and 1,015 nm (h); (c,f,i) Grain size statistics of the SEM images on the left; The scale bar in the SEM pictures is 2 µm.

Figure 6.3 SEM pictures of the thermal-annealed and solvent-annealed 300 nm thick perovskite films after different annealing duration from 5 to 60 min. Scale bar is 2 µm.
The dynamic grain growth process of thermal annealing and solvent annealing of a 300 nm thick perovskite films was studied by varying thermal and solvent annealing time from 0 min. to 60 min. The SEM surface images are shown in Figure 6.3. The average grain size versus time is summarized in Figure 6.4a. Due to the quick reaction of PbI$_2$ and MAI and quick crystallization of MAPbI$_3$, the as-prepared perovskite films were polycrystalline with a small average grain size of 125 nm. The grain size of both thermal-annealed and solvent-annealed films grew with increased annealing time. The grain size increase was fast in the first 20 min, and then slowed down and saturated with further annealing. The grain size of the solvent-annealed film grew much faster than the thermal-annealed films. A solvent-annealing for 20 min. increased the average grain size to 400 nm, which was already larger than the film thickness, while thermal-annealing for 60 min. only increased the grain size to 260 nm, smaller than the film thickness.

Figure 6.4 (a) Average grain size versus annealing time for the 300 nm thick perovskite films; (b) XRD patterns of the thermal-annealed and solvent-annealed 300 nm thickness perovskite films; (c) Single path absorption of the perovskite films with different thicknesses.
The solvent annealing-induced crystallinity change was measured by XRD. Figure 6.4b shows the XRD results of the solvent-annealed and thermal-annealed 300 nm thick perovskite films. All of the XRD diffraction peaks of the solvent-annealed films were shaper than those of the thermal-annealed films, which indicates increased crystallinity with less low-dimensional defects and/or larger grain size with less scattering of grain boundaries. The relative intensity of the diffraction peaks from the different planes did not change, indicating that the grain crystal orientation of the solvent-annealed film should not change during the solvent annealing process. The absorption spectra of the perovskite films with different thicknesses were also measured, and the result is shown in Figure 6.4c. The increased band-edge absorption, around 750 nm, should be due to the improved crystallinity and/or the full reaction of precursors under the facilitation of DMF vapor.

Hall Effect measurements were conducted on the 300 nm thick films to determine the morphology-correlated electric property change. It showed that all of the perovskite films were p-type. After solvent annealing, the hole mobility increased from 30 cm$^2$/V·s to 45 cm$^2$/V·s; and the extrinsic hole concentration decreased from $1.8 \times 10^{14}$ cm$^{-3}$ to $6.2 \times 10^{13}$ cm$^{-3}$. Both variations can be ascribed to the larger grains with better crystallinity and decreased grain boundary density in the solvent-annealed films.

6.4. Device structure and performance

Photovoltaic devices were fabricated to evaluate the influence of improved crystallinity and enlarged grain size on device performance. The devices were structured of ITO/PEDOT:PSS/PCBM (10 nm)/C$_{60}$ (20 nm)/BCP (8 nm) /Al (100 nm). The device
area was 9.6 mm$^2$, determined by the overlap of the cathode and anode. In order to avoid the overestimation of the photocurrent density by piping effect, an aperture size of 8 mm$^2$ was used to define the light absorption area. Double fullerene layers were used, because they can passivate the defects with different depths at both the perovskite surface and the grain boundaries in a complementary way.\textsuperscript{165,166} Figure 6.5 shows the SEM cross-section images of the thermal-annealed and solvent-annealed devices with a perovskite layer thickness around 1,015 nm. As one can see, the grains in the thermal-annealed device are smaller than the film thickness, while the grains in the solvent-annealed film are so large that a single grain can connect the cathode and anode. It can be inferred that, in the solvent-annealed perovskite devices, most of the photo-generated charges can reach the electrodes without encountering grain boundaries, which should significantly reduce charge loss by recombination at grain boundaries in thick perovskite film devices.

![Figure 6.5](image)

