

Cite this: *Nanoscale*, 2015, 7, 9427

Received 24th March 2015,

Accepted 23rd April 2015

DOI: 10.1039/c5nr01864a

www.rsc.org/nanoscale

Efficient and stable planar heterojunction perovskite solar cells with an MoO₃/PEDOT:PSS hole transporting layer†

Fuhua Hou,^{a,b} Zisheng Su,^{*a} Fangming Jin,^{a,b} Xingwu Yan,^{a,b} Lidan Wang,^{*c} Haifeng Zhao,^a Jianzhuo Zhu,^d Bei Chu^{*a} and Wenlian Li^a

A solution processed MoO₃/PEDOT:PSS bilayer structure is used as the hole transporting layer to improve the efficiency and stability of planar heterojunction perovskite solar cells. Increased hole extraction efficiency and restrained erosion of ITO by PEDOT:PSS are demonstrated in the optimized device due to the incorporation of an MoO₃ layer.

Perovskite solar cells based on organometal halide light absorbers have been considered as a promising photovoltaic technology owing to their direct bandgap, high absorption coefficient, long exciton diffusion length, and excellent charge transport properties that led to their superb power conversion efficiency (PCE).^{1–16} Since the first report on a long-term durable solid-state perovskite solar cell with a PCE of 9.7% in 2012,³ great improvement in the cell performance have been created in the past three years. The perovskite solar cells have two typical architectures: meso-superstructured and planar heterojunction (PHJ). The PHJ perovskite solar cell has a much simpler device structure with the perovskite sandwiched between hole- and electron-conductors, which avoids the pore-filling problem and the high temperature process for the preparation of the metal oxide scaffold layer. Poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is usually used as the hole transporting layer (HTL) in PHJ perovskite solar cells.^{17–25} However, the acidic PEDOT:PSS can etch indium tin oxide (ITO) and decompose perovskite, which results in poor stability of the devices.¹⁶ Some other robust materials, such as poly(*N*-9'-heptadecan-yl-2,7-carbazole-*alt*-5,5'-(4',7'-di(thien-2-yl)-

2',1',3'-benzothiadiazole)),²⁶ NiO_x,^{27–30} graphene oxide,^{16,31} and PbS,³² have been adopted as the alternatives to PEDOT:PSS. However, their PCEs are still lower than those of state-of-the-art ones based on PEDOT:PSS.^{21,25} Apart from PCE, stability is another main factor limiting the practical application of perovskite solar cells. However, it has rarely been of concern.

MoO₃ is one of the most promising HTL materials because of its non-toxicity and ambient condition stability. However, we have found that perovskite solar cells with an MoO₃ HTL exhibit a low PCE due to low coverage of perovskite films deposited on MoO₃. A similar result has been found by Jeng *et al.*¹⁷ Chen *et al.*³³ and Shao *et al.*³⁴ respectively used an MoO₃:PEDOT:PSS composite film as the HTL in a polymer solar cell to take advantage of both the highly conductivity of PEDOT:PSS and the ambient condition stability of MoO₃, and eventually both PCE and stability were improved. In such a configuration, direct contact between PEDOT:PSS and ITO still occurs, which cannot fully restrain the erosion of ITO by PEDOT:PSS. Besides, the highly acidic aqueous MoO₃ solution prepared in their studies may accelerate the erosion process.

In this work, an MoO₃/PEDOT:PSS bilayer structure is used as the HTL for inverted CH₃NH₃PbI₃/C₆₀ PHJ perovskite solar cells. MoO₃ solutions were prepared by a milder thermal decomposition solution method. The insertion of an MoO₃ layer between ITO and PEDOT:PSS not only increases the hole-extraction efficiency from CH₃NH₃PbI₃ to the ITO electrode but also completely eliminates direct contact between ITO and PEDOT:PSS. These two effects result in an increase of PCE and stability, respectively, for the perovskite solar cell compared with the pristine PEDOT:PSS based reference device. The as-prepared optimized device exhibits a PCE of 12.78%, and a maximum PCE of 14.87% is obtained for the device after a short storage under ambient conditions in the dark. More importantly, the device retains 93% of its initial PCE, compared to almost full failure for the reference device after they were stored under ambient conditions in the dark for 10 days.

