

# ***Improvement of Photovoltaic Properties of Solar Cells with Organic and Inorganic Films Prepared by Meniscus Coating Technique***

Anusit Kaewprajak

Graduate School of Energy Science

2019

The development of renewable energy technologies has been extensively studied to utilize alternative energy sources cleaner and cheaper than traditional fossil fuels.<sup>1</sup> Moreover, using fossil fuels include oil, coal, and natural gas are causing an environmental problem, such as air pollution, global warming, and climate change.<sup>2</sup> Therefore, the renewable energy technologies have become an urgent need to affordable, reliable, sustainable and modern energy from clean sources. Among renewable energy, solar energy is the most abundantly available natural resource on the earth. The irradiation of solar energy on the earth is approximately 175,000 TWh, this is more than 10,000 times of the total energy consumption of human.<sup>3</sup> There have been several ways to convert solar energy to electrical energy. However, direct conversion of the solar energy to electrical energy in a one-step process can be achieved by using the photovoltaic device. The first time of conversion of solar energy into electricity by photovoltaic effect was observed by Edmond Becquerel in 1839.<sup>4-5</sup> The first success of a silicon *p-n* junction solar cell with a power conversion efficiency (*PCE*) approximately 6% was reported by Chapin *et al.* in 1954.<sup>6</sup> The development of solar cell technologies has been increased to reduce fabrication cost and improve the efficiency of solar cells.

Currently, research of new photovoltaic technologies such as dye-sensitized, organic, quantum dots and perovskite solar cells (PSCs) have been extensively studied. Those solar cells can be fabricated by using only simple printing technique based on solution process. The solution-based coating techniques for solution-processed thin-film solar cells have been

attracted to improve their crystallinity, morphology, and performance of the photovoltaic devices for the sake of reduction of the cost and the time for preparations in large area.<sup>7-11</sup> Many solutions of coating techniques have been proposed and applied for linear motion of the substrate against the meniscus of the solution with constant velocity such as dip coating,<sup>12-13</sup> doctor blading,<sup>14-15</sup> and slot-die coating.<sup>16-17</sup> Among various solution-based coating techniques to prepare the thin-films, the convective deposition method is one of the promising strategies because of its well-ordered, rapid, low material consumption, easy setup, and scalable fabrication of thin-films for large area.<sup>18-20</sup>

When considering about coating process of organic bulk heterojunction (BHJ) solar cells, the microphase-separated structure and the molecular orientation of organic semiconductors is very important for the photovoltaic performance. The addition of additives in polymers and fullerenes have been used for optimizing the morphology of BHJ.<sup>21</sup> The high boiling point solvents are the most generally applied in polymer blends such as 1,8-diiiodooctane (DIO)<sup>22-24</sup>, 1,8-dibromooctane<sup>25</sup> and 1,2,4-trichlorobenzene (124-TCB).<sup>26-27</sup> It is well known that the additive of DIO 3 v% is the most efficient ratio for optimization the nanoscale morphology of the BHJ based solar cells.<sup>28-32</sup> The DIO additive can selectively dissolve fullerenes, which aggregates to smaller domains and promote a better donor-acceptor network into smaller domains.<sup>33-34</sup> However, the addition of DIO into BHJ cannot improve molecular packing and orientation of polymer.<sup>33</sup> Among the various strategies, one of the best effective techniques to improve the molecular orientation of semiconducting polymer is directional solidification by using a solidifying solvent such as 1,3,5-trichlorobenzene (135-TCB).<sup>35-38</sup> This technique requires solidifying solvent as supporting reagent for nucleation and orientation of the polymer. The improvement of the molecular orientation of organic semiconductors is very important for the enhancement of optical and electrical properties of organic active layer in organic solar cells. As expected, taking account for the advantageous points of directional solidification and convective deposition; a combination of two coating techniques will create more controllable in terms of nucleation density, directions of solidification, microphase-separated structure, and morphology of the polymer blend films.

