Improvement in power conversion efficiency and long-term lifetime of organic photovoltaic cells by using bathophenanthroline/molybdenum oxide as compound cathode buffer layer

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ABSTRACT

We demonstrate response and lifetime improvements for organic photovoltaic (OPV) by using organic bathophenanthroline (Bphen) and inorganic molybdenum oxide (MoO_3) as a compound cathode buffer layer (CBL). Not only power conversion efficiency (PCE) increases by 27% but also working and storage lifetimes extend at least 10 and 60 times respectively comparing with PV cell with 5 nm thick Bphen as CBL. The optimized PV structure is ITO/CuPc (20 nm)/C_{60} (40 nm)/Bphen (2 nm)/MoO_3 (5 nm)/Al and the CBL of the reference device is 5 nm Bphen without MoO_3 layer. The achievement of PV performance and lifetime improvement by introducing such a compound CBL is attributed to appropriate level alignment between C_{60}, Bphen and MoO_3, and stable inorganic MoO_3 can prevent from superior oxygen and moisture diffusion into the C_{60} acceptor layer. The detailed working mechanism of the compound Bphen/MoO_3 CBL in the OPV cells is also argued.

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1. Introduction

Since Tang's initial discovery of the donor–acceptor organic photovoltaic (OPV) cells based on small molecule planar hetero-junction, OPV cells have received increasing attentions in the hope of their application as a renewable, cheaper, and economical power source compared to their inorganic counterparts [1–3]. Significant efforts have been devoted in recent years to improve the power conversion efficiency (PCE); however, there are relatively few studies that develop ways to improve stability of OPV cells, which is also a huge problem restricting the application of OPV cells [4,5]. Therefore, there is a great deal of interest in introducing useful structures into OPV cells to gain both high PV response and long-term lifetime.

Cathode buffer layer (CBL) can play an important role in protecting excitons and holes to reach to cathode surface, thus avoiding quenching of the excitons and holes by the cathode surface states. Besides, CBL can assist in establishing an ohmic contact between acceptor and cathode [6,7]. The most commonly used CBLs, such as thin bathocuproine (BCP) [8] and bathophe-nanthroline (Bphen) [9], are intensively used as general exciton blocking layer (EBL). Since wide energy gap semiconductors transport carriers via cathode damage which is induced during metal deposition process, they are unsuitable to be used as thick EBL, which is a disadvantage in improving the working lifetime of OPV cells. Although the defect states induced by cathode deposition are beneficial for electron transport, heat-deposited Al atoms may still damage C_{60} acceptor. For the stability of OPV cells, it is well known that the predominant degradation mechanism is attributed to the entrance of ambient gases such as oxygen or moisture into the cells, and the major diffusion route of ambient gas is through the top cathode [10,11]. One of the important reasons for OPV cell degradation is the markedly reduced con-ductivity of C_{60} film due to the entrance of ambient gases into the active layer. So it is necessary to develop new cell structure to prevent C_{60} from the damage induced by heat-deposited Al and entrance of ambient gases. On the other hand, it is recognized that MoO_3 has been widely used as anode buffer layer (ABL) to modify indium tin oxide (ITO) either for OLEDs [12,13] or for OPV cells [14–17] due to its hole injection property and increasing work

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function of ITO anode. At the same time, different groups, however, have reported vastly different functions of MoO_3, such as enhancing electrical conductivity of organic hole-transporting layer [18], preventing an unwanted chemical reaction between ITO and the active layer [19], reducing the electron leakage current [20], forming a Schottky barrier [21] and so on.

In the present article, $Bphen/MoO_3$ is used as a compound CBL in OPV cells, in which thinner Bphen can transport electrons by tunneling mechanism and MoO_3 could protect against contamination of Al atoms to C_{60} film and block the moisture and oxygen gas in air to diffuse into OPV cells. Such a CBL is different from traditional single Bphen or BCP because the CBL can integrate strongpoint of organic and inorganic semiconductors. As a result, a maximum PCE of 1.62% for the optimized $ITO/CuPc/C_{60}/Bphen/MoO_3/Al$ cell is obtained, which increases by 27% compared with the reference cell with 5 nm Bphen. More importantly, optimized cell offers enlarged working lifetime. As the PCE of the reference cell is decreased to 0, the improving cell still maintains 73% of the initial PCE under a constant illumination of 50 mW/cm². Besides, the storage lifetime increases at least 60 times, and keeps 60% of initial PCE after the cell is conserved for 2 months in an ambient condition, while the cell without compound CBL degrades very quickly and no PCE can be detected in 24 h. In addition to CuPc-donor OPV cells, we also construct Rubrene donor based cells with the structure $ITO/MoO_3/Rubrene/C_{60}/Bphen/MoO_3/Al$, which can be another forceful evidence for improving device performance by the compound CBL. For optimized Rubrene donor-cell, PCE is improved by 20% comparing with its reference cell, reaching to a PCE of 2.87%.