\textbf{Figure 6.5} Cross-section SEM images of the thermal-annealed (a) and solvent-annealed (b) perovskite films with thickness of 1,015 nm.
Figure 6.6a-h show the photocurrent curves as well as the EQE of the device with perovskite thickness from 160 nm to 1,015 nm, and the device performances are shown in Table 6.1. When the perovskite film is thinner than 300 nm, which is comparable to the grain size of both thermal-annealed and solvent-annealed perovskite films, the photo-generated carriers are expected to be effectively extracted out without severe recombination, since there would be fewer grain boundaries along the charge transportation paths. In this case, the photocurrent of the solvent-annealed devices had only slightly higher photocurrent than the thermal-annealed devices. The $J_{SC}$ of 16-17 mA/cm$^2$ from the thin perovskite film devices were relatively small because of insufficient absorption in the red spectrum region. The $J_{SC}$ of the solvent-annealed device kept increasing with the thickness due to stronger absorption evidenced by the dramatically increased EQE in the 550-800 nm spectral range. It reached a maximum value of 21.1 mA/cm$^2$ in the devices with a perovskite film thickness of 630 nm. For the thermal-annealed devices, the $J_{SC}$ and FF increased slightly with an increased perovskite film thickness to 300 nm. However, the $J_{SC}$ and FF of the thermal-annealed devices decreased when the thickness of the perovskite films was further increased to surpass the invariable grain size. It is derived that the charge recombination at these grain boundaries severely reduced the device performance. If all of the photo-generated charges were collected by the diffusion of charges to electrodes, the charge diffusion length of the solvent-annealed perovskite films would be larger than 1 µm, much longer than the thermal-annealed film of around 300 nm. According to the solvent annealing working principle, any solvent with large solubility to MAI and PbI$_2$ should also worked well for solvent annealing. DMSO was also tested, which verified this scenario. The PCE of a
630 nm thick devices was increased to 15.6% by using DMSO as the solvent for annealing. This result proved that solvent annealing approach is universal.

**Figure 6.6** Photocurrent characteristics (a-d) of the perovskite devices with film thickness of 250 nm, 300 nm, 630 nm, and 1,015 nm, respectively. (e-h) EQE of the perovskite devices with film thicknesses. Black circle line: thermal annealing; red circle line: solvent annealing; blue circle line: IQE; green line: transmittance of the glass/ITO substrate.

**Table 6.1** The performances of perovskite solar cell devices with different film thickness fabricated by thermal or solvent annealing processes. (Based on ten devices of each category)

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Treatment</th>
<th>$J_{SC}$</th>
<th>$V_{OC}$ (V)</th>
<th>$FF$ (%)</th>
<th>PCE (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>630 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,015 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(nm)</td>
<td>(mA/cm²)</td>
<td>average</td>
<td>best</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>----------</td>
<td>---------</td>
<td>------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>TA</td>
<td>16.2±0.5</td>
<td>73.7±1.5</td>
<td>10.9±0.4</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SA</td>
<td>16.9±0.4</td>
<td>76.4±1.2</td>
<td>11.7±0.5</td>
<td>12.2</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>TA</td>
<td>18.7±0.6</td>
<td>77.0±1.2</td>
<td>13.3±0.6</td>
<td>13.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SA</td>
<td>29.7±0.5</td>
<td>79.4±1.0</td>
<td>14.2±0.7</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>TA</td>
<td>18.2±0.5</td>
<td>71.4±1.0</td>
<td>11.9±1.0</td>
<td>12.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SA</td>
<td>20.3±0.4</td>
<td>78.4±1.2</td>
<td>14.1±1.0</td>
<td>15.1</td>
<td></td>
</tr>
<tr>
<td>430</td>
<td>TA</td>
<td>16.4±0.6</td>
<td>61.0±1.0</td>
<td>10.0±1.0</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SA</td>
<td>20.3±0.4</td>
<td>76.1±1.0</td>
<td>14.1±0.8</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td>630</td>
<td>TA</td>
<td>16.8±0.8</td>
<td>69.5±0.8</td>
<td>10.5±1.0</td>
<td>11.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SA</td>
<td>21.0±0.5</td>
<td>76.0±1.5</td>
<td>15.1±0.5</td>
<td>15.6</td>
<td></td>
</tr>
<tr>
<td>1,015</td>
<td>TA</td>
<td>13.6±0.6</td>
<td>53.4±1.0</td>
<td>7.0±1.2</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SA</td>
<td>20.5±0.4</td>
<td>74.3±1.0</td>
<td>14.0±0.8</td>
<td>14.8</td>
<td></td>
</tr>
</tbody>
</table>

It is noted that all of the solvent-annealed devices had large FF of around 75-80\%.

This can be understood by the fact that the average grain size of the solvent-annealed film was always larger than the thickness of the film, so that the charges could transport and be collected through a single grain without encountering grain boundaries. The device efficiency of the solvent-annealed perovskite solar cells with different thicknesses stayed above 14.5\% with the thickness varied from 250 nm to 1,015 nm.