For planar PSCs, the development of the electron transport layer is one of the most important keys to improving photovoltaic performance and stability. In conventional planar PSCs, titanium dioxide ( $\text{TiO}_2$ ) has been widely used as an effective electron transport layer.<sup>39-40</sup> However,  $\text{TiO}_2$  has some drawbacks such as poor conductivity<sup>41</sup> and low electron mobility.<sup>42</sup> Those disadvantages resulted in the limitation of the electron extraction from perovskite to  $\text{TiO}_2$  layer and the limited photovoltaic performance of the devices. Many researchers introduced the methods to improve the electron extraction from perovskite to  $\text{TiO}_2$  such as doping of  $\text{TiO}_2$  with  $\text{Zn}^{2+}$ ,  $\text{Y}^{3+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Mo}^{6+}$ , and  $\text{NH}_4^+$ ,<sup>43-45</sup> insertion of interlayer with  $\text{ZnS}$ ,  $\text{C}_{70}$ ,  $\text{In}_2\text{S}_3$ , and  $\text{SnO}_2$  as bilayer systems,<sup>39, 42, 46-47</sup> and loading of nanomaterials onto  $\text{TiO}_2$  with carbon quantum dots and carbon nanotubes as the composites.<sup>41, 48</sup> Wang *et al.*<sup>49</sup> applied  $\text{CsPbCl}_3:\text{Mn}$  quantum dots as the down conversion layer onto the front side of the PSCs to improve the performance and the stability of planar PSCs. This method showed significant enhancement of the *EQE* response in the UV region and improvement of the stability under the UV irradiation of the planar PSCs. While  $\text{AgInS}_2$  is a I-III-VI<sub>2</sub> semiconductor with its band gap in the range from 1.8 eV to 2.2 eV.<sup>50-51</sup> This material has alternative potentials as the light absorber and the fluorescent materials.<sup>52-54</sup> It was also found that the annealing of the  $\text{AgInS}_2$  film at 500 °C in air brought the improvement of charge mobilities up to around  $6.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .<sup>55-56</sup> Therefore,  $\text{AgInS}_2$  is one of the expecting materials for the improvement of solar cells through mixing with  $\text{TiO}_2$  as the electron transport layer followed by the annealing at 500 °C in air. As expected, taking account for the advantageous points of  $\text{AgInS}_2$  quantum dots in  $\text{TiO}_2$  as electron transport layer will create more effects on the performance and the stability of the planar PSCs in terms of promoting the electron extraction, enhancing the light harvesting and down conversion.

As has been indicated, all the methods presented above as the effective ways to improve optical and electrical properties, both of organic and inorganic materials to enhance the performance of the organic solar cells and planar PSCs.

In this work, convective deposition technique was applied for preparation of organic and inorganic thin films for two kinds of solar cell, one was organic thin-film solar cell, and another was perovskite type solar cell. For preparation of the active layer of the organic thin-

film solar cells, solidifying reagent was added to the mixture of conducting polymer and fullerene to regulate the nucleation density, directions of solidification, microphase-separated structure, homogeneous distribution, and surface morphology of the bulk heterojunction during the thin-film making process. By taking the convective deposition method, improvement of the photovoltaic parameters ( $J_{sc}$ ,  $V_{oc}$ ,  $FF$ , and  $PCE$ ) of the organic thin-film solar cells were attained. On the other hand, in order to prepare the electron transporting layer of the perovskite type solar cells by the convective deposition technique, quantum dots (QDs) were added to the solution of titanium tetra(isopropoxide)s as the precursor solution of  $TiO_2$  and enhancement of the photocurrent generation both in the uv and the visible regions were observed after the addition of QDs. In other words, the combination of convective deposition technique and solidifying reagents or quantum dots led to the improvement of crystallinity, morphology, extent of contacts between the polymer and fullerene, or between the perovskite and  $TiO_2$ , and resulted in the enhancement of the photovoltaic performance of the devices.

For organic solar cells, the combination of directional solidification and convective deposition techniques were applied for preparation of polymer:fullerene as active layer for organic photovoltaic (OPV) cells. The polymers and fullerenes in this study composed of poly[*N*-9'-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT), Poly[4,8-bis(5-(2-ethylhexyl) thiophen-2-yl)benzo [1,2-b;4,5-b']dithiophene-2,6-diyl-*alt*-(4-(2-ethylhexyl)-3-fluorothieno [3,4-b]thiophene)-2-carboxylate-2-6-diyl)] (PTB7-Th), and [6,6]-phenyl  $C_{71}$  butyric acid methyl ester (PC<sub>71</sub>BM). The 1,3,5-trichlorobenzene (135-TCB) was used as solidifying solvent.