MoO₃ solutions were synthesized by a thermal decomposition method following the procedure reported by Murase *et al.*³⁵ Ammonium heptamolybdate (NH₄)₆Mo₇O₂₄·4H₂O was

^aState Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P. R. China. E-mail: suzs@ciomp.ac.cn, chub@ciomp.ac.cn

^bUniversity of Chinese Academy of Sciences, Beijing 100039, P. R. China

^cState Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China. E-mail: wangld@ciac.ac.cn

^dCollege of Science, Yanshan University, Qinhuangdao 066004, P. R. China

†Electronic supplementary information (ESI) available: AFM images of the MoO₃ and MoO₃/PEDOT:PSS films, XRD patterns of CH₃NH₃PbI₃, and *J*–*V* curves of the devices. See DOI: 10.1039/c5nr01864a

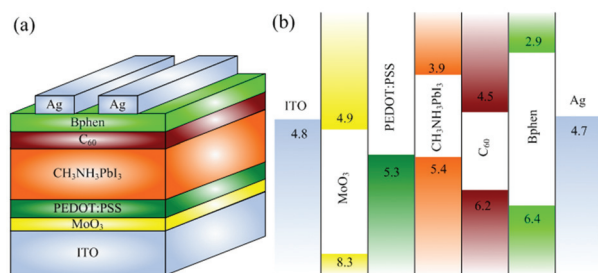


Fig. 1 (a) Structure and (b) schematic energy level diagram of the devices.

dissolved in deionized water and vigorously stirred at 80 °C for 60 min in an open round-bottom flask to let the generated NH₃ volatilize in air. The resulting solution was diluted with deionized water to various concentrations (0.2, 0.5, 1.0, and 2.0 wt%) and was used to form MoO₃ films.

Devices were fabricated on patterned ITO coated glass substrates with a sheet resistance of 15 Ω sq⁻¹. The perovskite solar cells have a structure of ITO/MoO₃/PEDOT:PSS/CH₃NH₃PbI₃/C₆₀/4,7-diphenyl-1,10-phenanthroline (Bphen)/Ag, as shown in Fig. 1(a); for reference, a device without MoO₃ layers was also fabricated. The ITO substrates were routinely cleaned, followed by UV-ozone treatment for 15 min. Before depositing MoO₃ layers, ITO substrates were heated on a hot plate at 100 °C for 5 min to vaporise the residual organic solvent. The MoO₃ solutions with different concentrations were spin-coated at 4000 rpm for 40 s on hot ITO substrates and then annealed at 100 °C for 10 min. PEDOT:PSS (Clevios P-VP Al4083) was passed through a 0.45 μm filter and deposited onto MoO₃ layers or ITO substrates by spin-coating at 5000 rpm for 40 s, and then the samples were dried at 120 °C for 15 min, which forms a PEDOT:PSS layer of about 40 nm. PbI₂ and CH₃NH₃I were dissolved in *N,N*-dimethylformamide and 2-propanol with concentrations of 460 and 50 mg ml⁻¹, respectively. The PbI₂ solution was heated at 100 °C for around 10 min before use to make sure that PbI₂ can be fully dissolved. The hot PbI₂ solution was spun on PEDOT:PSS substrates at 2000 rpm for 30 s. Then they were transferred onto a hot plate quickly and dried at 100 °C for 3 min. The CH₃NH₃I solution was spun on top of dried PbI₂ films at 2000 rpm for 30 s at room temperature. The spin coated PbI₂/CH₃NH₃I stacking films were then put on the top of a hot plate that pre-heated at 100 °C in the ambient conditions. Around 25 μL of dimethylsulfoxide (DMSO) solvent was added at the edge of a petri dish and quickly covered the perovskite layers to form the DMSO vapor atmosphere. This annealing process continued for 2 h, which formed CH₃NH₃PbI₃ layers of about 350 nm. All the above fabrication procedures were performed under an ambient atmosphere. Finally, the devices were completed by thermal evaporating 40 nm C₆₀, 5 nm Bphen, and 80 nm Ag in sequence in a vacuum chamber at a pressure of 5 × 10⁻⁴ Pa without breaking vacuum. The deposition rate and the layer thickness were monitored *in situ* using oscillating quartz monitors. The evaporation rates were kept at 1 Å s⁻¹ for C₆₀