There is an obvious trend in that the EQE spectra near the absorption edge increases and the whole spectra becomes more flat as the thickness of the film increases. This is due to the increased single path absorption of the thicker perovskite films. As
shown in Figure 6.4c, the single path absorption reached above 90% across the whole absorption spectrum when the perovskite film was thicker than 630 nm. The average EQE reached 83% for the 630 nm thick devices. The trough of EQE at around 520 nm was caused by the reflection of the glass/ITO substrate, as shown in Figure 6.6g. Assuming all of the light transmitted through ITO/glass was absorbed by the perovskite films, the IQE, calculated by dividing the EQE with the transmittance, of the 630 nm thick device reached 95% on average, with the peak IQE reaching 100% at around 600 nm (Figure 6.6g). This indicates that the limitation on further photocurrent enhancement is the reflection of incident sunlight by the glass/ITO or other interfaces of the perovskite devices. It is thus expected that $J_{SC}$ can be further increased to 25.0 mA/cm$^2$ by applying an antireflective coating.

Since the photocurrent hysteresis was shown to be a major issue in accurate characterization of device efficiency, we measured a solvent-annealed high efficiency device by changing the scanning directions and different scanning rates. No photocurrent hysteresis was observed with different scanning rates or scanning directions. In order to verify the measured efficiency is right, we measured steady-state photocurrent output at the maximum power point (0.82 V). The steady state photocurrent represents the actual power output and should be used to accurately characterize the device efficiency. As shown in Figure 6.7c, the photocurrent rose quickly to maximum, and the steady state current is the same with what measured from the photocurrent scanning. The photocurrent was stable.
Figure 6.7 Photocurrent curves of a best performing device with (a) different scanning directions, and (b) different scanning rates measured from negative to positive bias. (c) Steady-state photocurrent output at the maximum power point (0.82 V).

6.5. Origin of the efficiency enhancement

In order to determine the origin of the efficiency enhancement of the solvent-annealed devices, we used thermal admittance spectroscopy (TAS) to measure trap density of states (tDOS) reduction induced by increased crystallinity and grain size. The 1,015 nm thick perovskite devices were used for this study. TAS is an established and effective technique to measure the trap density in thin film solar cells.\textsuperscript{168,169} The experiment details and calculations of the tDOS can be found in the Method section. As shown in Figure 6.8a, the tDOS of the solvent-annealed device was 2~7 times smaller than the thermal-annealed device. The measured surface trap density is in the same order magnitude with that derived by photoluminescence lifetime study.\textsuperscript{170} It has been established in another of our studies that the charge traps in this energy band originate from the grain boundary by the fact that the diffusion of fullerene into the grain boundaries effectively reduce the trap density in this band.\textsuperscript{166} The total trap density,
calculated by integrating the $t\text{DOS}$ in this band, of the solvent-annealed device is $1.8 \times 10^{16}$ m$^{-3}$ which is more than three-time smaller than that of the thermal-annealed device of $5.3 \times 10^{16}$ m$^{-3}$. If grain boundary has same density of traps in both films, the total trap density of the solvent-annealed film should be 16 times smaller than in the thermal-annealed film because the grain size is 4 times larger. This indicates the nature of the grain boundaries in both types of films is different, and it is possible that fullerene can diffuse longer in the thermal-annealed films along the grain boundaries to passivate the traps. As shown in Figure 6.5, the grains of the solvent-annealed film are more compact so that it is harder for the fullerene to diffuse. This result clearly verifies that the charge trap density is dramatically reduced by the much smaller total grain boundary areas in the solvent-annealed films which have much larger grain size.

Figure 6.8 Trap density of states calculated from the thermal admittance spectroscopy measurement; (b) Photovoltage decay under 0.3 Sun illumination measured by TPV; (c) Photocurrent decay measured by TPC.

In order to examine the effect of the reduced $t\text{DOS}$ on the performance of the device, both charge recombination lifetime and charge extraction time were measured by TPV and TPC techniques, respectively. As shown in Figure 6.8b, the charge
recombination lifetime of the solvent-annealed device was increased to 7.2 µs, compared to 1.7 µs in the thermal-annealed device, under 0.3 sun illumination at open circuit voltage condition. We also measured the device under illumination using impedance spectroscopy and derive the charge recombination lifetime, which yielded consistent results with TPV measurement. The reduced trap density also resulted in larger carrier mobility, which further resulted in quicker charge extraction. As shown in Figure 6.8c, the charge extraction time measured at zero bias decreased to 0.25 µs for the solvent-annealed device, compared with 0.57 µs for the thermal-annealed device, which corresponds to an increase of transit mobility by 2.3 times. The rising time of the photocurrent of the thermal-annealed device is longer than that of the solvent-annealed device, which also demonstrates the higher trap density in the thermal-annealed device. It is noted that the ratio of Hall mobility increase (1.5 times) is smaller than the transit mobility increase. This might be due to that the Hall mobility measures the in-plane conduction of the carriers, and the TPC measures carrier transportation along the out-of-plane direction, while the grain structures in these two directions are different. Nevertheless, there is a disparity of carrier mobilities measured by these two methods, which is not understood yet. The charge carrier diffusion length was estimated by the diffusivity (D) and carrier lifetime. The diffusivity was calculated from the drift mobility measured by TPC using the Einstein relationship: $D = \mu k_B T / e$, where $\mu$ is the drift mobility, $k_B$ is Boltzmann constant and $T$ is the absolute temperature. The carrier lifetime was estimated from the TPV measurement, which gives the low limit of the charge recombination lifetime because the carrier concentration at $V_{OC}$ is larger than time-resolved photoluminescence measurement due to the charge injection. The calculated
carrier diffusion length of the solvent-annealed device is 886 nm which is close to the maximum film thickness, and around four times longer than that in the thermal annealed devices of 282 nm. All these facts including increased charge recombination lifetime, decreased charge extraction time and increased carrier diffusion length can be ascribed to the increased grain size and crystallinity of the perovskite films by solvent annealing.