The combination of directional solidification and convective deposition techniques were demonstrated for preparation of organic thin-film solar cells with PCDTBT and PC<sub>71</sub>BM as the active layer. The coating conditions of the concentration of 135-TCB were ranged from 0 to 500 mg mL<sup>-1</sup> in dichlorobenzene (DCB) followed by the mixing with PCDTBT:PC<sub>71</sub>BM. The effects of 135-TCB as the solidifier in the polymer blend on the optical property, morphology, hole mobility of the polymer blended films and photovoltaic performance were investigated. The nucleation density and directional solidification of PCDTBT:PC<sub>71</sub>BM films were controlled by the amount of 135-TCB and the coating

direction of convective deposition. This fabrication technique can induce directional crystallization of 135-TCB along the coating direction. From the result of cross-polarized optical microscopic images of PCDTBT:PC<sub>71</sub>BM thin films prepared by convective deposition with different concentrations of 135-TCB when the concentration of 135-TCB was over 250 mg mL<sup>-1</sup>, anisotropic thin films with fibrous structures were observed. However, the concentration of 135-TCB more than 100 mg mL<sup>-1</sup> might be not appropriate for OPVs fabrication because of the large domain sizes of the fibrous structures and high roughness values of the PCDTBT:PC<sub>71</sub>BM films. Therefore, the optimum amount of 135-TCB in PCDTBT:PC<sub>71</sub>BM bulk heterojunction (BHJ) solar cells in this case is 20 mg mL<sup>-1</sup>. The improvement of the photovoltaic performance by using 135-TCB is presumably ascribed to following three reasons: Firstly, the improvement of the light absorption and the external quantum efficiency spectra, which shifted to a longer wavelength region. That enhanced the generation of photocurrent. Secondly, the improvement of morphology and phase separation of PCDTBT and PC<sub>71</sub>BM made a formation of good continuous pathway for carrier transportation. Thirdly, the improvement of orientation and mobility of the PCDTBT:PC<sub>71</sub>BM films, which enhanced the charge collection to the electrode. The highest hole mobility of  $1.48 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was obtained when 135-TCB was 20 mg mL<sup>-1</sup>. The photovoltaic cell with 135-TCB at 20 mg mL<sup>-1</sup> showed the highest *FF* and *J<sub>sc</sub>*, brought the highest *PCE* of 3.89 %. That is a 30% improvement of efficiency as compared to the device without 135-TCB (*PCE* of 2.99 %).

The effect of binary additives of DIO and 135-TCB on phase separation and molecular orientation of PTB7-Th:PC<sub>71</sub>BM films for the improvement of the photovoltaic performance were investigated. The solvent additive in this study compose of 135-TCB 30 mg mL<sup>-1</sup>, DIO 3 v%, and binary additives of DIO 3 v% + 135-TCB 30 mg mL<sup>-1</sup>. It was found that the addition of binary additives into PTB7-Th:PC<sub>71</sub>BM blend improved the phase separated state of PTB7-Th:PC<sub>71</sub>BM film into small domain sizes with a homogeneous distribution and a continuous interpenetrating network. The PTB7-Th:PC<sub>71</sub>BM films with 135-TCB 30 mg mL<sup>-1</sup> and binary additives indicated the improvement of the out-of-plane orientation. The improvement of the out-of-plane orientation in PTB7-Th:PC<sub>71</sub>BM film is

beneficial to the charge transport along the out-of-plane direction of the active layer in OPVs. As a result, the photovoltaic parameters were improved by using DIO 3 v% + 135-TCB 30 mg mL<sup>-1</sup> as binary additives. The OPVs with DIO 3 v% + 135-TCB 30 mg mL<sup>-1</sup> indicated better diode characteristics with the highest  $RR$  of  $51.7 \times 10^3$  and lower leakage current, which exhibited lowest  $R_s$  and highest  $R_p$ . The  $PCE$  of the device with binary additives was increased up to 7.4% as compared with that of without the additives ( $PCE$  of 3.0%) and with DIO 3 v% ( $PCE$  of 6.9%).

For perovskite solar cells, convective deposition techniques were applied for preparation of composite films of titanium dioxide (TiO<sub>2</sub>) and silver-indium-sulfide (AgInS<sub>2</sub>) quantum dots as single layer and dual electron transport layer for the planar perovskite solar cells (PSCs).

The effect of AgInS<sub>2</sub> quantum dots in TiO<sub>2</sub> as the electron transport layer of the planar PSCs for the improvement of the photovoltaic performance and the stability were investigated. It was observed that the average value of the root mean square of the surface roughness of the electron transport layer was slightly reduced by the addition of AgInS<sub>2</sub> into TiO<sub>2</sub>. The electron mobility of the electron transport layer was enhanced from  $1.34 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> to  $2.05 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> after the addition of AgInS<sub>2</sub>. The external quantum efficiency ( $EQE$ ) of the device with TiO<sub>2</sub>:AgInS<sub>2</sub> was improved in the region from 300 nm to 750 nm as compared with that of the device without AgInS<sub>2</sub>. This result was separately caused by following two factors: one was the efficient light harvesting by AgInS<sub>2</sub> in the region from 300 nm to 450 nm, and another was the improvement of the charge transfer from perovskite layer to TiO<sub>2</sub> through AgInS<sub>2</sub> in the region from 450 nm to 750 nm. The power conversion efficiency of the device was increased from 11.9% to 13.8% by the addition of AgInS<sub>2</sub> at 0.8 mg mL<sup>-1</sup> into TiO<sub>2</sub>. Storage of the PSCs with or without AgInS<sub>2</sub> with encapsulation in air resulted in long stability for 200 days in terms of the  $PCEs$ , which were kept relatively 111% and 92% as compared with the initial values, respectively. Addition of AgInS<sub>2</sub> into TiO<sub>2</sub> brought the improvement of the durability against the photodegradation.