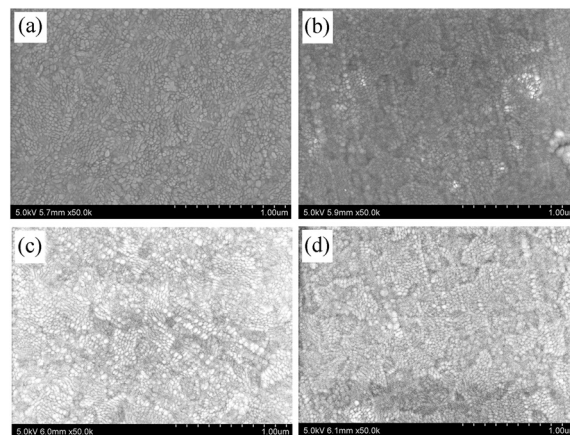


Fig. 2 SEM images of MoO₃ films on ITO substrates prepared from (a) 0.2 wt%, (b) 0.5 wt%, (c) 1.0 wt%, and (d) 2.0 wt% MoO₃ solutions.

and Bphen and 10 Å s⁻¹ for the Ag cathode. The device area is 0.18 cm², determined by the overlap of the cathode and anode electrodes.

X-ray diffraction (XRD) patterns were recorded with a Rigaku D/Max-2500 diffractometer using Cu Kα radiation (λ = 1.54 Å). Transmission spectra were recorded on a Shimadzu UV-3101 spectrophotometer. Scanning electron microscopy (SEM) images were obtained using a Hitachi S4800 field emission scanning electron microscope. The surface topographies were imaged with a Bruker MultiMode 8 atomic force microscope (AFM) in tapping mode. Current-voltage (*J*-*V*) characteristics of the devices were measured with a Keithley 2400 source meter both in the dark and under illumination of a Xe lamp light source with an AM 1.5 G filter, and the irradiation intensity was certified to be 100 mW cm⁻². The voltage scans were swept from short circuit to forward bias with a rate of 0.05 V s⁻¹. The incident photon to current conversion efficiency (IPCE) spectra were recorded with a Stanford SR803 lock-in amplifier under monochromatic illumination. All measurements were performed under ambient conditions.

Fig. 2 shows SEM images of MoO₃ layers on ITO substrates deposited from MoO₃ solutions with concentrations of 0.2, 0.5, 1.0, and 2.0 wt%, which forms MoO₃ films of about 4.2, 8.7, 16.2, and 38.6 nm, respectively, as determined by spectroscopic ellipsometry. Due to the thin and discontinued morphology of MoO₃ films prepared with 0.2 and 0.5 wt% MoO₃ solutions, as discussed below, their thicknesses may have a large deviation. The morphology of MoO₃ films prepared from a 0.2 wt% MoO₃ solution shows little difference from that of bare ITO substrate. However, the root mean square (RMS) roughness of the ITO substrate decreases from 2.54 to 1.02 nm, as shown in AFM images in Fig. S1.† This means that small MoO₃ clusters may fill the gaps between ITO crystals. With the concentration of MoO₃ increased to 0.5 wt% and 1.0 wt%, an ultrathin and continued morphology with an RMS roughness of 0.94 and 1.15 nm, respectively, can be evidently observed for the MoO₃ films. Further increase of the concentration results in the formation of a smooth MoO₃ film. Conse-

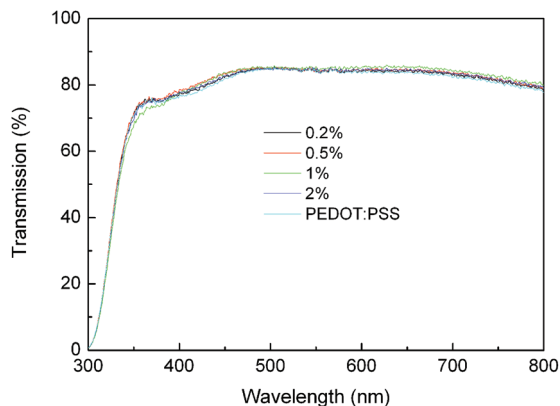


Fig. 3 Transmission spectra of the MoO₃/PEDOT:PSS and pristine PEDOT:PSS films.

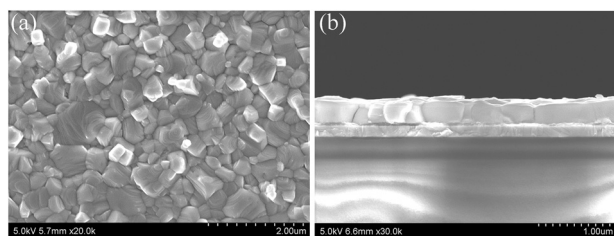


Fig. 4 (a) Typical top-surface and (b) cross-sectional SEM images of CH₃NH₃PbI₃ films deposited on an ITO/MoO₃/PEDOT:PSS substrate.

quently, the RMS roughness of the film decreases to 0.45 nm with an MoO₃ concentration of 2.0 wt%.