In summary, solvent annealing was first reported to be an effective method to increase the organolead triiodine perovskite grain size and crystallinity, which resulted in significant material electronic property improvement and performance enhancement of the photovoltaic devices. The effective charge diffusion length of the solvent-annealed MAPbI₃ films was increased to longer than 1 µm, much longer than the previously reported 300 nm. The highest device efficiency reached 15.6%, and device efficiency stayed above 14.5% as the perovskite thickness increased to 1,015 nm.
Chapter 7 Switchable perovskite solar cells

In this chapter, we will show that diode and photocurrent direction of OTP devices can be switched repeatedly by a small field of <1 V/µm for both vertical and lateral structure photovoltaic devices. The switchable photocurrent, generally observed in ferroelectric material based devices, reached 20.1 mA/cm² under one sun illumination in the vertical structure OTP devices, which is four orders of magnitude larger than that in ferroelectric photovoltaic devices. The lateral photovoltaic devices with 125 devices connected in series have an open circuit voltage of 47 V under a quarter sun illumination. The field switchable photovoltaic effect can be explained by the reversible ion-drift induced switchable p-i-n structures. The demonstration of switchable OTP photovoltaics and electric-field manipulated doping paves the way for new perovskite photovoltaic device designs such as homojunction solar cells, and opens up new applications for perovskite devices, such as both electrically- and optically-readable memristors and circuits.

7.1. Switchable perovskite photovoltaics with vertical structure

The vertical structure device has a layered structure of ITO/PEDOT:PSS/Perovskite/Au as shown in Figure 7.1a, where the MAPbI₃ perovskite layer was formed by the interdiffusion of PbI₂ and MAI stacking layers. The as-prepared devices with 300 nm thick perovskite films have a $J_{SC}$ of 8.5 mA/cm² and $V_{OC}$ of 0.18 V (Figure 7.1b), despite that the work function of PEDOT:PSS and Au electrodes are almost the same. This might be due to the different interfacial electronic structures at the perovskite/PEDOT:PSS and perovskite/Au contacts.
Figure 7.1 J-V characteristics of the as-prepared vertical structure devices with the structure of ITO/PEDOT:PSS)/Perovskite (300 nm)/Au. Scanning rate was 0.14 V/s and the scanning direction was labeled in the figure.

A large memristive effect from these devices was identified both in the dark and under illumination, which showed a scanning history dependent current output. The diode direction can be switched during the scanning process in the dark as shown in Figure 7.2b. The on/off ratio of the dark current is \(>10^3\) and \(>10^2\) at a bias of -1.0 V and 0.7 V, respectively. The devices can also be poled by a constant bias pulse with a duration of 5~30 s. The device with a perovskite layer thickness of 1,015 nm was switched by a small bias of 1.0 V, which corresponds to a minimal poling electric field of < 1 V/µm.\(^{174} \)
Figure 7.2 Vertical structure photovoltaic devices and their switching behavior. a, Schematics of the vertical structure device. Dark current (b) and photocurrent hysteresics (c) of the devices under continuous current sweeping at a rate of 0.14 V/s between -2.5 V and 2.5 V. The arrows in the figure show the scanning direction. d, Open circuit voltage of the device recorded after repeated poling by ±2.5 V bias for more than 750 circles. Only the first ten and last ten circles were shown.

The switchable diode in the dark resulted in a giant switchable photovoltaic effect under illumination. In contrast to the switchable photovoltaics using bismuth ferrite materials with $J_{SC}$ typically on the order of $\mu$A/cm$^2$, the $J_{SC}$ of the OTP devices was switched between 18.6 and -20.1 mA/cm$^2$ (Figure 7.2b) under one sun illumination,
which is comparable to that of the optimized perovskite solar cells$^{130,131,133,175-177}$. This indicates that most of the photogenerated excitons dissociated to free charges in the perovskite layer even without an electron or hole accepting layer, and the free charges were efficiently collected by the electrodes regardless of the diode directions. The photocurrents showed varied hysteresis loops with changed scanning rates, while the $J_{SC}$ remained almost unchanged and the $V_{OC}$ was around 0.15 V lower at a lower scanning rate of 0.25 V/s. The photocurrent direction after poling remained unchanged after storing the device for two months under ambient illumination in the glove box (Figure 7.3). Two devices were negatively and positively poled, respectively, under a steady bias of 2.5 V for about ten seconds. After that, the devices were kept under ambient illumination in a glove box and no further poling was applied during the test. In order to eliminate the influence of scanning voltage, we only test the $J_{SC}$ to identify the stability of current direction.