2. Experiments methods

Patterned ITO coated glass substrates with a sheet resistance of 20 Ω/sq were routinely cleaned and treated in an ultraviolet-ozone chamber for 20 min immediately before loading into a high vacuum chamber ($\sim 5 \times 10^{-4}$ Pa). The evaporating rates were kept at 0.5–1 Å/s for organic layers and MoO_3 layer, and 10–15 Å/s for Al cathode. The current–voltage characteristics were measured using a programmable source meter (Keithley 2400) in the dark and under illumination of 100 mW/cm² with AM 1.5G simulated solar spectrum from a solar simulator. All measurements were carried out at room temperature and under ambient conditions without encapsulation. We fabricated two series of cells, and they are referred to be as series-1 and series-2; the former's donor is CuPc and donor of the latter cell is Rubrene. More detailed structure will be described in the next section. The PV devices were consecutively illuminated under a 50 mW/cm² iodine–tungsten lamp in open circuit state for working lifetime measurements which is corresponding to ISOS-L-1 in Ref. [22] Storage lifetime measurements were performed in dark under laboratory ambient at room temperature in open circuit state which is corresponding to ISOS-D-1 in Ref. [22].

3. Results and discussion

Fig. 1(a) and (b) depicts schematic structure of two series cells based on CuPc and Rubrene series, respectively. Note that for series-1 MoO_3 ABL is not used, which is attributed to poor effect of MoO_3 anode buffer layer on performance of CuPc cells [15].

Fig. 2(a) and (b) shows the typical current–voltage (I–V) characteristics of improved and corresponding reference cells under 1 sun (100 mW/cm²) AM 1.5G simulated solar illumination. We can observe that optimized cell structures are ITO/CuPc (20 nm)/C_{60} (40 nm)/Bphen (2 nm)/MoO_3 (5 nm)/Al and ITO/
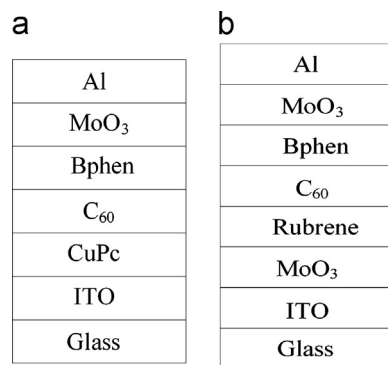

Fig. 1. Schematic structures of two series cells based on (a) CuPc and (b) Rubrene.