The  $\text{TiO}_2/\text{TiO}_2:\text{AgInS}_2$  QDs as the dual electron transport layers of the planar heterojunction PSCs was prepared for the improvement of the photovoltaic performance and the stability of the devices. From the results in Chapter 4, the best performance of the device with  $\text{TiO}_2:\text{AgInS}_2$  QDs under reverse scan showed the lower  $FF$ ,  $RR$ , and  $R_p$  than the device with pristine  $\text{TiO}_2$ . Therefore, in Chapter 5 the  $\text{TiO}_2/\text{TiO}_2:\text{AgInS}_2$  QDs as the dual electron transport layers was used for the improvement of the device performance and diode characteristics. It was demonstrated that the addition of  $\text{AgInS}_2$  into  $\text{TiO}_2$  indicated a reduction of pinholes at the interspace of the grains of the  $\text{TiO}_2$ . The PL intensity of the perovskite film deposited on  $\text{TiO}_2/\text{TiO}_2:\text{AgInS}_2$  QDs was quenched by the addition of  $\text{AgInS}_2$  QDs into  $\text{TiO}_2$ . Those results of quenching were probably caused by the improved efficiencies of electron transfer and extraction from the perovskite layer to the electron transport layer. Moreover, a rectification ratio ( $RR$ ) of the planar PSCs were improved by using  $\text{TiO}_2/\text{TiO}_2:\text{AgInS}_2$  QDs as dual electron transport layers. As a result, fill factor ( $FF$ ) and power conversion efficiency ( $PCE$ ) of the device with  $\text{TiO}_2/\text{TiO}_2:\text{AgInS}_2$  QDs ( $1.6 \text{ mg mL}^{-1}$ ) increased up to 0.77 and 17.5% as compared with  $FF$  (0.73) and  $PCE$  (16.3%) of the device with  $\text{TiO}_2$  single layer. The device with  $\text{TiO}_2/\text{TiO}_2:\text{AgInS}_2$  QDs as dual electron transport layers showed the improvement of the external quantum efficiency in the wavelength region from 300 nm to 750 nm as compared with that of the device with  $\text{TiO}_2$  single layer. This result probably caused by the enhancement of light harvesting by  $\text{AgInS}_2$  QDs and the enhancement of the charge transfer from the perovskite layer to the dual electron transport layers. The long-term stability of the PSC with the dual electron transport layers was confirmed when  $1.6 \text{ mg mL}^{-1}$  of  $\text{AgInS}_2$  was added, which was followed by the encapsulation and improvement of the retained  $PCE$  after the storage of the device in air for 15 days from 11% to 34% was also observed. As has been indicated, the  $\text{TiO}_2/\text{TiO}_2:\text{AgInS}_2$  QDs as dual electron transport layers not only brought the improvement of photovoltaic performance but also the durability against the photodegradation.

As has been indicated, the combination of directional solidification and convective deposition techniques for preparation of organic thin-film solar cells and preparation of inorganic composite thin-films with  $\text{TiO}_2$  precursor and QDs by convective deposition

techniques were investigated in this work. Throughout this work, it was found that the combination of directional solidification and convective deposition techniques was effective for improving both optical properties and electrical properties of the active layer. The directional crystallization of solidifying reagent was regulated along with the coating direction. The nucleation density was also controlled by changing the amount of solidifying reagent in the bulk heterojunction films. While in the case of inorganic composite thin films, homogeneous distribution of QDs with uniform thickness, and good physical contact with FTO substrates were realized by taking convective deposition method. Addition of QDs reduced the surface roughness, enhanced the electron mobility and improved the efficiency of the electron extraction from the active layer of perovskite through the electron transport layer. Furthermore, the long-term stability of the devices was confirmed when QDs was added by the convective deposition, which was followed by the encapsulation and improvement of the retained PCE after the storage of the device in air. This result implies that the addition of QDs into the electron transport layers not only brought the improvement of photovoltaic performance but also the durability against the photodegradation. Therefore, the convective deposition technique can be effective method for preparation of organic and inorganic thin-films for solar cells for improvement of optical property, electrical property, and long-term stability of semiconducting materials.