![Figure 7.3](image)

Figure 7.3 The stability test of short circuit current for the ITO/PEDOT:PSS/Perovskite/Au vertical structure device after positive and negative
poling. (The $J_{SC}$ were normalized by the value measured 24 h after the fabrication of the device (18.2 mA/cm$^2$ and -19.0 mA/cm$^2$).

The $V_{OC}$ was switched between 0.42 V and -0.73 V. There is a variation in $J_{SC}$ and $V_{OC}$ from different devices; and some of them showed a larger $V_{OC}$ close to 0.9 V but a relatively smaller $J_{SC}$ of 8 mA/cm$^2$. The average $V_{OC}$ and $J_{SC}$ of the vertical structure devices were ±0.65 V and ±18.5 mA/cm$^2$, respectively.$^{174}$ A positive poling (electric field pointing from PEDOT:PSS to Au) resulted in a positive $V_{OC}$. A typical device was switched more than 750 times with the $V_{OC}$ in the first 10 and last 10 poling circles shown in Figure 7.2c. The photocurrent direction of the device can survive after 750 poling circles. After positive poling, the $V_{OC}$ remained almost constant at 0.42 V, while the $V_{OC}$ after negative poling showed switching fatigue from 0.73 V to 0.21 V. The switchable photovoltaic phenomenon was universally demonstrated using other organolead trihalide perovskite materials, such as CH$_3$NH$_3$PbI$_3$-$x$Cl$_x$, HC(NH$_2$)$_2$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$, and with many other top electrodes including nickel, gallium and platinum, but not Al or Ag, due to the severe chemical reaction of perovskite with Al and Ag.$^{174}$

### 7.2. Switchable perovskite photovoltaics with Lateral structure

We continued to demonstrate the switchable photovoltaic effect in lateral structure devices because of the very low electric field of 1 V/µm needed for poling and the absence of electrode selectivity shown in the vertical structure devices. For lateral photovoltaic devices, the Au stripe arrays were first fabricated on glass substrates by photolithography, i.e. the 50 nm thick Au layer was thermally deposited on a pre-
patterned photoresist layer, and then the photoresist was removed by acetone. The positive photoresistor, Shipley S-1813, was used. **Figure 7.3a** schematically shows that the photovoltaic device has a lateral symmetric structure of Au/OTP/Au/OTP/…, where tens to hundreds of cells are connected in series. The resulted Au stripe patterns have a length of 3 mm, and spacing of 8 µm (**Figure 7.3b**). The total width of the lateral photovoltaic devices connected in series composing of 125 cells is ~1.4 mm. Perovskite films were then fabricated on these substrates with the same method as in vertical device fabrication. The thickness of the perovskite films for both vertical and lateral structure device is 300 nm, excepting those specially labeled.

**Figure 7.4** Lateral structure photovoltaic devices and their switching behavior. a, Schematics of the lateral structure devices. b, A Au stripe array under microscope (reflective mode), where the electrode spacing ($d$) shown in the enlarged image (bottom) is 8 µm. The lateral photovoltaic devices connected in series were fabricated by depositing uniform perovskite films (300 nm) on preformed Au stripe electrodes with spacing between 8 and 100 µm.
As shown in Figure 7.5a, the non-poled device had no photovoltaic effect with zero $V_{OC}$ because of the symmetrical electrodes, while the poled single cell showed a $V_{OC}$ of 0.48 V under 0.25 sun illumination after poling at 10 V for ~100 s. The photovoltaic direction after poling was consistent with that of vertical structure devices. The photovoltaic direction was flipped by a reversed poling bias. The $J_{SC}$ of the device with 8 µm electrode spacing is 0.1 mA/cm$^2$. The smaller $J_{SC}$ in the lateral structure devices is due to the much larger electrode spacing than the charge diffusion length in perovskite materials$^{141,143}$. The largest absolute $V_{OC}$ and $J_{SC}$ value reached 0.88 V and 0.11 mA/cm$^2$, and the average $V_{OC}$ and $J_{SC}$ of the lateral structure devices were ±0.50 V and ±0.075 mA/cm$^2$ respectively. As shown in Figure 7.5b, the $V_{OC}$ of lateral photovoltaic devices connected in series is the sum of each unit cell, while the $J_{SC}$ remains almost constant, indicating a uniform performance of each unit cell. A large $V_{OC}$ of 47 V was observed for the devices with 125 unit cells connected in series under illumination of 25 mW/cm$^2$.