MoO_3 (10 nm)/Rubrene (20 nm)/C_{60} (40 nm)/Bphen (2 nm)/MoO_3 (5 nm)/Al, respectively, and 5 nm thick Bphen layers are used for both two reference cells. Optimized series-1 and -2 OPV cells offer maximum PCEs of 1.62% and 2.87%, and are respectively enhanced by 27% and 20% comparing with their respective reference cells. In order to understand the working mechanism of $Bphen/MoO_3$ CBL, devices with different thicknesses of Bphen and MoO_3 are fabricated. Tables 1 and 2 summarize the PV performances for series-1 and series-2 cells, in which the thicknesses of Bphen and MoO_3 are changed. We can see that 2 nm Bphen plays a very important role in two series improved cells. That is, when 2 nm Bphen layer is not used in CuPc- and Rubrene-OPV cells, PCEs decrease by 60% and 80% for CuPc and Rubrene cells, which are even much lower than those for the respective reference cells. We consider that the poor PV performance can be ascribed to the formation of a new cell of MoO_3/C_{60} [23]. This new organic Schottky barrier PV cell provides a reversed PV response, which inevitably decreases the performance of the forward OPV cell. It is also found that when MoO_3 thickness is fixed at 5 nm and the thickness of Bphen increases from 2 nm to 10 nm, the PCE drastically decreases from the maximum to nearly 0. This phenomenon indicates that 5 nm MoO_3 CBL can absolutely prevent Al atom from entering into Bphen layer so that Bphen layer cannot be damaged by heat-deposited Al and damage state cannot be induced. It is impossible for electron transport to occur by tunneling process with a Bphen layer as thick as 10 nm. We also observe that the PCEs decrease when thickness of MoO_3 continues to rise, which is attributed to the increase in cell resistances induced by too thick MoO_3 layer. Thus we select 2 nm Bphen/5 nm MoO_3 to be CBLs for fabricating improved cells. Fig. 3 displays the schematic energy-level diagram for electron transport process in the OPV cell with 2 nm Bphen/5 nm MoO_3. The LUMO and HOMO levels (units in eV) are cited from Ref. [16] for MoO_3, Ref. [24] for Bphen, Ref. [25] for CuPc and Ref. [26] for C_{60}. It seems that the electrons can pass through 2 nm Bphen layer efficiently by tunneling mechanism [8,27] and then the electrons transport via LUMO level of MoO_3 reaching to Al cathode as the appropriate level alignment between C_{60}, Bphen and MoO_3 for electron transport. This can be understood as below. Due to the occurrence of interfacial dipole effect, there is a ~3 eV shift of the vacuum level [28], so that the LUMO level of MoO_3 just lies near the LUMO of C_{60} level and the work function of Al, which could benefit for the electron transport. On the other hand, MoO_3 is an inorganic semiconductor with n-type structure and the majority carriers are electrons, and generally hole-injection at anode side of OPV cells is actually via electron extraction from the HOMO of hole transporter (or donor) through the MoO_3 conduction band to anode [16]. Thus we infer that electron transport should also happen via the LUMO level of MoO_3.

Not only improvements in above PV performances are achieved but also working lifetime is enlarged by using the compound CBL
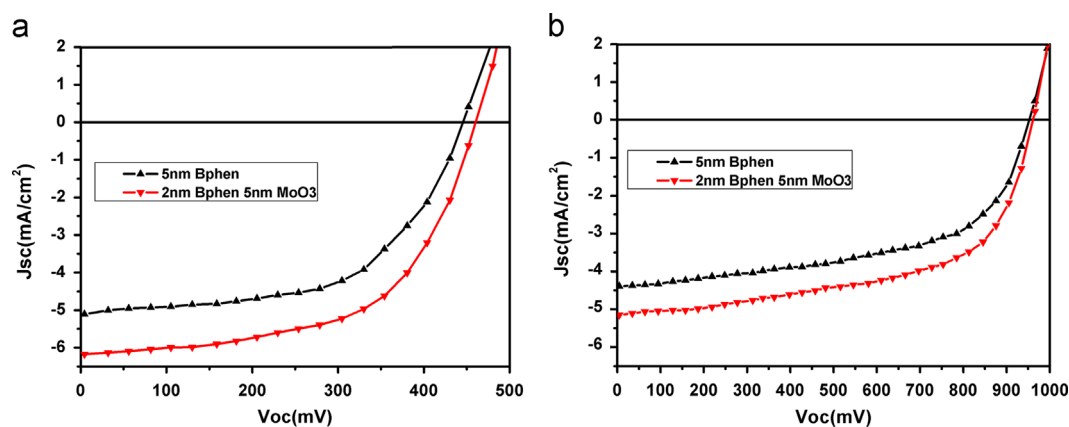
Fig. 2. The typical current–voltage (*I–V*) characteristics of optimized OPV cells and the reference cells of (a) series-1 for CuPc system and (b) series-2 for Rubrene system under 1 sun AM 1.5G simulated solar illumination.

Table 1
PV performances of series-1 cells with CuPc donor, in which the thicknesses of Bphen and MoO$_3$ are changed.

Bphen (nm)/MoO$_3$ (nm)	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	PCE (%)
Bphen (2)	4.64	445	0.545	1.11
Bphen (5)	5.09	447	0.563	1.27
Bphen (2)/MoO$_3$ (5)	6.17	461	0.574	1.62
Bphen (2)/MoO$_3$ (10)	5.25	433	0.502	1.13
Bphen (2)/MoO$_3$ (20)	4.78	412	0.449	0.88
Bphen (0)/MoO$_3$ (5)	2.09	413	0.382	0.32
Bphen (5)/MoO3 (5)	5.83	456	0.555	1.46
Bphen (10)/MoO$_3$ (5)	0.004	401	0.137	2.30E-4