## References

- (1) Sansaniwal, S. K.; Sharma, V.; Mathur, J. Energy and Exergy Analyses of Various Typical Solar Energy Applications: A Comprehensive Review. *Renewable and Sustainable Energy Reviews* **2018**, *82*, 1576-1601.
- (2) Sampaio, P. G. V.; González, M. O. A. Photovoltaic Solar Energy: Conceptual Framework. *Renewable and Sustainable Energy Reviews* **2017**, *74*, 590-601.
- (3) Moosavian, S. M.; Rahim, N. A.; Selvaraj, J.; Solangi, K. H. Energy Policy to Promote Photovoltaic Generation. *Renewable and Sustainable Energy Reviews* **2013**, *25*, 44-58.
- (4) Williams, R. Becquerel Photovoltaic Effect in Binary Compounds. *The Journal of Chemical Physics* **1960**, *32*, 1505-1514.
- (5) Hersch, P.; Zweibel, K. *Basic photovoltaic principles and methods*; SERI/SP-290-1448; Solar Energy Research Inst., Golden, CO (USA): 1982/02/01/, 1982.



- (6) Chapin, D. M.; Fuller, C. S.; Pearson, G. L. A New Silicon p-n Junction Photocell for Converting Solar Radiation into Electrical Power. *Journal of Applied Physics* **1954**, *25*, 676-677.
- (7) Diao, Y.; Shaw, L.; Bao, Z.; Mannsfeld, S. C. B. Morphology Control Strategies for Solution-Processed Organic Semiconductor Thin Films. *Energy & Environmental Science* **2014**, *7*, 2145-2159.
- (8) Diao, Y.; Tee, B. C. K.; Giri, G.; Xu, J.; Kim, D. H.; Becerril, H. A.; Stoltenberg, R. M.; Lee, T. H.; Xue, G.; Mannsfeld, S. C. B.; Bao, Z. Solution Coating of Large-Area Organic Semiconductor Thin Films with Aligned Single-Crystalline Domains. *Nature Materials* **2013**, *12*, 665-671.
- (9) Giri, G.; DeLongchamp, D. M.; Reinspach, J.; Fischer, D. A.; Richter, L. J.; Xu, J.; Benight, S.; Ayzner, A.; He, M.; Fang, L.; Xue, G.; Toney, M. F.; Bao, Z. Effect of Solution Shearing Method on Packing and Disorder of Organic Semiconductor Polymers. *Chemistry of Materials* **2015**, *27*, 2350-2359.
- (10) Bae, S.-H.; Zhao, H.; Hsieh, Y.-T.; Zuo, L.; De Marco, N.; Rim, You S.; Li, G.; Yang, Y. Printable Solar Cells from Advanced Solution-Processible Materials. *Chem* **2016**, *1*, 197-219.
- (11) He, M.; Li, B.; Cui, X.; Jiang, B.; He, Y.; Chen, Y.; O'Neil, D.; Szymanski, P.; Ei-Sayed, M. A.; Huang, J.; Lin, Z. Meniscus-Assisted Solution Printing of Large-Grained Perovskite Films for High-Efficiency Solar Cells. *Nature Communications* **2017**, *8*, 16045.
- (12) Hu, Z.; Zhang, J.; Xiong, S.; Zhao, Y. Performance of polymer solar cells fabricated by dip coating process. *Solar Energy Materials and Solar Cells* **2012**, *99*, 221-225.
- (13) Wu, K.; Li, H.; Li, L.; Zhang, S.; Chen, X.; Xu, Z.; Zhang, X.; Hu, W.; Chi, L.; Gao, X.; Meng, Y. Controlled Growth of Ultrathin Film of Organic Semiconductors by Balancing the Competitive Processes in Dip-Coating for Organic Transistors. *Langmuir* **2016**, *32*, 6246-6254.
- (14) Sankaran, S.; Glaser, K.; Gärtner, S.; Rödlmeier, T.; Sudau, K.; Hernandez-Sosa, G.; Colsmann, A. Fabrication of polymer solar cells from organic nanoparticle dispersions by doctor blading or ink-jet printing. *Organic Electronics* **2016**, *28*, 118-122.
- (15) Schilinsky, P.; Waldauf, C.; Brabec, C. J. Performance Analysis of Printed Bulk Heterojunction Solar Cells. *Advanced Functional Materials* **2006**, *16*, 1669-1672.
- (16) Pérez-Gutiérrez, E.; Lozano, J.; Gaspar-Tánori, J.; Maldonado, J.-L.; Gómez, B.; López, L.; Amores-Tapia, L.-F.; Barbosa-García, O.; Percino, M.-J. Organic Solar Cells all Made by Blade and Slot-Die Coating Techniques. *Solar Energy* **2017**, *146*, 79-84.
- (17) Machui, F.; Lucera, L.; Spyropoulos, G. D.; Cordero, J.; Ali, A. S.; Kubis, P.; Ameri, T.; Voigt, M. M.; Brabec, C. J. Large Area Slot-Die Coated Organic Solar Cells on Flexible Substrates with Non-Halogenated Solution Formulations. *Solar Energy Materials and Solar Cells* **2014**, *128*, 441-446.
- (18) Kumnorkaew, P.; Ee, Y.-K.; Tansu, N.; Gilchrist, J. F. Investigation of the Deposition of Microsphere Monolayers for Fabrication of Microlens Arrays. *Langmuir* **2008**, *24*, 12150-12157.
- (19) Kumnorkaew, P.; Gilchrist, J. F. Effect of Nanoparticle Concentration on the Convective Deposition of Binary Suspensions. *Langmuir* **2009**, *25*, 6070-6075.