To exploit the effects of the MoO₃ layer on the morphology of the upper PEDOT:PSS layers, AFM images of PEDOT:PSS layers are investigated and shown in Fig. S2.† The RMS roughnesses are 1.02, 1.06, 1.08, and 1.05 nm, respectively, for the PEDOT:PSS layers deposited on bare ITO and MoO₃ layers prepared from MoO₃ solutions with concentrations of 0.2, 0.5, 1.0, and 2.0 wt%. The PEDOT:PSS layers deposited on bare ITO and MoO₃ layers present comparable RMS roughness; this should be attributed to the fact that the thickness of the PEDOT:PSS layer is much larger than the roughness of ITO and MoO₃ layers. The comparable RMS roughness suggests that the insertion of an MoO₃ layer may not affect the growth of PEDOT:PSS and hence perovskite films. Fig. 3 displays the transmission spectra of the PEDOT:PSS films with and without an MoO₃ layer. Because MoO₃ has nearly no absorption in the visible region, almost identical transmissions are found for the films. This suggests that the introduction of a thin MoO₃ layer has little effect on the optical field distribution of the devices if the same device geometry were used.

Fig. 4 shows the typical top-surface and cross-sectional SEM images of the CH₃NH₃PbI₃ film deposited on an ITO/MoO₃/PEDOT:PSS substrate. A homogeneous and pin-hole free morphology with a grain size of up to 800 nm is found for the CH₃NH₃PbI₃ layer. Such a morphology ensures a high charge

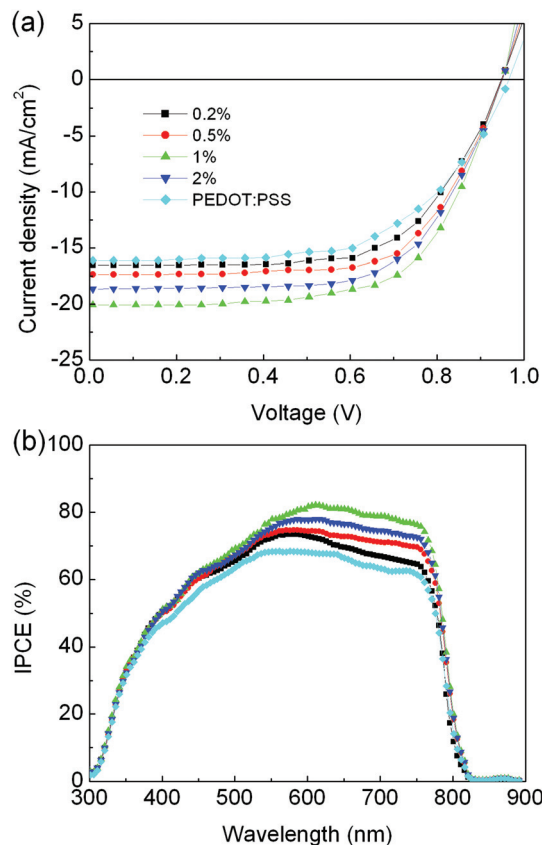


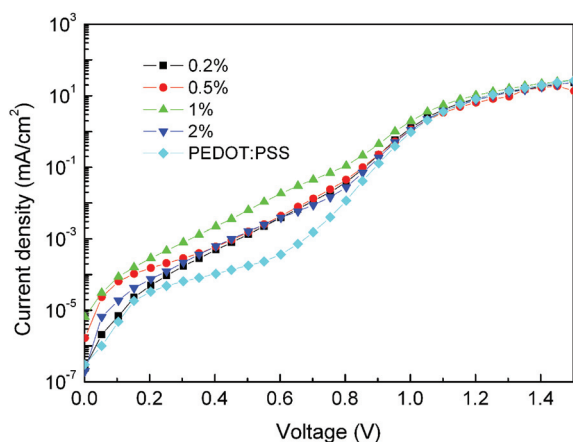
Fig. 5 (a) *J*-*V* characteristics and (b) IPCE spectra of the devices with different MoO₃/PEDOT:PSS and pristine PEDOT:PSS HTLs.

mobility and a low electron-hole recombination in thick perovskite solar cells. Fig. S3† shows the XRD pattern of the CH₃NH₃PbI₃ film. Diffraction peaks of 2θ at about 14.22°, 28.53°, 32.03°, 40.82° and 43.28° are found, which can be assigned to the (110), (220), (310), (314), and (330) planes of CH₃NH₃PbI₃, respectively. The higher number of diffraction peaks indicates that the CH₃NH₃PbI₃ films prepared are highly crystalline.¹⁴ Furthermore, no diffraction peaks of PbI₂ are found, indicating good conversion from the precursors to perovskite and high purity of this perovskite film.