Table 2
PV performances of series-2 cells with Rubrene donor, in which the thicknesses of Bphen and MoO$_3$ are changed.

| Bphen (nm)/MoO$_3$ (nm)	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	PCE (%)
Bphen (2)	4.19	919	0.538	2.07
Bphen (5)	4.39	954	0.572	2.39
Bphen (2)/MoO$_3$ (5)	5.06	961	0.591	2.87
Bphen (2)/MoO$_3$ (10)	4.27	892	0.508	1.93
Bphen (2)/MoO$_3$ (20)	3.66	878	0.481	1.54
Bphen (0)/MoO$_3$ (5)	2.34	346	0.279	0.22
Bphen (5)/MoO$_3$ (5)	4.64	956	0.549	2.44
Bphen (10)/MoO$_3$ (5)	0.004	851	0.110	4.56E-4

Fig. 3. Schematic energy-level diagram for electron transport process in the OPV cell with 2 nm Bphen/5 nm MoO$_3$. The LUMO and HOMO levels (units in eV) are cited from Ref. [16] for MoO$_3$, Ref. [24] for Bphen, Ref. [25] for CuPc and Ref. [26] for C$_{60}$.

as shown in Fig. 4. We note that if we define lifetime as the degradation time of 50% initial PCE, the working lifetime of the improved cell is enlarged by 10 times than that of the reference cell. As the lifetime of reference cell decreases to zero, the improved cell still offers a PCE of 73%. Besides, the storage lifetime (not shown here) increases at least 60 times, and the improved cell maintains 60% of the initial PCE after being stored in an ambient condition for 2 months, while the cell without a MoO$_3$ layer degrades very quickly in less than 24 h. It is pointed out that there seems an enormous discrepancy between device working and storage lifetimes. Taking into account that under the continued illumination condition a cell surface temperature of 50 °C is observed, we conjecture that such a high temperature condition under iodine–tungsten lamp illumination could destroy the structure of organic molecules.

As can be seen from Fig. 4(b) that, obvious initial increases in V_{oc} are observed in the both cells, which is in accordance with previous reports [5] and can be attributed to the energy offset increasing between HOMO$_{CuPc}$/LUMO$_{C_{60}}$ under exposure with
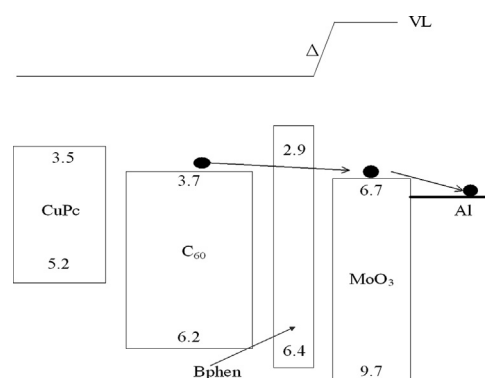
ambient gas [29]. At the same time, due to diffusion of the ambient gas, C$_{60}$-LUMO level shifts away from the Fermi level, resulting in a reduction of C$_{60}$ conductivity by several orders of magnitude [30]. Besides, upon exposure to ambient gas, the energy band bending in C$_{60}$ increases considerably from 0.3 to 0.8 eV [31]; excitons generated in the C$_{60}$ layer could diffuse to the interface of C$_{60}$/CBL and readily dissociated at the interface due to the strong built-in electric field formed from the orbital bending near the junction. All these are in good consistence with J_{sc}, and FF drastically decreases as observed for the Bphen only cell. But the cell with a compound CBL shows only a mild degradation, and it can be explained that by considering that MoO$_3$ as a stable inorganic semiconductor material, it should have a stronger ability of preventing the entrance of moisture and oxygen over pure Bphen CBL. In addition, direct contact between Al film and organic active layer may be unstable due to the formation of Al–C bond, which could result in poor charge extraction at the cathode side and therefore a reduction in J_{sc} and PCE [32,33]. Insertion of a MoO$_3$ layer can effectively prevent diffusion of Al into the organic layer and thus eliminate the formation of the insulating layer that degrades the device performance.