- (20) Kumnorkaew, P.; Weldon, A. L.; Gilchrist, J. F. Matching Constituent Fluxes for Convective Deposition of Binary Suspensions. *Langmuir* **2010**, *26*, 2401-2405.
- (21) Liao, H.-C.; Ho, C.-C.; Chang, C.-Y.; Jao, M.-H.; Darling, S. B.; Su, W.-F. Additives for morphology control in high-efficiency organic solar cells. *Materials Today* **2013**, *16*, 326-336.
- (22) Liang, Y.; Xu, Z.; Xia, J.; Tsai, S.-T.; Wu, Y.; Li, G.; Ray, C.; Yu, L. For the Bright Future—Bulk Heterojunction Polymer Solar Cells with Power Conversion Efficiency of 7.4%. *Advanced Materials* **2010**, *22*, E135-E138.
- (23) Lee, H.-S.; Ahn, H.; Woong Jo, J.; Kim, B.; Jung Son, H. Synergistic effects of solvent and polymer additives on solar cell performance and stability of small molecule bulk heterojunction solar cells. *Journal of Materials Chemistry A* **2016**, *4*, 18383-18391.
- (24) Liu, Z.; Ju, H.; Lee, E.-C. Improvement of polycarbazole-based organic bulk-heterojunction solar cells using 1,8-diiodooctane. *Applied Physics Letters* **2013**, *103*, 133308.
- (25) Huang, D.; Li, Y.; Xu, Z.; Zhao, S.; Zhao, L.; Zhao, J. Enhanced performance and morphological evolution of PTB7:PC71BM polymer solar cells by using solvent mixtures with different additives. *Physical Chemistry Chemical Physics* **2015**, *17*, 8053-8060.
- (26) Fang, G.; Liu, J.; Fu, Y.; Meng, B.; Zhang, B.; Xie, Z.; Wang, L. Improving the nanoscale morphology and processibility for PCDTBT-based polymer solar cells via solvent mixtures. *Organic Electronics* **2012**, *13*, 2733-2740.
- (27) Alem, S.; Graddage, N.; Lu, J.; Kololuoma, T.; Movileanu, R.; Tao, Y. Flexographic printing of polycarbazole-based inverted solar cells. *Organic Electronics* **2018**, *52*, 146-152.
- (28) Dkhil, S. B.; Pfanmüller, M.; Bals, S.; Koganezawa, T.; Yoshimoto, N.; Hannani, D.; Gaceur, M.; Videlot-Ackermann, C.; Margeat, O.; Ackermann, J. Square-Centimeter-Sized High-Efficiency Polymer Solar Cells: How the Processing Atmosphere and Film Quality Influence Performance at Large Scale. *Advanced Energy Materials* **2016**, *6*, 1600290.
- (29) Li, N.; Brabec, C. J. Air-Processed Polymer Tandem Solar Cells with Power Conversion Efficiency Exceeding 10%. *Energy & Environmental Science* **2015**, *8*, 2902-2909.
- (30) Xie, Y.; Hu, X.; Yin, J.; Zhang, L.; Meng, X.; Xu, G.; Ai, Q.; Zhou, W.; Chen, Y. Butanedithiol Solvent Additive Extracting Fullerenes from Donor Phase To Improve Performance and Photostability in Polymer Solar Cells. **2017**.
- (31) Yang, X.; Zheng, F.; Xu, W.; Bi, P.; Feng, L.; Liu, J.; Hao, X. Improving the Compatibility of Donor Polymers in Efficient Ternary Organic Solar Cells via Post-Additive Soaking Treatment. *ACS Applied Materials & Interfaces* **2017**, *9*, 618-627.
- (32) Jain, N.; Chandrasekaran, N.; Sadhanala, A.; Friend, R. H.; McNeill, C. R.; Kabra, D. Interfacial Disorder in Efficient Polymer Solar Cells: the Impact of Donor Molecular Structure and Solvent Additives. *Journal of Materials Chemistry A* **2017**, *5*, 24749-24757.
- (33) Lou, S. J.; Szarko, J. M.; Xu, T.; Yu, L.; Marks, T. J.; Chen, L. X. Effects of Additives on the Morphology of Solution Phase Aggregates Formed by Active Layer