Fig. 5(a) shows the *J*-*V* curves of the perovskite solar cells with different MoO₃ layers. Each curve is averaged over 6 devices. Table 1 summarizes the detailed parameters extracted from the *J*-*V* curves. The pristine PEDOT:PSS based reference device shows a short-circuit current (*J*_{SC}), open-circuit voltage (*V*_{OC}), fill factor (FF), and PCE of 16.11 mA cm⁻², 0.97 V, 0.63, and 9.81%, respectively. The MoO₃/PEDOT:PSS based devices exhibit a similar *V*_{OC} compared with the reference device, indicating that the devices have identical CH₃NH₃PbI₃ bulk and PEDOT:PSS/CH₃NH₃PbI₃ interface properties. However, both *J*_{SC} and FF of the devices increase with the increase of the concentration of MoO₃, indicating an improved charge collection efficiency and a decreased electron-hole recombination probability. Further increases in the concentration results in slight decreases of both *J*_{SC} and FF. The optimized device fabricated

Table 1 Photovoltaic parameters of the devices with different HTLs

Device	MoO ₃ concentration (wt%)	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF	PCE (%)	R_s (Ω cm ⁻²)	R_p (k Ω cm ⁻²)
MoO ₃ /PEDOT:PSS	0.2	16.53 ± 1.83	0.95 ± 0.01	0.66 ± 0.05	10.28 ± 1.71	9.17	2.87
MoO ₃ /PEDOT:PSS	0.5	17.35 ± 0.89	0.96 ± 0.07	0.66 ± 0.03	10.93 ± 1.87	6.49	2.32
MoO ₃ /PEDOT:PSS	1.0	20.06 ± 1.23	0.96 ± 0.02	0.67 ± 0.03	12.78 ± 0.57	7.75	3.08
MoO ₃ /PEDOT:PSS	2.0	18.65 ± 2.36	0.95 ± 0.03	0.66 ± 0.06	11.74 ± 0.74	11.24	2.59
PEDOT:PSS	—	16.11 ± 2.48	0.97 ± 0.03	0.63 ± 0.04	9.81 ± 1.97	9.48	2.90

**Fig. 6** Dark current of the devices with different MoO₃/PEDOT:PSS and pristine PEDOT:PSS HTLs.

with 1.0 wt% MoO₃ shows a J_{SC} , V_{OC} , FF, and PCE of 20.06 mA cm⁻², 0.96 V, 0.67, and 12.78%, respectively. Compared with the reference device, the PCE is increased by more than 30%. Fig. 5(b) shows the IPCE spectra of the devices. A broad response with a value of about 80% at 600–800 nm is obtained for the optimized device. The calculated J_{SC} from its IPCE is 19.95 mA cm⁻², which is within the error compared with that from the J - V curve. Fig. S4† shows the J - V curves measured with different scanning rates of one of the devices fabricated with 1.0 wt% MoO₃. Negligible difference is found in these curves.

To understand the origin of the improved device performance, dark currents of the devices are compared in Fig. 6. It can be found that the dark currents of the MoO₃/PEDOT:PSS based devices are higher than those of the reference device, which indicates that the hole collection efficiency is improved. Consequently, the series resistance (R_s) is reduced, while the shunt resistance (R_p) is comparable to that of the reference device, as listed in Table 1. The highest dark current is found in the device based on 1.0 wt% MoO₃, which corresponds to the highest PCE among the devices. Fig. 1(b) shows the schematic energy diagram of the devices, and energy level data are cited from the literature.^{17,36} Although MoO₃ has a low conduction and valence bands of 4.9 and 8.3 eV, respectively, holes can be extracted through the gap-states formatted in the oxygen vacancies. Thus the increased hole extraction efficiency

can be attributed to the Ohmic contact at the ITO/MoO₃ interface due to electron transfer from ITO to MoO₃ and/or band bending and built-in field formation at the MoO₃/PEDOT:PSS interface.^{37,38} However, the dark current decreases in the device based on 2.0 wt% MoO₃. Thus the hole extraction efficiency is reduced, which results in the increase of electron–hole recombination in the device and hence the R_s . This can be attributed to the high resistance of a thick MoO₃ layer.³⁵ As a result, both J_{SC} and FF of the device are decreased. Besides, the reflection losses at the ITO/MoO₃ interface may also cause a decrease in J_{SC} because of the high refractive index of MoO₃ compared to that of ITO.^{35,39}