4. Conclusions

In summary, a compound Bphen/MoO$_3$ is firstly introduced to the cathode side as a CBL. Such a compound CBL extends device stability greatly and increases PCE to some extent. PV response improvement is attributed to appropriate level alignment between
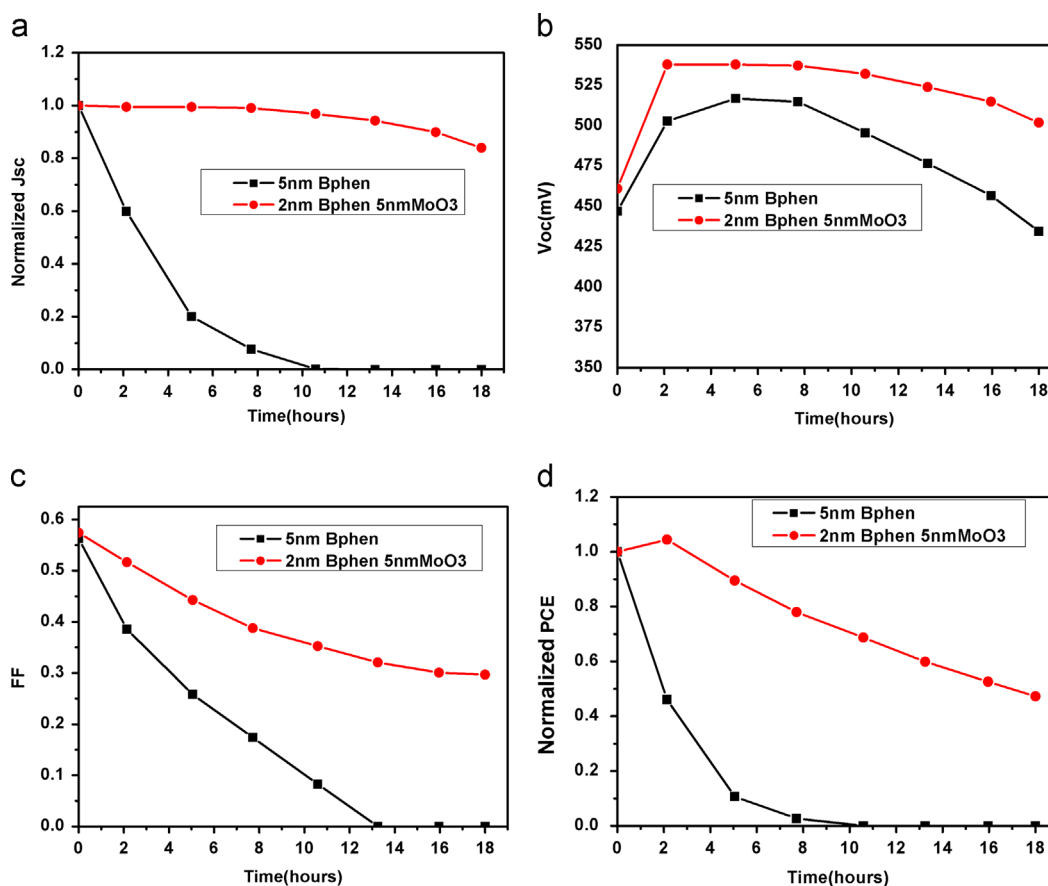
Fig. 4. Comparison of the (a) short circuit current (J_{sc}), (b) open circuit voltage (V_{oc}), (c) fill factor (FF), and (d) PCE as a function of working time for the cells with different CBLs under consecutive 50 mW/cm^2 illumination with iodine–tungsten lamp (ISOS-L-1 in Ref. [22]).

C_{60}, Bphen and MoO$_3$ for the electron collection. The lifetime increase is because of a stronger ability of MoO$_3$ in preventing the entrance of moisture and oxygen and in avoiding direct contact between Al film and organic active layer. The organic/inorganic based compound CBL can exert respective advantages. Thinner Bphen could induce LUMO/HOMO levels to have a more feasible level alignment for electron transport and MoO$_3$ layer can block moisture and oxygen gas to enter C_{60} and avoid the formation of Al–C bond between organic layer and Al. Our findings provide an interesting way to use organic/inorganic based compound CBL in OPV cells for improving PV response and lifetime. It is expected that inorganic semiconductor may be a promising material that can be used in OPVs as a CBL.

Acknowledgments

References

[1] C.W. Tang, Two-layer organic photovoltaic cell, Applied Physics Letters 48 (1986) 183–185.

[2] E.D. Kosten, J.H. Atwater, J. Parsons, A. Polman, H.A. Atwater, Highly efficient GaAs solar cells by limiting light emission angle, Light: Science and Applications 2 (2013) e45.