- Components of High-Efficiency Organic Solar Cells. *Journal of the American Chemical Society* **2011**, *133*, 20661-20663.
- (34) Lu, L.; Yu, L. Understanding Low Bandgap Polymer PTB7 and Optimizing Polymer Solar Cells Based on It. *Advanced Materials* **2014**, *26*, 4413-4430.
- (35) Brinkmann, M.; Wittmann, J. C. Orientation of Regioregular Poly(3-hexylthiophene) by Directional Solidification: A Simple Method to Reveal the Semicrystalline Structure of a Conjugated Polymer. *Advanced Materials* **2006**, *18*, 860-863.
- (36) Brinkmann, M.; Rannou, P. Effect of Molecular Weight on the Structure and Morphology of Oriented Thin Films of Regioregular Poly(3-hexylthiophene) Grown by Directional Epitaxial Solidification. *Advanced Functional Materials* **2007**, *17*, 101-108.
- (37) Brinkmann, M.; Aldakov, D.; Chandezon, F. Fabrication of Oriented and Periodic Hybrid Nanostructures of Regioregular Poly(3-hexylthiophene) and CdSe Nanocrystals by Directional Epitaxial Solidification. *Advanced Materials* **2007**, *19*, 3819-3823.
- (38) Hamidi-Sakr, A.; Schiefer, D.; Covindarassou, S.; Biniek, L.; Sommer, M.; Brinkmann, M. Highly Oriented and Crystalline Films of a Phenyl-Substituted Polythiophene Prepared by Epitaxy: Structural Model and Influence of Molecular Weight. *Macromolecules* **2016**, *49*, 3452-3462.
- (39) Zhou, Y.-Q.; Wu, B.-S.; Lin, G.-H.; Li, Y.; Chen, D.-C.; Zhang, P.; Yu, M.-Y.; Zhang, B.-B.; Yun, D.-Q. Enhancing Performance and Uniformity of Perovskite Solar Cells via a Solution-Processed C<sub>70</sub> Interlayer for Interface Engineering. *ACS Applied Materials & Interfaces* **2017**, *9*, 33810-33818.
- (40) Ruankham, P.; Sagawa, T. Dopant-Free  $\pi$ -Conjugated Polymers as Hole-Transporting Materials for Stable Perovskite Solar Cells. *Journal of Materials Science: Materials in Electronics* **2018**, *29*, 9058-9066.
- (41) Li, H.; Shi, W.; Huang, W.; Yao, E.-P.; Han, J.; Chen, Z.; Liu, S.; Shen, Y.; Wang, M.; Yang, Y. Carbon Quantum Dots/TiO<sub>x</sub> Electron Transport Layer Boosts Efficiency of Planar Heterojunction Perovskite Solar Cells to 19%. *Nano Letters* **2017**, *17*, 2328-2335.
- (42) Song, S.; Kang, G.; Pyeon, L.; Lim, C.; Lee, G.-Y.; Park, T.; Choi, J. Systematically Optimized Bilayered Electron Transport Layer for Highly Efficient Planar Perovskite Solar Cells ( $\eta = 21.1\%$ ). *ACS Energy Letters* **2017**, *2*, 2667-2673.
- (43) Zheng, H.; Liu, G.; Zhu, L.; Ye, J.; Zhang, X.; Alsaedi, A.; Hayat, T.; Pan, X.; Dai, S. Enhanced Performance and Stability of Perovskite Solar Cells Using NH<sub>4</sub>I Interfacial Modifier. *ACS Applied Materials & Interfaces* **2017**, *9*, 41006-41013.
- (44) Wang, H.-H.; Chen, Q.; Zhou, H.; Song, L.; Louis, Z. S.; Marco, N. D.; Fang, Y.; Sun, P.; Song, T.-B.; Chen, H.; Yang, Y. Improving the TiO<sub>2</sub> Electron Transport Layer in Perovskite Solar Cells Using Acetylacetonate-Based Additives. *Journal of Materials Chemistry A* **2015**, *3*, 9108-9115.
- (45) Lv, M.; Lv, W.; Fang, X.; Sun, P.; Lin, B.; Zhang, S.; Xu, X.; Ding, J.; Yuan, N. Performance Enhancement of Perovskite Solar Cells with a Modified TiO<sub>2</sub> Electron Transport Layer Using Zn-Based Additives. *RSC Advances* **2016**, *6*, 35044-35050.