To assess the new device architecture, an aging test was performed to check how the MoO₃ buffer layer affects the device performance over time. Unencapsulated solar cells with different HTLs were stored under ambient conditions (humidity of about 30% and temperature of 25 °C) in the dark. Samples were only illuminated during the regular measurements. Fig. 7 shows the changes of J_{SC} , V_{OC} , FF, and PCE as a function of the ageing time, where the parameters are averaged over 6 devices. All devices exhibit a significant increase of the four key photovoltaics within the first 100 h. Although the mechanisms are not clearly understood, one of the possible reasons is the further growth of the perovskite grains during this period, and a similar phenomenon has been found by other groups.^{40,41} As a result, the optimized device based on 1.0 wt% MoO₃ shows a J_{SC} , V_{OC} , FF, and PCE of 21.49 mA cm⁻², 1.00 V, 0.69, and 14.87%, respectively, as shown in Fig. S5.† Such a PCE is one of the highest values reported for inverted PHJ perovskite solar cells.^{21–26} Although the PCE of the reference device is also increased, the maximum PCE is only 11.87%, which is still significantly lower than that of the optimized device with an MoO₃ layer. Then the devices with a thicker MoO₃ layer (1.0 and 2.0 wt%) show an excellent stability. The device based on 1.0 wt% MoO₃ retains 93% of its initial PCE for 10 days. In contrast, the devices with a thin MoO₃ layer (0.2 and 0.5 wt%) and without an MoO₃ layer present a fast degradation, and the reference device is almost a complete failure within 10 days. As the incorporation of an MoO₃ layer does not affect the growth of PEDOT:PSS and CH₃NH₃PbI₃ films, the different stabilities of the devices are not related to the PEDOT:PSS/CH₃NH₃PbI₃ interface and the bulk of CH₃NH₃PbI₃ but to the ITO/PEDOT:PSS interface. The acidic PEDOT:PSS was reported that can etch ITO,⁴² which may result in diffusion of indium to PEDOT:PSS and

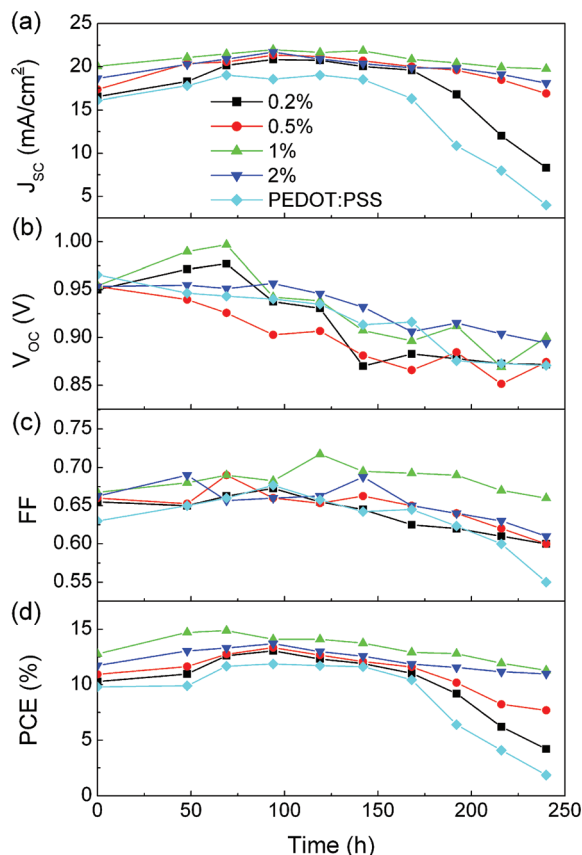


Fig. 7 (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) PCE values as a function of aging time of the devices with different MoO_3 /PEDOT:PSS and pristine PEDOT:PSS HTLs.

$\text{CH}_3\text{NH}_3\text{PbI}_3$ layers and then deteriorates device performance. Thus the excellent stability of the device with a thicker MoO_3 layer can be attributed to the successful restricted erosion of ITO by the acidic PEDOT:PSS because the direct contact between these two layers is completely obstructed by the inserted MoO_3 layer.