**Figure 7.5** a, Photocurrents of the device before and after negative and positive poling for a single cell measured at a sweeping rate of 0.05 V/s under 0.25 sun illumination; The arrows in the figure show the scanning direction. b, Photocurrents of the lateral
photovoltaic devices connected in series measured at a sweeping rate of ~0.05 V/s for each cell. The poling of the lateral photovoltaic devices were conducted by either poling each cell individually or simply poling the whole area between the first and last electrodes.

### 7.3. Origin of the switchable perovskite photovoltaic effect

In order to find out the origin of the switchable photovoltaic effect in OTP devices, we examined three possible mechanisms which have been reported for switchable photovoltaic or memristor behavior, which was also speculated to result in photocurrent hysteresis with a changed photocurrent scanning direction and scanning rate in some perovskite photovoltaic devices:\[178: 1) ferroelectricity of the photoactive layer\[179; 2) charge traps in the active layer’s surface\[178,180; and 3) motion and accumulation of ions induced doping effect\[171,181. Some theoretical calculation predicted strong ferroelectricity of MAPbI\(_3\) with a polarization charge density on the order of 38 C/m\(^2\)\[182,183. However, no ferroelectric polarization was detected from these devices with comparable voltage scanning rates as in photovoltaic study when they were measured at both room temperature and 77 K (Figure 7.6).\[174 PFM imaging and hysteresis loop measurements did not show anything resembling ferroelectric activity in the MAPbI\(_3\) perovskite films as shown in Figure 7.6, i.e. there were weak PFM amplitude and phase signals and no hysteresis switching activity, despite the application of a much higher bias than in the switchable photovoltaic studies. In addition, the ferroelectric photovoltaic effect can be excluded by the non-changed photovoltage with respect to the electrode spacing in the lateral structure devices, (Figure 7.7) and diminished switching behavior at reduced temperature. Our finding does not rule out ferroelectricity in MAPbI\(_3\) in principle as more
measurements (such as temperature-dependent dielectric and structural testing) are required to clarify this issue. The charge-trapping mechanism can also be excluded because it cannot explain the flipped photovoltage and photocurrent direction, and the persistent photocurrent output long after poling shown in Figure 7.3.
**Figure 7.6** Ferroelectric polarization loops measured at room temperature (a) and at 77 K (b) scanned at the same frequency of photovoltaic switch process. c, PFM topology (c), amplitude (e) and phase (f) images of the perovskite (300 nm). d, Representative PFM hysteresis loops (phase and amplitude) signal for any location on the film surface.

**Figure 7.7** Normalized I-V curves of lateral Au/OTP/Au solar cells with different electrode-separating distances (d) at a illumination of 0.25 sun.

It was previously reported that similar halide containing perovskites, such as CsPbCl$_3$ and CsPbBr$_3$, are good halide ion vacancy conductors at elevated temperatures$^{184}$. We ascribe switchable photovoltaic to the ion drift under the electric field in the perovskite layer. Theoretical calculation predicted the V$_{Pb}^+$ and V$_{MA}^+$ could result in $p$-type doping, while the V$_{I'}$ result in $n$-type doping in MAPbI$_3^{185,186}$, which was verified experimentally by us in the study of composition dependent self-doping behavior in MAPbI$_3^{187}$. In this scenario, the electric field drives the drift of charged V$_{I'}$, V$_{Pb}^+$ and/or
$V_{MA}^*$, which have low formation energy in MAPbI$_3^{185,186}$, to the area near electrode and forms the $p$-$i$-$n$ structure.

**Figure 7.8** Switchable photovoltaic model and mechanism study. a-b, Schematics of ion drift in perovskite during poling, and the accumulated ions in the perovskite near the electrodes induced $p$- and $n$-doping; c, Energy diagram of the $p$-$i$-$n$ structure after poling.

Our scenario for the switchable photovoltaic is illustrated in **Figure 7.8a-b** using vertical structure devices as an example. The positively charged ions or vacancies moved to the Au side during positive poling and accumulated there, which caused $n$-doping in perovskite at the Au side. Similarly, the left negative space charge layer can $p$-dope the perovskite layer close to PEDOT:PSS, which forms a $p$-$i$-$n$ homojunction structure. A reversed bias can flip the $p$-$i$-$n$ structure to $n$-$i$-$p$ by driving the ions or ion vacancies to drift in the opposite direction. The memristive dark- and photo-current hysteresis can also be well explained by the time-dependent drift of ions under the field$^{188}$. 