[3] Y.H. Su, Y.F. Ke, S.L. Cai, Q.Y. Yao, Surface plasmon resonance of layer-by-layer gold nanoparticles induced photoelectric current in environmentally-friendly plasmon-sensitized solar cell, Light: Science and Applications 1 (2012) e14.

[4] M.F. Lo, T.W. Ng, S.L. Lai, F.L. Wong, M.K. Fung, S.T. Lee, C.S. Lee, Operation stability enhancement in organic photovoltaic device by a metal doped organic exciton blocking layer, Applied Physics Letters 97 (2010) 143304.

[5] M.F. Lo, T.W. Ng, S.L. Lai, M.K. Fung, S.T. Lee, C.S. Lee, Stability enhancement in organic photovoltaic device by using polymerized fluorocarbon anode buffer layer, Applied Physics Letters 99 (2011) 033302.

[6] Q.L. Song, C.M. Li, M.L. Wang, X.Y. Sun, X.Y. Hou, Role of buffer in organic solar cells using C_{60} as an acceptor, Applied Physics Letters 90 (2007) 071109.

[7] M. Vogel, S. Doka, C. Breyer, M.C. Lux-Steiner, K. Fostiropoulos, On the function of a bathocuproine buffer layer in organic photovoltaic cells, Applied Physics Letters 89 (2006) 163501.

[8] P. Peumans, V. Bulovic, S.R. Forrest, Efficient photon harvesting at high optical intensities in ultrathin organic double–hetero-structure photovoltaic diodes, Applied Physics Letters 76 (2000) 2650–2652.

[9] M.Y. Chan, C.S. Lee, S.L. Lai, M.K. Fung, F.L. Wong, H.Y. Sun, K.M. Lau, S.T. Lee, Efficient organic photovoltaic devices using a combination of exciton blocking layer and anodic buffer layer, Journal of Applied Physics 100 (2006) 094506.

[10] K. Norrman, N.B. Larsen, F.C. Krebs, Lifetimes of organic photovoltaics: combining chemical and physical characterisation techniques to study degradation mechanisms, Solar Energy Materials and Solar Cells 90 (2006) 2793–2814.

[11] F.C. Krebs, K. Norrman, Analysis of the failure mechanism for a stable organic photovoltaic during 10,000 h of testing, Progress in Photovoltaics: Research and Applications 15 (2007) 697–712.

[12] S. Tokito, K. Noda, Y. Taga, Metal oxides as a hole-injecting layer for an organic electroluminescent device, Journal of Physics D: Applied Physics 29 (1996) 2750–2753.

[13] H. Lee, S.W. Cho, K. Han, P.E. Jeon, C.N. Whang, K. Jeong, K. Cho, Y. Yi, The origin of the hole injection improvements at indium tin oxide/molybdenum trioxide/ N,N′-bis(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl- 4,4′-diamine interfaces, Applied Physics Letters 93 (2008) 043308.

[14] D.Y. Kim, J. Subbiah, G. Sarasqueta, F. So, H. Ding, Irfan, Y. Gao, The effect of molybdenum oxide interlayer on organic photovoltaic cells, Applied Physics Letters 95 (2009) 093304.

[15] I. Hancox, P. Sullivan, K.V. Chauhan, N. Beaumont, L.A. Rochford, R.A. Hatton, T.S. Jones, The effect of a MoOx hole-extracting layer on the performance of organic photovoltaic cells based on small molecule planar heterojunctions, Organic Electronics 11 (2010) 2019–2025.

[16] M. Kroeger, S. Hamwi, J. Meyer, T. Riedl, W. Kowalsky, A. Kahn, Role of the deep-lying electronic states of MoO$_3$ in the enhancement of hole-injection in organic thin films, Applied Physics Letters 95 (2009) 123301.

[17] G. Chen, H. Sasabe, Z. Wang, X.F. Wang, Z.R. Hong, Y. Yang, J. Kido, Co-evaporated bulk heterojunction solar cells with > 6.0% efficiency, Advanced Materials 24 (2012) 2768–2773.

[18] T. Matsushima, C. Adachi, Enhanced hole injection and transport in molybdenum-dioxide-doped organic hole-transporting layers, Journal of Applied Physics 103 (2008) 034501.

[19] V. Shrotriya, G. Li, Y. Yao, C.W. Chu, Y. Yang, Transition metal oxides as the buffer layer for polymer photovoltaic cells, Applied Physics Letters 88 (2006) 073508.