Conclusions

In summary, inverted PHJ perovskite solar cells are fabricated with an MoO_3 /PEDOT:PSS bilayer HTL. The incorporation of an MoO_3 layer does not affect the growth of PEDOT:PSS but dramatically improves the PCE and stability of the devices. The as-prepared optimized device shows a PCE of 12.78%, which is increased by about 30% as compared with the reference device based on pristine PEDOT:PSS. The improvement is attributed to the increased hole collection efficiency with an MoO_3 layer. A maximum PCE of 14.87% is obtained for the device after a short storage under ambient conditions in the dark, which is one of the highest PCEs reported for inverted PHJ perovskite solar cells. More importantly, only 7% degradation in PCE is observed for the optimal device and almost complete failure of

the reference device for storage under ambient conditions for 10 days. This work has provided a simple strategy to simultaneously improve the PCE and stability of PHJ perovskite solar cells.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (61376062 and 61376022), Science and Technology Development Plan of Jilin Province (20140201094JC), and Education Department of Hebei Province (QN20131103).

Notes and references

- 1 A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *J. Am. Chem. Soc.*, 2009, **131**, 6050.
- 2 J. H. Im, C. R. Lee, J. W. Lee, S. W. Park and N. G. Park, *Nanoscale*, 2011, **3**, 4088.
- 3 H. S. Kim, C. R. Lee, J. H. Im, K. B. Lee, T. Moehl, A. Marchioro, S. J. Moon, R. Humphry-Baker, J. H. Yum, J. E. Moser, M. Gratzel and N. G. Park, *Sci. Rep.*, 2012, **2**, 591.
- 4 M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, **338**, 643.
- 5 S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza and H. J. Snaith, *Science*, 2013, **342**, 341.
- 6 G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Gratzel, S. Mhaisalkar and T. C. Sum, *Science*, 2013, **342**, 344.
- 7 A. Mei, X. Li, L. Liu, Z. Ku, T. Liu, Y. Rong, M. Xu, M. Hu, J. Chen, Y. Yang, M. Gratzel and H. Han, *Science*, 2014, **345**, 295.
- 8 H. Zhou, Q. Chen, G. Li, S. Luo, T. B. Song, H. S. Duan, Z. Hong, J. You, Y. Liu and Y. Yang, *Science*, 2014, **345**, 542.
- 9 D. Liu and T. L. Kelly, *Nat. Photonics*, 2013, **8**, 133.
- 10 M. Liu, M. B. Johnston and H. J. Snaith, *Nature*, 2013, **501**, 395.
- 11 N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo and S. I. Seok, *Nature*, 2015, **517**, 476.
- 12 J. Burschka, N. Pellet, S. J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Gratzel, *Nature*, 2013, **499**, 316.
- 13 Z. Xiao, C. Bi, Y. Shao, Q. Dong, Q. Wang, Y. Yuan, C. Wang, Y. Gao and J. Huang, *Energy Environ. Sci.*, 2014, **7**, 2619.
- 14 C.-H. Chiang, Z.-L. Tseng and C.-G. Wu, *J. Mater. Chem. A*, 2014, **2**, 15897.
- 15 C. Bi, Y. Shao, Y. Yuan, Z. Xiao, C. Wang, Y. Gao and J. Huang, *J. Mater. Chem. A*, 2014, **2**, 18508.
- 16 J. S. Yeo, R. Kang, S. Lee, Y. J. Jeon, N. Myoung, C. L. Lee, D. Y. Kim, J. M. Yun, Y. H. Seo, S. S. Kim and S. I. Na, *Nano Energy*, 2015, **12**, 96.