Figure 7.9 a, Schematic image of the devices with some part of the Au electrodes peeled off. The scanning area is also marked as a dashed rectangle in the image; b-c, KPFM potential image of the perovskite/Au areas after positive and negative poling of the perovskite layers (300 nm).

To test this scenario, we first measured the doping caused band-bending in perovskite close to the top Au electrode after poling in the vertical structure devices by Kelvin probe force microscopy (KPFM). The $p$- or $n$-doping should induce an increase or reduction of the work function for the perovskite top surface, respectively, as illustrated by the energy diagram in Figure 7.9a. The long retention of the diode direction indicates that the poling induced composition change or work function change is stable after poling. Au electrodes could be easily peeled off by a scotch tape, which exposed the poled perovskite films. Figure 7.9a illustrated the films used for the KPFM study, where some unp Peeled Au areas were intentionally left as work function reference. As shown in Figure
The work function of the perovskite films was ~0.22 V lower than that of Au after positive poling, and comparable to that of Au after negative poling, which agreed well with the energy diagram in Figure 7.8c and thus supports the proposed doping mechanism. The surface topography showed no obvious change in the poling areas which excluded the effect of topography to the surface potential measurement. The discrepancy of the perovskite work function change with $V_{OC}$ can be explained by the possible surface contamination by the residues of Au after peeling and/or by moisture/oxygen because the KPFM measurement was conducted in air. Finally, semiconductor doping generally causes photoluminescence (PL) quench, which was also observed for the $p$- and $n$-doped perovskite region close to both Au and PEDOT:PSS sides, as shown in Figure 7.10a-b.

**Figure 7.10** a-b, Photoluminescence from the thin perovskite layers close to either a PEDOT:PSS electrode or Au electrode. A thin gold electrode (25 nm) was used as the top electrode so the PL emission from the perovskites close to both electrodes can be measured, and a blue light (405 nm) was used to excite only the 25 nm thick perovskite layer close to the electrodes (estimated by the extinction coefficient) of the 1,015 nm
thick device. The PL measurement was conducted in-situ during the poling process to exclude other PL changing factors. The peak at 710 nm in Figure 7.10a is from ITO.

Another conclusive evidence for the drift of ions during the poling process comes from the observation of composition and morphology changes during the poling of a lateral structure device. In this study, the device was intentionally poled for a much longer time (2 hours) than was needed for the doping effect so that the change in perovskite composition/morphology was discernable. The transparency of the perovskite film was monitored in-situ under an optical microscopy, as illustrated by the measurement setup in Figure 7.11a. The dynamic process was recorded on video using a time-accelerated mode, and several snapshots were shown in Figure 7.11b. The perovskite stripe area close to the anode side became more and more transparent, and the morphology in this area was completely different from other areas with many pin-holes appearing,\textsuperscript{174} which indicates the drift of ions from the anode side. The loss of perovskite material on the anode side indicated that the drifting ions were $V_{\text{Pb}}^+$ and/or $V_{\text{MA}}^\ast$.

Figure 7.11 In-situ monitoring of the material change in a poling process. a, Illustration of the setup used for the in-situ monitoring of the poling process using a lateral structure
device. b, Snapshots of the in-situ recorded video which shows changed perovskite material close to the anode side during the poling process. The electrical field applied on the perovskite film was \( \sim 1.2 \, \text{V/\mu m} \).

The extensive dynamic poling process study of the device under varied electric field, temperature, and perovskite film morphology supported the mechanism of field driven ion drift for the photovoltaic switching, as shown in Figure 7.12. Here, a train of voltage pulses with duration of 0.95 s were applied on the devices and the \( J_{SC} \) was recorded after each pulse. An elevated temperature and/or applied electric field (by changing either the applied bias or perovskite film thickness) accelerated the poling process (Figure 7.12a-b), while the poling was almost frozen at temperature below 0 °C (Figure 7.12c). The poling became more difficult (Figure 7.12d-f) in the device with much larger perovskite grain size which was formed by a solvent-annealing process. This can be explained by the reduced vacancy concentration in the solvent-annealed perovskite films due to less grain boundaries because the solvent-annealing increased the grain size from 300 nm to 600–1000 nm\textsuperscript{167}. The device performance statistics during the dynamic poling process with different measurement condition and film morphology is shown in Figure 7.12g. These results confirmed that the switchable photovoltaic behavior of the devices is due to the ion drift.
**Figure 7.12** Dynamic poling process of the ITO/PEDOT:PSS/Perovskite (300 nm)/Au vertical structure devices at (a) varied electrical field, (b-c) temperature and (d-f) with different film morphology. The thickness of the films in d-f is 1,015 nm. (g) $J_{SC}$ versus poling time of the devices with different film annealing processes and measurement temperatures. The devices were measured under 0.1 sun when measured at 60 °C. The error bar showed the device performance variation based on the statistics of five devices of each category. And the scanning rate in Figure 7.12 was 0.14 V/s.