[20] N. Li, B.E. Lassiter, R.R. Lunt, G. Wei, S.R. Forrest, Open circuit voltage enhancement due to reduced dark current in small molecule photovoltaic cells, Applied Physics Letters 94 (2009) 023307.

[21] M.L. Zhang, H. Wang, H.K. Tian, Y.H. Geng, C.W. Tang, Bulk heterojunction photovoltaic cells with low donor concentration, Advanced Materials 23 (2011) 4960–4964.

[22] M.O. Reese, S.A. Gevorgyan, M. Jørgensen, E. Bundgaard, S.R. Kurtz, D.S. Ginley, D.C. Olson, M.T. Lloyd, P. Morvillo, E.A. Katz, A. Elschner, O. Haillant, T.R. Currier, V. Shrotriya, M. Hermenau, M. Riede, K.R. Kirov, G. Trimmel, T. Rath, O. Inganas, F. Zhang, M. Andersson, K. Tvingstedt, M. Lira-Cantu, D. Laird, C. McGuiness, S. Gowrisanker, M. Pannone, M. Xiao, J. Hauch, R. Steim, D.M. DeLongchamp, R. Rosch, H. Hoppe, N. Espinosa, A. Urbina, G. Yaman-Uzunoglu, J. Bonekamp, A.J.J.M.V. Breemen, C. Girotto, E. Voroshazi, F.C. Krebs, Consensus stability testing protocols for organic photovoltaic materials and devices, Solar Energy Materials and Solar Cells 95 (2011) 1253–1267.

[23] M.L. Zhang, Irfan, H.J. Ding, Y.L.Gao, C.W. Tang, Organic Schottky barrier photovoltaic cells based on MoOx/C60, Applied Physics Letters 96 (2010) 183301.

[24] M.Y. Chan, C.S. Lee, S.L. Lai, M.K. Fung, F.L. Wong, H.Y. Sun, K.M. Lau, S.T. Lee, Efficient organic photovoltaic devices using a combination of exciton blocking layer and anodic buffer layer, Journal of Applied Physics 100 (2006) 094506.

[25] P. Peumans, A. Yakimov, S.R. Forrest, Small molecular weight organic thin-film photodetectors and solar cells, Journal of Applied Physics 93 (2003) 3693–3723.

[26] K.L. Mutolo, E.I. Mayo, B.P. Rand, S.R. Forrest, M.E. Thompson, Enhanced open-circuit voltage in subphthalocyanine/C60 organic photovoltaic cells, Journal of the American Chemical Society 128 (2006) 8108–8109.

[27] B. Yu, F. Zhu, H.B. Wang, G. Li, D.H. Yan, All-organic tunnel junctions as connecting units in tandem organic solar cell, Journal of Applied Physics 104 (2008) 114503.

[28] J. Li, Q.Y. Bao, H.X. Wei, Z.Q. Xu, J.P. Yang, Y.Q. Li, S.T. Lee, J.X. Tang, Role of transition metal oxides in the charge recombination layer used in tandem organic photovoltaic cells, Journal of Materials Chemistry 22 (2012) 6285–6290.

[29] W. Ng, M.F. Lo, Y.C. Zhou, Z.T. Liu, C.S. Lee, O. Kwon, S.T. Lee, Ambient effects on fullerene/copper phthalocyanine photovoltaic interface, Applied Physics Letters 94 (2009) 193304.

[30] A. Hamed, Y.Y. Sun, Y.K. Tao, R.L. Meng, P.H. Hor, Effects of oxygen and illumination on the in situ conductivity of C60 thin films, Physical Review B 47 (1993) 10873–10880.

[31] Q.D. Yang, T.W. Ng, M.F. Lo, F.Y. Wang, N.B. Wong, C.S. Lee, Effect of water and oxygen on the electronic structure of the organic photovoltaic, The Journal of Physical Chemitry 116 (2012) 10982–10985.

[32] M.D. Wang, F.Y. Xie, W.G. Xie, S.Z. Zheng, N. Ke, J. Chen, N. Zhao, J.B. Xu, Device lifetime improvement of polymer-based bulk heterojunction solar cells by incorporating copper oxide layer at Al cathode, Applied Physics Letters 98 (2011) 183304.

[33] M. Jørgensen, K. Norrman, F.C. Krebs, Stability/degradation of polymer solar cells, Solar Energy Materials and Solar Cells 92 (2008) 686–714.