- 17 J. Y. Jeng, Y. F. Chiang, M. H. Lee, S. R. Peng, T. F. Guo, P. Chen and T. C. Wen, *Adv. Mater.*, 2013, **25**, 3727.
- 18 K. Sun, J. Chang, F. H. Isikgor, P. Li and J. Ouyang, *Nanoscale*, 2015, **7**, 896.
- 19 O. Malinkiewicz, A. Yella, Y. H. Lee, G. M. Espallargas, M. Graetzel, M. K. Nazeeruddin and H. J. Bolink, *Nat. Photonics*, 2014, **8**, 128.
- 20 C. Zuo and L. Ding, *Nanoscale*, 2014, **6**, 9935.
- 21 J. You, Y. Yang, Z. Hong, T. B. Song, L. Meng, Y. Liu, C. Jiang, H. Zhou, W. H. Chang, G. Li and Y. Yang, *Appl. Phys. Lett.*, 2014, **105**, 183902.
- 22 Z. Xiao, Q. Dong, C. Bi, Y. Shao, Y. Yuan and J. Huang, *Adv. Mater.*, 2014, **26**, 6503.
- 23 J. Seo, S. Park, Y. C. Kim, N. J. Jeon, J. H. Noh, S. C. Yoon and S. I. Seok, *Energy Environ. Sci.*, 2014, **7**, 2642.
- 24 C. W. Chen, H. W. Kang, S. Y. Hsiao, P. F. Yang, K. M. Chiang and H. W. Lin, *Adv. Mater.*, 2014, **26**, 6647.
- 25 W. Nie, H. Tsai, R. Asadpour, J. C. Blancon, A. J. Neukirch, G. Gupta, J. J. Crochet, M. Chhowalla, S. Tretiak, M. A. Alam, H. L. Wang and A. D. Mohite, *Science*, 2015, **247**, 522.
- 26 Q. Lin, A. Armin, R. C. R. Nagiri, P. L. Burn and P. Meredith, *Nat. Photonics*, 2015, **9**, 106.
- 27 J. H. Kim, P. W. Liang, S. T. Williams, N. Cho, C. C. Chueh, M. S. Glaz, D. S. Ginger and A. K. Y. Ken, *Adv. Mater.*, 2015, **27**, 695.
- 28 J. Y. Jeng, K. C. Chen, T. Y. Chiang, P. Y. Lin, T. D. Tsai, Y. C. Chang, T. F. Guo, P. Chen, T. C. Wen and Y. J. Hsu, *Adv. Mater.*, 2014, **26**, 4107.
- 29 J. Cui, F. Meng, H. Zhang, K. Cao, H. Yuan, Y. Cheng, F. Huang and M. Wang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 22862.
- 30 Z. Zhu, Y. Bai, T. Zhang, Z. Liu, X. Long, Z. Wei, Z. Wang, L. Zhang, J. Wang, F. Yan and S. Yang, *Angew. Chem., Int. Ed.*, 2014, **53**, 12571.
- 31 Z. Wu, S. Bai, J. Xiang, Z. Yuan, Y. Yang, W. Cui, X. Gao, Z. Liu, Y. Jin and B. Sun, *Nanoscale*, 2014, **6**, 10505.
- 32 L. Hu, W. Wang, H. Liu, J. Peng, H. Cao, G. Shao, Z. Xie, W. Ma and J. Tang, *J. Mater. Chem. A*, 2015, **3**, 515.
- 33 L. Chen, P. Wang, F. Li, S. Yu and Y. Chen, *Sol. Energy Mater. Sol. Cells*, 2012, **102**, 66.
- 34 S. Shao, J. Liu, J. Bergqvist, S. Shi, C. Veit, U. Würfel, Z. Xie and F. Zhang, *Adv. Energy Mater.*, 2013, **3**, 349–355.
- 35 S. Murase and Y. Yang, *Adv. Mater.*, 2012, **24**, 2459.
- 36 J. Meyer, R. Khalandovsky, P. Görrn and A. Kahn, *Adv. Mater.*, 2011, **23**, 70.
- 37 T. Matsushima, Y. Kinoshita and H. Murata, *Appl. Phys. Lett.*, 2007, **91**, 253504.
- 38 D. Y. Kim, J. Subbiah, G. Sarasqueta, F. So, H. Ding, Irfan and Y. Gao, *Appl. Phys. Lett.*, 2009, **95**, 093304.
- 39 A. Hadipour, D. Cheyins, P. Heremans and B. P. Rand, *Adv. Energy Mater.*, 2011, **1**, 930.
- 40 G. Sfyri, C. V. Kumar, D. Raptis, V. Dracopoulos and P. Lianos, *Sol. Energy Mater. Sol. Cells*, 2015, **134**, 60.
- 41 S. N. Habisreutinger, T. Leijtens, G. E. Eperon, S. D. Stranks, R. J. Nicholas and H. J. Snaith, *Nano Lett.*, 2014, **14**, 5561.
- 42 M. P. de Jong, L. J. van IJzendoorn and M. J. A. de Voigt, *Appl. Phys. Lett.*, 2000, **77**, 2255.