### 7.4. Conclusion
In summary, the best device parameters in the single layer vertical structure devices after poling approached that of optimized multiple-layer devices with both electron and hole transporting layers. This work points to a new direction of perovskite solar cell design using controlled doping of perovskite for homojunction solar cells, reducing device fabrication complexity. The lateral structure device is particularly interesting because it eliminates the need for transparent electrodes, but its efficiency is still limited by the charge carrier diffusion length in present perovskite materials. Further improvement in crystal quality and surface passivation techniques will help to resolve this issue. The perovskite memristors reported here can be read-out by not only electrical pulse but also optical pulses\(^{179}\). This work paved the way for a new approach to doping perovskite using electric pulse so that a doping pattern can be programmed and directly written using scanning probe microscopy for memristor array fabrication, which might open up a new application for perovskite materials for optoelectronic computational devices, as viewing the memristors is increasingly being pursued for computing\(^{189,190}\).
Chapter 8 Summary

To conclude, the research work in this thesis is an effort to enhance the efficiency of both organic solar cells and organic-inorganic perovskite solar cells. Various techniques have been developed for both organic and organic-inorganic hybrid perovskite solar cells to improve their efficiency.

For the organic solar cell, we first studied the crystallinity of the P(VDF-TrFE) layer on the performance of organic solar cells. Our results showed that the ferroelectric phase (beta-phase) is critical to enhance the device efficiency. Amorphous P(VDF-TrFE) films show almost no ferroelectricity and act as regular dielectric layers in the OPV devices. Usually the P(VDF-TrFE) film need to be thermal annealed above its curie temperature to get ferroelectric phase, which is not compatible to many low band gap polymer systems. Then we synthesized the crystalline P(VDF-TrFE) nanocrystals, which can be spin coated on top of any polymer:fullerene films without thermal annealing. The efficiency of the PCDTBT:PCBM based solar cells was increased from 5.3% to 6.7%. We went further to use a small polar molecule, TPACA, to increase the efficiency of organic solar cells. One unique property of TPACA molecule is that it can be simply blended in the processing solvent DCB, and do the spin coating together with polymer and PCBM in one step. After poling, the dipoles of TPACA molecules can be aligned, and the built-in potential of the device was increased by about 0.2 V.

To address the issue of the random morphology of polymer:fullerene films fabricated by spin coating process, we developed a solvent fluxing technique to form the graded BHJ with fullerene rich at the top surface. It is a universal technique that was
applicable to all the polymer:fullerene systems we tested. The PCE of the organic solar cells we tested were increased by 15%-50%, with the highest efficiency reached 8.6% for PBDTTT-CT:[70]PCBM system. We did through characterizations on the origin of the efficiency enhancement by the graded BHJ. It is confirmed that the bimolecular recombination was greatly reduced.

For the organic-inorganic hybrid perovskite solar cells, we developed a novel two-step inter-diffusion method to fabricate the continuous and compact perovskite film. The average PCE is 14.5% and 85% of the devices have efficiency above 14%. We also developed a solvent annealing approach to increase the grain size and crystallinity of the perovskite films. After solvent annealing of the perovskite film, the average grain sizes were increased to be comparable to film thickness so that most photo-generated charges can be extracted within single grain without crossing grain boundaries. The long charge diffusion length, over 1 μm, enables high efficiency devices based on thick perovskite films. A high PCE of 15.6% was achieved using the 630 nm thick MAPbI₃ perovskite film under one sun illumination, and the efficiency kept above 14.5% when the thickness changes from 250 nm to over 1 μm. The high tolerance of the efficiency on the film thickness after solvent annealing would enable it one of the most promising treatments for perovskite toward its commercialization.

We found a novel phenomenon that, in OTP-based photovoltaic devices with vertical and lateral cell configuration, the photocurrent direction can be switched repeatedly by applying a small electric field of <1 V/μm. The switchable photocurrent reached 20.1 mA/cm² under one sun illumination in OTP devices with vertical architecture. The lateral photovoltaic devices with 125 devices connected in series have
an open circuit voltage of 47 V under a quarter sun illumination. The origin of the efficiency enhancement was found to be due to the ion electro-migration. This finding opened up a new application of OTP materials: memristors. And the perovskite memristors can be read-out not only electrically but also optically, which might open a new application of perovskite materials for optoelectronic computation devices, since the memristors are increasingly pursued for computing.
References:


17 Guo, J. M., Ohkita, H., Benten, H. & Ito, S. Charge Generation and Recombination Dynamics in Poly(3-hexylthiophene)/Fullerene Blend Films with