- (46) Ke, W.; Stoumpos, C. C.; Logsdon, J. L.; Wasielewski, M. R.; Yan, Y.; Fang, G.; Kanatzidis, M. G. TiO<sub>2</sub>-ZnS Cascade Electron Transport Layer for Efficient Formamidinium Tin Iodide Perovskite Solar Cells. *Journal of the American Chemical Society* **2016**, *138*, 14998-15003.
- (47) Hou, Y.; Chen, X.; Yang, S.; Zhong, Y. L.; Li, C.; Zhao, H.; Yang, H. G. Low-Temperature Processed In<sub>2</sub>S<sub>3</sub> Electron Transport Layer for Efficient Hybrid Perovskite Solar Cells. *Nano Energy* **2017**, *36*, 102-109.
- (48) Batmunkh, M.; Macdonald Thomas, J.; Shearer Cameron, J.; Bat-Erdene, M.; Wang, Y.; Biggs Mark, J.; Parkin Ivan, P.; Nann, T.; Shapter Joseph, G. Carbon Nanotubes in TiO<sub>2</sub> Nanofiber Photoelectrodes for High-Performance Perovskite Solar Cells. *Advanced Science* **2017**, *4*, 1600504.
- (49) Wang, Q.; Zhang, X.; Jin, Z.; Zhang, J.; Gao, Z.; Li, Y.; Liu, S. F. Energy-Down-Shift CsPbCl<sub>3</sub>:Mn Quantum Dots for Boosting the Efficiency and Stability of Perovskite Solar Cells. *ACS Energy Letters* **2017**, *2*, 1479-1486.
- (50) Torimoto, T.; Adachi, T.; Okazaki, K.-i.; Sakuraoka, M.; Shibayama, T.; Ohtani, B.; Kudo, A.; Kuwabata, S. Facile Synthesis of ZnS-AgInS<sub>2</sub> Solid Solution Nanoparticles for a Color-Adjustable Luminophore. *Journal of the American Chemical Society* **2007**, *129*, 12388-12389.
- (51) Liu, B.; Li, X.; Zhao, Q.; Ke, J.; Tadé, M.; Liu, S. Preparation of AgInS<sub>2</sub>/TiO<sub>2</sub> Composites for Enhanced Photocatalytic Degradation of Gaseous O-Dichlorobenzene under Visible Light. *Applied Catalysis B: Environmental* **2016**, *185*, 1-10.
- (52) Han, J.; Liu, Z.; Guo, K.; Ya, J.; Zhao, Y.; Zhang, X.; Hong, T.; Liu, J. High-Efficiency AgInS<sub>2</sub>-Modified ZnO Nanotube Array Photoelectrodes for All-Solid-State Hybrid Solar Cells. *ACS Applied Materials & Interfaces* **2014**, *6*, 17119-17125.
- (53) Anantha Sunil, M.; Thota, N.; Deepa, K. G.; Jampana, N. Sulfurization of Sputtered Ag-In Precursors for AgInS<sub>2</sub> Solar Cell Absorber Layers. *Thin Solid Films* **2015**, *595*, 5-11.
- (54) P. Kadlag, K.; Patil, P.; Rao, M. J.; Datta, S.; Nag, A. Luminescence and Solar Cell from Ligand-Free Colloidal AgInS<sub>2</sub> Nanocrystals. *CrystEngComm* **2014**, *16*, 3605-3612.
- (55) Akaki, Y.; Kurihara, S.; Shirahama, M.; Tsurugida, K.; Kakeno, T.; Yoshino, K. Structural and Electrical Characterization of AgInS<sub>2</sub> Thin Films Grown by Single-Source Thermal Evaporation Method. *Journal of Materials Science: Materials in Electronics* **2005**, *16*, 393-396.
- (56) Akaki, Y.; Kurihara, S.; Shirahama, M.; Tsurugida, K.; Seto, S.; Kakeno, T.; Yoshino, K. Structural, Electrical and Optical Properties of AgInS<sub>2</sub> Thin Films Grown by Thermal Evaporation Method. *Journal of Physics and Chemistry of Solids* **2005**, *66*, 1858-1861.